
***Glasnik hemičara i tehnologa
Bosne i Hercegovine***

***Bulletin of the Chemists and Technologists
of Bosnia and Herzegovina***

Print ISSN: 0367-4444
Online ISSN: 2232-7266



38

Juli 2012

**Prirodno-matematički fakultet Sarajevo
Faculty of Science Sarajevo**

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Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

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The journal is published semiannual, and full text version of the papers published are available free of cost at http://www.pmf.unsa.ba/hemija/Glasnik-WEB/glasnik_eng.html.



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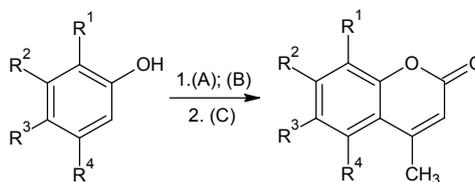
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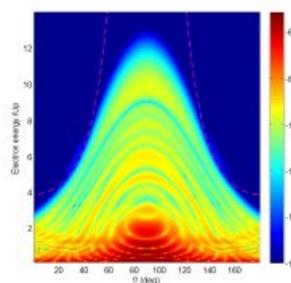
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	IRM ¹ -1		IRM-2		ILC ²	
	KUP ³	XRF ⁴	KUP	XRF	KUP	XRF
	588.5	588.0	583.9	582.5	588.2	589.0
	588.8	585.3	583.0	584.2	587.6	582.4
	588.4	588.9	583.9	588.4	588.2	588.2
	588.6	587.1	583.5	585.1	587.7	589.9
Au (%)	588.4	588.8	583.3	583.9		
	588.3	586.8	583.5	585.6		
	588.8	587.8	583.7	582.0		
	588.7	586.4	583.5	587.0		
	588.9	588.5	583.4	586.7		
	588.4	585.6	583.3	582.1		

¹Internal Reference Material; ²International Inter-laboratory comparisons; ³Cupellation Method; ⁴X-ray Fluorescent Analysis Method

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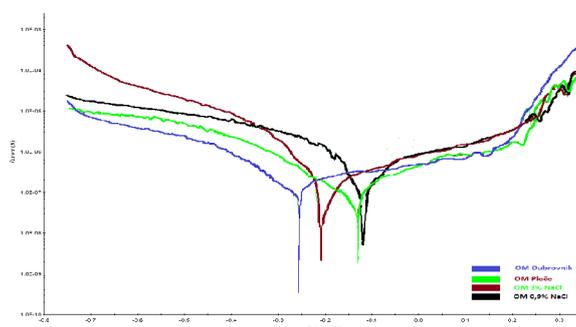
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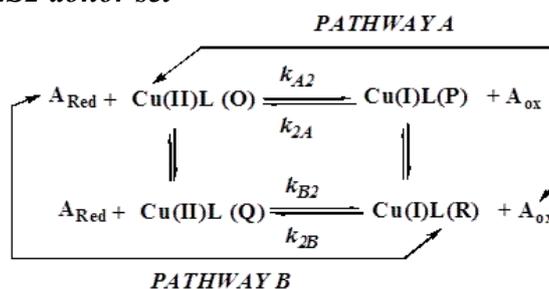
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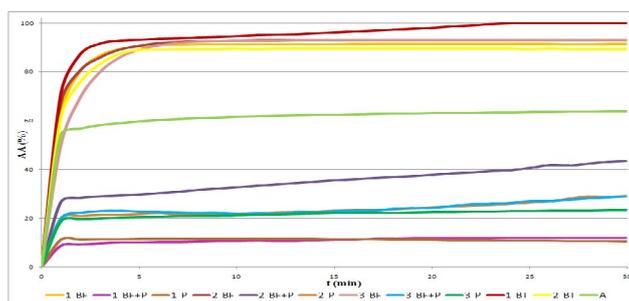
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	Number of urine donors	Interval of Hg concentrations (ng/mL)	Mean concentrations of Hg (ng/mL)
Consumers of 5 to 20 cigarettes per day	16	0.33 – 1.91	0.79
Consumers of 20 to 40 cigarettes per day	12	0.12 – 2.65	0.65
Consumers of 40 to 60 cigarettes per day	1	1.20	1.20

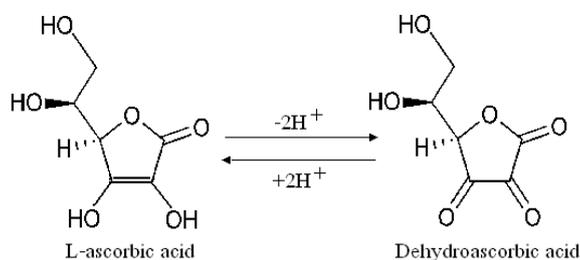
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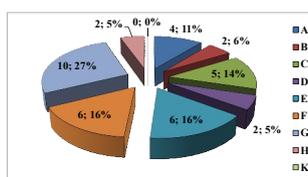
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na Prirodno-matematičkom Fakultetu Univerziteta u Sarajevu
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Poštovani korisniče,

Pred Vama je 38. broj časopisa „GLASNIK HEMIČARA I TEHNOLOGA BOSNE I HERCEGOVINE“, u izdanju Prirodno-matematičkog fakulteta u Sarajevu. Da smo imali sreće da nam Bog dodijeli civilizovanije okruženje, ovo bi bio, makar, 58. broj, a ovaj tekst ne bi ni postojao. Barbarski pokušaji s brda da se unište sva civilizacijska dostignuća u našoj Zemlji rezultirali su, nažalost, ozbiljnim zastojem u razvoju hemije, hemijske tehnologije i naučnih oblasti i disciplina koje se oslanjaju na hemiju, kao i teško nadoknadivim zastojem u naučno-stručnim publicističkim aktivnostima u cijeloj BiH, a u Sarajevu pogotovo. Bez obzira na sve te teškoće, naučna i stručna radoznalost ovdašnjih hemičara kao i neophodan, a prisutan, entuzijizam i potreba da se razvijaju i napreduju, nisu izostale. Rezultati naučnih i stručnih istraživanja naših kadrova saopštavani su u ovakvim naučnim časopisima u našem bližem okruženju, ali i daleko izvan njega. S obzirom na kapacitete današnjih hemičara, a posebno na njihovu mladost i dobru obučenost, nije više dovoljno pojedinačno nastupati i publikovati, makar to bilo u okvirima respektabilnih naučnih svjetskih institucija i uglednih referentnih časopisa. Ta praksa treba da bude nastavljena kad god je to korisno za našu sredinu i ljude, ali se postepeno mora fokusirati na ugradnju dostignutih znanja u našu hemijsku stvarnost.

Danas se mora ovom poslu pristupati sa platforme sistematskog i sistemskog pristupa nauci, a rezultati tog pristupa moraju biti publikovani i u domaćim, vlastitim, naučno-stručnim glasilima. I pored činjenice da je savremeni Svijet postao „mali“ u mnogo aspekata, pa i u naučnoj informatici, nastavak pojavljivanja ovog GLASNIKA daće doprinos svijetu nauke sa bosansko-hercegovačkih izvora, prije svega iz Sarajeva, ali i iz ostalih univerzitetskih i naučno-istraživačkih centara u BiH.

Sa željom da ovo glasilo postane respektabilna naučno-stručna publikacija, koja će afirmisati našu sredinu, Zemlju i ljude u hemiji i srodnim granama nauke i time ostvariti željene ciljeve, preporučujemo vam da intenzivirate svoje naučne aktivnosti, a o njihovim rezultatima informišete našu i svjetsku naučnu javnost publikujući i u ovom GLASNIK-u.

Redakcija GLASNIK-a

ZAŠTO (PONOVO) IZLAZIMO?

Poštovani korisniče,

Prvi broj ovog časopisa, simboličnog imena – GLASNIK, kojim su se hemičari (profesori sarajevskog Univerziteta, srednjih i viših škola, inženjeri – hemije i tehnologije, nastavnici osnovnih škola i hemijski tehničari, iz svih dijelova tadašnje NR Bosne i Hercegovine) željeli uključiti u svijet nauke i prakse, pojavio se daleke 1952. godine, nakon završenih redakcijskih poslova, 29. februara te prestupne godine. Odluka da se izdaje Glasnik Društva hemičara NR BiH donesena je na 1. Glavnoj Skupštini Društva hemičara NR BiH, za 1951. godinu, koja je održana 11.11. te godine u Sarajevu. Glavni urednik bio je prof. dr Mladen Deželić, a odgovorni urednik, prof. Husnija Kurt. “U našem će GLASNIKU biti štampani originalni naučni radovi, stručni članci koji će obrađivati problematiku hemijske privrede i nastave, zatim referati i interesantne bilješke iz hemijske nauke i tehnike” stoji u dijelu Zapisnika sa Skupštine pod stavkom.”Društvene edicije”. Treba napomenuti da su entuzijasti hemičari iz tog vremena, kao jednu od uvodnih djelatnosti Društva, organizovali dva predavanja Nobelovca Lavoslava Ružičke u amfiteatru Medicinskog fakulteta u Sarajevu, 24.4.1950. godine.

Tokom 40 godina izašlo je 37 brojeva Glasnika, koji je mijenjao izdavača, urednike i redakcije, ali je gore citirane i dodatne zadatke uspješno izvršavao. Između ostalog, GLASNIK je poticao i pratio razvoj obrazovanja hemičara u Republici, posebno visokog, do dva tehnološka fakulteta, pedagoških škola i akademija, većeg broja afirmisanih katedara iz hemije na više fakulteta u BiH. Iz Katedre za prirodne nauke na Filozofskom fakultetu u Sarajevu izrastao je Odsjek za hemiju Prirodno-matematičkog fakulteta, koji društvu obezbjeđuje stručnjake inženjerskog i nastavničkog profila iz hemije. Posebno poglavlje predstavlja neraskidiva veza GLASNIKA, Društva i Hemijskog instituta, o čijoj izgradnji je bilo govora na spomenutoj Skupštini. Stalna Komisija Društva, sastavljena od univerzitetskih profesora, bila je jezgro Odbora za izgradnju Instituta za hemiju i fiziku pri Univerzitetu u Sarajevu. Za razvoj hemije, hemijske tehnologije, hemijske industrije i obrazovanja đaka i studenata iz hemije bilo je neophodno obezbjeđivati i vlastite kadrove hemičara koji će taj razvoj nositi, pored nekih, već afirmisanih profesora iz drugih razvijenijih univerzitetskih centara u tadašnjoj državi. U Glasniku su publikovali svoje radove, u najvećem stepenu, svi hemičari iz Bosne i Hercegovine, i ne samo oni, koji su kasnije bili okosnica većine hemijskih aktivnosti u navedenim, privrednim i društvenim, djelatnostima.

Pred Vama je, dakle, 38. broj časopisa „GLASNIK HEMIČARA I TEHNOLOGA BOSNE I HERCEGOVINE“, u izdanju Prirodno-matematičkog fakulteta Univerziteta u Sarajevu. Da smo imali sreće da nam Bog dodijeli civilizovanije okruženje, ovo bi bio, makar, 58. broj, a ovaj tekst ne bi ni postojao. Barbarski pokušaji s brda da se unište sva civilizacijska dostignuća u našoj Zemlji rezultirali su, nažalost, ozbiljnim zastojem u razvoju hemije, hemijske tehnologije i naučnih oblasti i disciplina koje se oslanjaju na

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Eto zašto ponovo pred javnost izlazi naš „GLASNIK“.



Three novel 4-methylcoumarin derivatives

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Article info

Received: 02/11/11
Accepted: 13/01/12

Keywords:

4-methylcoumarins
Pechmann synthesis
Benzoylation

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Abstract: Substituted 4-methylcoumarins are synthesized from phenols and ethyl acetoacetate via Pechmann condensation, then, using common method for benzoylation, three novel coumarin derivatives were obtained: 4-methyl-2-oxo-2*H*-chromen-6-yl benzoate (**2a**), 4,5-dimethyl-2-oxo-2*H*-chromen-7-yl benzoate (**2b**), and 4-methyl-2-oxo-2*H*-chromen-7,8-diyl benzoate (**2c**). The structures of novel coumarins were characterized by elemental analysis, GC/MS, NMR, and IR techniques.

INTRODUCTION

Organic compounds containing coumarin moiety (2*H*-1-chromen-2-one) are widely distributed in nature. Coumarin and its derivatives have been essentially found in green plants belonging to the family of Rutaceae and Umbelliferae. These compounds can be obtained from plants by different extraction methods. Many compounds containing 2*H*-1-chromen-2-one subunit exhibit useful and diverse biological activity and find their application in pharmaceuticals, fragrances, agrochemicals and insecticides (Sethna, and Shah, 1945). Due to their physical properties they have also been used as organic scintillators and dispersed fluorescent and laser dyes. Therefore, the chemical synthesis of coumarin derivatives is done to fulfill their requirements in numerous applications.

Chemically, coumarins can be synthesized by several synthetic routes such as Pechmann, Perkin, Knoevenagel, Reformatsky and Wittig reactions (Sethna, and Shah, 1945). However, due to simple and relatively inexpensive starting materials, the Pechmann reaction has been widely used for the syntheses of coumarins.

Many coumarins have been found to be effective in scavenging activity against reactive oxygen species such as superoxide radicals, hydroxyl radicals, and inhibit lipid peroxidations (Liu, Yu, and Liu, 1999; Kaneko, Baba, and Matsuo, 2003; Ćavar, Kovač, Maksimović, 2009).

Therefore, these facts have been stimulating to synthesize novel 4-methylcoumarin derivatives.

EXPERIMENTAL

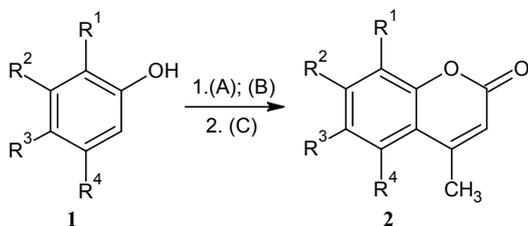
Materials

All chemicals used were purchased from the Sigma-Aldrich chemical company.

Synthesis of 4-methylcoumarin derivatives

The synthesis of coumarins was carried out according to the slightly modified Pechmann method (Russell and Frye, 1941; Vogel, Tatchell, Furnis, et al., 1996; Manhas, Ganguly, Mukherjee, et al., 2006; Kumar, Saini, and Sandhu, 2007; Mandhane, Joshi, Ghawalkar, et al., 2009), which involves the condensation of different phenols with β -keto esters in the presence of acidic condensing agents,

such as concentrated sulphuric acid and anhydrous aluminum chloride. Hydroxy-derivatives of 4-methylcoumarin were benzoylated in order to obtain the corresponding benzoxy-derivatives of 4-methylcoumarin (**2a-c**). Esterification reaction was carried out using benzoyl chloride in basic media (Figure 1)



- 1a:** R¹=R²=R⁴=H, R³=OH **2a:** R¹=R²=R⁴=H, R³=OCOPh
1b: R¹=R⁴=CH₃, R³=H, R²=OH **2b:** R¹=R⁴=CH₃, R³=H, R²=OCOPh
1c: R¹=R²=OH, R³=R⁴=H **2c:** R¹=R²=OCOPh, R³=R⁴=H

Figure 1: Pechman synthesis of 4-methylcoumarins. Reagents and conditions: (A) concentrated sulfuric acid, ethylacetoacetate, 0-10°C, reaction time 60 min; (B) polyphosphoric acid, ethyl acetoacetate, 75-80°C, reaction time 25 min; (C) benzoyl chloride, 5% sodium hydroxide, 25°C, reaction time 30 min.

Spectroscopic analyses of 4-methylcoumarins

Synthesized 4-methylcoumarins were identified by the determination of melting points on Kofler microscope hot stage apparatus (Model No. 220392, Reichert), using elemental analysis on CHN Analyzer (Perkin-Elmer 2400), GC/MS and NMR techniques.

The GC/MS (Hewlett-Packard GC 6890 series II and MSD 6890 series II) conditions were as follows: a fused-silica HP-5 column (5% phenyl methyl siloxane; 30 m x 250 μm x 0.25 μm), carriers gas He (1.1 mL/min), temperature program: 20°C/min from 100°C to 270°C; the injection port temperature was 250°C; detector temperature 280°C. Ionization of the sample components was performed in the EI mode, (70 eV). The NMR spectra were recorded in CDCl₃, acetone-d₆ and DMSO-d₆ at 300.13 MHz using Bruker DPX 300 NMR spectrometer. Novel compounds were also characterized by IR spectroscopy, recording the spectra of solid samples in KBr pellets on Perkin-Elmer spectrum BX FTIR system.

RESULTS AND DISCUSSION

The condensation of phenols and acetoacetic ester provided the 4-methylcoumarin and its derivatives. The concentrated sulfuric acid and polyphosphoric acid have been used as the condensing agents.

The yields of obtained 4-methylcoumarins were, in general, very high regardless of the structural variations of phenol substrates (**1a-c**). Substrates having electron-donating groups in the *para* position to the site of electrophilic substitution, gave maximum yields under mentioned reaction conditions.

The 4-methylcoumarin esters were prepared in high yields using benzoylation as a common method for esterification of organic compounds. In contrast to the Pechmann condensation, there is no correlation to the position of the hydroxy group in the coumarin molecule.

The purity of synthesized 4-methylcoumarins was determined by GC/MS technique. All samples were

dissolved in acetone. They showed appreciable purity which was confirmed by elemental analysis. Data obtained from elemental analysis were in agreement with the calculated data. Structural confirmation was done using ¹H NMR, ¹³C NMR and EI mass spectrometric methods.

The ¹H NMR spectra showed characteristic chemical shifts: 3-H δ 5.99-6.92, 4-methyl protons at δ 2.15-2.46, and protons from benzenoid part of molecule at δ 6.57-7.65, for all of the synthesized compounds. Benzoxy group attached to the aromatic part of coumarin molecules showed resonance peaks at δ 7.35-8.12. Observed results are in agreement with those found in the literature (Borsche, 1907; Mali and Yadav, 1977; Khan, Saify, Begum, et al., 2003).

The ¹³C NMR spectra showed characteristic peaks of C-2 at δ 161.39-162.76, C-3 at δ 111.24-115.54, C-4 at δ 152.23-154.62, C-5 at δ 107.92-136.53, C-6 at δ 110.92-156.53, C-7 at δ 115.82-161.74, C-8 at δ 99.57-135.45, C-8a at δ 143.72-156.24, and C-4a at δ 112.28-121.92. Chemical shifts for aromatic carbon atoms were in a wide span due to the resonance influence of electron-acceptor substituent groups attached to the particular carbon atom. Benzoxy group displayed chemical shifts at δ 166.04-167.17 for carbonyl atom and at δ 129.12-133.72 for C-atoms from phenyl-group. Observed results are in agreement with those found in literature (Mital, Gupta, and Jain, 1972; Sojka, 1975; Chang and Floss, 1977).

Finally, the structures of synthesized 4-methylcoumarins were supported by their EI mass spectra. All compounds showed characteristic molecular [M]⁺ peaks, *m/z* 280 (**2a-b**), and *m/z* 400 (**2c**). Moreover, all examined compounds displayed characteristic fragmentation of coumarin structure, such as [M - HC=O]⁺. Observed results are in agreement with those found in literature (Desai and Mavani, 1942; Mali and Yadav, 1977, Woods and Sapp, 1962; Khan et al., 2003).

The IR spectra showed characteristic absorption bands for stretching of ester groups (1720 cm⁻¹), and for stretching of lactone C=O group (1680-1700 cm⁻¹). Other significant absorption bands were noted at 2900-3100 cm⁻¹ (medium stretching of aromatic C-H bonds), and at 1590 cm⁻¹ (weak stretching of aromatic C=C bonds).

Analytical and spectral characteristics of the novel compounds are given below.

4-Methyl-2-oxo-2H-chromen-6-yl benzoate; syn: 6-benzoxy-4-methyl-2-oxo-2H-chromen (2a). Yield 59%. m.p. 110-115°C. Anal. calcd for C₁₇H₁₂O₄: C 72.85, H 4.32; found: C 72.48, H 4.47. MS (EI; 70 eV): *m/z* (%) 39 (3), 51 (6), 77 (29), 91 (4), 105 (100), 106 (8), 280 (4). ¹H-NMR (300.13 MHz; DMSO-d₆): δ 8.06 (dd, *J*₁ = 7.9 Hz, *J*₂ = 2.0 Hz, 2H), 7.72 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 7.67 (d, *J*₂ = 2.1 Hz, 1H), 7.46 (dd, *J*₁ = 8.0 Hz, *J*₂ = 7.9 Hz, 2H), 7.35 (d, *J*₁ = 7.6 Hz, 1H), 7.21 (dd, *J*₁ = 7.6 Hz, *J*₂ = 2.1 Hz 1H), 6.04 (s, 1H), 2.42 (s, 3H). ¹³C-NMR (300.13 MHz; CDCl₃): δ 167.17, 162.33, 152.99, 151.93, 149.75, 133.63, 130.95, 129.72-129.53, 129.32, 128.87, 120.65, 117.55, 114.90, 113.49, 21.32. IR (ν_{max}/cm⁻¹; KBr): 3060-3100, 1720, 1688, 1480, 1225, 840.

4,5-dimethyl-2-oxo-2H-chromen-7-yl benzoate; syn: 7-benzoxy-4-methyl-2-oxo-2H-chromen (2b). Yield 72%. m.p. 152-153°C. Anal. calcd for C₁₈H₁₂O₄: C 73.46, H 4.79; found: C 74.12, H 5.09. MS (EI; 70 eV): *m/z* (%) 51 (6), 77 (27), 105 (100), 106 (8), 294 (3). ¹H-NMR (300.13 MHz; DMSO-d₆): δ 8.02 (dd, *J*₁ = 7.8 Hz, *J*₂ = 2.1 Hz, 2H), 7.64 (dd, *J*₁ = 7.9 Hz, *J*₂ = 2.1 Hz, 1H), 7.53 (dd, *J*₁ = 7.9 Hz, *J*₂ = 7.8 Hz, 2H), 7.03 (d, *J*₁ = 2.6 Hz, 1H), 6.76 (d, *J*₁ = 2.6 Hz, 1H), 5.93

(s, 1H), 2.43 (s, 3H), 2.24 (s, 3H). $^{13}\text{C-NMR}$ (300.13 MHz; CDCl_3): δ 167.17, 162.59, 154.63 -153.96, 135.92, 133.63, 130.95, 129.92 -129.53, 129.32-128.97, 117.40, 116.67, 115.56, 105.40, 21.37, 20.73. IR ($\nu_{\text{max}}/\text{cm}^{-1}$; KBr): 3260, 1816, 1700-1720, 1272, 1224, 696.

4-methyl-2-oxo-2H-chromen-7,8-diyl benzoate; syn: 7,8-dibenzoxy-4-methyl-2-oxo-2H-chromen (2c). Yield 76%. m.p. 139-140°C. Anal. calcd for $\text{C}_{18}\text{H}_{12}\text{O}_4$: C 72.00, H 4.04; found: C 72.11, H 4.03. MS (EI; 70 eV): m/z (%) 51 (15), 77 (36), 105 (100), 106 (8), 198 (9). $^1\text{H-NMR}$ (300.13 MHz; DMSO-d_6): δ 8.09 - 7.51 (m, 10H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 5.94 (s, 1H), 2.26 (s, 3H). $^{13}\text{C-NMR}$ (300.13 MHz; CDCl_3): δ 166.14, 165.47, 166.49, 153.42, 148.99-148.13, 133.83-133.43, 132.02, 131.15 -130.75, 129.92-129.53, 129.32-128.91, 122.40, 117.75, 117.02, 112.24, 22.09. IR ($\nu_{\text{max}}/\text{cm}^{-1}$; KBr): 2980, 1700-1720, 1590-1610, 1350-1390, 1000-1015.

CONCLUSIONS

This study presents the synthesis and characterization of three novel 4-methylcoumarin derivatives. After effective Pechman condensation, esterification of 4-methylcoumarins has been performed, and all of coumarin derivatives were obtained in high yields.

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Summary/Sažetak

Substituirani 4-metilkumarini su sintetizirani Pechmanovom metodologijom gdje se vrši kondenzacija fenola i etilacetoacetata uz prisustvo jakih kiselina kao katalizatora. Sintetizirani derivati 4-metilkumarina su dalje podvrgnuti benzoiliranju, pri čemu su sintetizirana tri nova derivata kumarina, i to: 4-metil-2-okso-2*H*-hromen-6-il benzoat (**3a**), 4,5-dimetil-2-okso-2*H*-hromen-7-il benzoat (**3b**) i 4-metil-2-okso-2*H*-hromen-7,8-diil benzoat (**3c**). Struktura novih kumarinskih derivata je potvrđena elementarnom analizom uzoraka, te GC/MS, NMR i IR tehnikama.



High-order above-threshold ionization and high-order harmonic generation of molecule: a way of its characterization

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Article info

Received: 19/10/2011

Accepted: 17/01/2012

Keywords:

Molecules
Symmetry
Interference
HOMO
(H)ATI spectra
HHG spectra

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Abstract: We investigate high-order above-threshold ionization (HATI) and high-order harmonic generation (HHG) of diatomic molecules having different symmetries by a strong laser field using modified molecular strong-field approximation. We present our results for N₂, O₂, H₂, and Ar₂ molecules. Their initial highest occupied molecular orbitals are characterized by 3σ_g, 1π_g, 1σ_g, and 5σ_u symmetry, respectively. By analyzing HATI and HHG spectra for different molecular orientation with respect to the laser polarization axis, and for different values of the electron or photon energies and electron emission angle, we are able to draw some conclusions about the molecular structure. The most noticeable feature of all molecular spectra is the existence of minima that are absent in the atomic case.

INTRODUCTION

Atomic and molecular nonlinear processes in a strong laser field have attracted a lot of attention in last years because of many applications in chemistry, physics, and biology. Using pump-probe techniques with ultrashort laser pulses, one can monitor molecular motion occurring on the femtosecond time scale and thus gain insight into the structure and the short-time dynamics of molecules. This concept has led to the birth of femtochemistry for which the 1999 Nobel Prize in chemistry was awarded to Ahmed Zewail (Zewail, 2000). Using femtosecond lasers in order to control motion in atoms and molecules on the femtosecond time scale was studied by

Wollenhaupt, Engel, and Baumert (2005). Also, in the physics, studying of different processes in the strong laser field is of great interest for a deeper understanding of the laser-matter interaction. Some of these phenomena take place within a fraction of the laser-field cycle, which, for near-infrared pulses, is on the time scale of hundreds of attoseconds. Sub-laser-cycle rescattered electron pulses were suggested as a tool for probing the molecular dynamics (Niikura, Légaré, Hasbani, *et al.*, 2002).

In this paper we focused on two processes that play important role in strong-field physics (Lein, 2007): high-order harmonic generation (HHG) and high-order above-threshold ionization (HATI). Both processes are explained in terms of

the semiclassical three-step model: (1) the atom (molecule) is ionized, (2) the ionized electron is accelerated by the laser field and driven back to its parent ion, and (3) the ionized electron rescatters off (for HATI) or recombines with (for HHG) the parent ion and high-energy electrons or high-order harmonic photons are emitted.

In the first step of these processes, the considered system absorbs more photons from the laser field than is necessary for ionization. The electron, liberated in such a way, can go directly to the detector. We call this process the direct above-threshold ionization (ATI). Owing to the influence of the laser field, the ionized electron may also return to the parent ion (second step) and elastically scatters off it (third step), before reaching the detector. In this process, the electron can absorb many more photons from the laser field than in the direct ATI. This process was named high-order ATI (HATI). For the HHG process, in the third step, the electron recombines with the parent ion and one high-energy photon is emitted. The energy spectra of HATI and HHG processes are characterized by a plateau which manifests itself as a broad energy interval of the spectrum in which the photoelectron (HATI) or photon (HHG) yield is practically constant. These intervals are followed by abrupt cutoffs.

One of the most useful theoretical approaches based on three-step model is the strong-field approximation (SFA) (see review article by Milošević, Paulus, Bauer, *et al.*, 2006). The SFA was originally formulated for the low-energy part of the ATI spectra. In order to describe high-energy plateau of the HATI spectra we have developed improved version of the SFA or ISFA (for example see Milošević, Hasović, Busuladžić, *et al.*, 2007). Within this approach we included one more interaction between the ionized electron and parent atomic ion.

While these phenomena in atomic media are well understood (see review article by Milošević and Ehlötzky, 2003, and references therein), there is a small number of papers devoted to their molecular analogs, especially for molecular HATI. Molecules are multicenter systems. As a consequence, additional two-center interferences appear in the third step, and, by analyzing the electron spectra or photon spectra, we can obtain information about the molecular structure and symmetry. The ionization can take place at any of the two or more different centers, causing interference structures in the electron spectrum, which will be presented in this paper. In fact, even direct ionization (direct ATI) without rescattering reveals the initial symmetry of the molecular system (Grasbon, Paulus, Chin, *et al.*, 2001). For example, the O₂ molecule shows a suppression in the low-energy electron spectra due to its π_g symmetry, while the N₂ molecule, having σ_g symmetry, does not show such a suppression (for a more recent experimental study see work by Okunishi, Shimada, Prümper, *et al.*, 2007). In the case of HHG process, the major step forward was the so-called tomographic reconstruction of molecular orbitals by Itatani, Levesque, Zeidler, *et al.* (2004) where, from the measured photon spectra at various orientations of the molecular axis, the highest occupied molecular orbital (HOMO) of N₂ was reconstructed. More details and references about molecular imaging can be found in recent review articles by Lein (2007) and by Lin, Le, Chen, *et al.*, (2010).

In this paper we gave brief review of our MSFA theory, which includes the most important results obtained for linear polarization case (Section 2). Our numerical results are presented in Section 3, and finally conclusion is given in Section 4. We used atomic system of units.

THEORY

HATI

We have developed a theory of ionization of diatomic molecules by a strong laser field within modified molecular strong-field approximation (Milošević, 2006). A diatomic molecule was considered as a three-particle system, which consists of two heavy atomic (ionic) centers and an electron. After separation of the center-of-mass coordinate, the dynamics of this system is reduced to the relative electronic and nuclear coordinates. We introduced two forms of molecular SFA, one with the field-free and other with the field-dressed initial molecular bound state.

We present here the final result for the dressed modified molecular SFA in length gauge for neutral homonuclear diatomic molecules. The rate of the ATI process with absorption of n photons from the laser field is equal to

$$w = 2\pi P_f |T_{fi}^{(0)}(n)|^2 \quad (1)$$

where the T -matrix element $T_{fi}^{(0)}(n)$ is the Fourier transform of an expression which is given by Eq. (52) in the paper by Milošević (2006). The ground-state molecular electronic wave function is presented as linear combination of atomic orbitals (LCAO) (Atkins and Friedman, 2001; Levine, 2000), i.e.

$$|\Psi_s^{(0)}\rangle = \sum_a c_{sa} |\psi_a^{(0)}\rangle \quad (2)$$

In our notation, the connection between the coefficients c_{sa} , depends on the symmetry of the considered molecule and is given by $c_{-1a} = s_{a\lambda} c_{1a}$, with

$$s_{a\lambda} = (-1)^{l_a - m_a} (-1)^{m_\lambda}, \quad (3a)$$

$$s_{a\lambda} = (-1)^{l_a - m_a} (-1)^{m_\lambda + 1}, \quad (3b)$$

for g and u symmetry, respectively. Here, m_λ is the projection of the orbital angular momentum on the internuclear axis. For example, for σ states it is $m_\lambda=0$, while for π states it is $m_\lambda=1$. The factor $(-1)^{l_a - m_a}$ comes from the inversion of the z coordinate of the second center. Using the above-described theory we reproduced key features of the most important experiment in which low-energy electrons or ATI electrons were collected (Busuladžić and Milošević, 2010).

In the previous papers (Busuladžić *et al.*, 2008), we have generalized this theory to include the rescattering of the ionized electron off the parent molecular ion. Following mentioned procedure we got two terms, first of them describes the direct ATI, and it was given by $T_{fi}^{(0)}(n)$. The second term, denoted by $T_{fi}^{(1)}(n)$, that corresponds to the rescattered electrons is a very complex function and can be presented as the Fourier transform of an expression given by Eq. (22) in the paper by Busuladžić, Gazibegović-Busuladžić, Milošević, *et al.* (2008). The total rate accounts for the coherent sum of the direct term ($T_{fi}^{(0)}(n)$) and rescattering one $T_{fi}^{(1)}(n)$, (Busuladžić *et al.*, 2008).

As the molecules are multicenter systems, the ionization as well as the rescattering can happen at different centers, causing interference structures in the electron spectrum. So, our matrix element T related to rescattering process can be decomposed into four terms

$$T^{(1)} = T^{++} + T^{+-} + T^{-+} + T^{--}. \quad (4)$$

The electron can tunnel out of either atom. These possibilities are denoted by superscript “+” or “-”. With T^{++} (T^{--}) we denote the T -matrix contribution of the electron which, after excursion in the continuum, rescatters at the same center “+” (“-”). The terms T^{+-} and T^{-+} , correspond to the cases where the electron is ionized and rescatters off different centers. It can be shown that our matrix element is proportional to $\cos\left[\left(\vec{p}_f - \vec{k}_{st}\right) \cdot \vec{R}_0 / 2\right]$, regardless of the symmetry of the atomic orbital of which the considered molecular orbital consists (Busuladžić, *et al.*, 2008). In the last equation \vec{p}_f is the final momentum of detected electron, \vec{k}_{st} is the stationary intermediate electron momentum between the ionization and rescattering (it is in the direction of the laser electric field vector) and \vec{R}_0 is the internuclear axis. Therefore, if we present the rescattering ionization rate in the (E_{pf}, θ) plane, we will have local minima if the condition

$$R_0 \left| p_f \cos \theta - k_{st} \cos \theta_L \right| = (2m + 1)\pi, \quad (5)$$

with m integer, is fulfilled. Here, θ is angle between the final momentum of detected electron and the internuclear axis, while θ_L is the angle between the internuclear axis and the laser polarization axis. This novel two-source two-rescattering-centers interference survives the focal averaging and even has been observed in experiments with unaligned molecules. Averaging over molecular orientations was considered in paper published by Milošević, Busuladžić, Gazibegović-Busuladžić, *et al.*, (2009).

For elliptical polarization the destructive interference condition still holds (Busuladžić, Gazibegović-Busuladžić and Milošević, 2009; Busuladžić, Gazibegović-Busuladžić and Milošević, 2010) but one should have in mind that \vec{k}_{st} is a complex solution of the saddle-point equations (Salières, Carré, Le Déroff, *et al.*, 2001).

HHG

Now, we will consider HHG process on molecular targets. For a $T=2\pi/\omega$ -periodic laser field the rate of emission of a harmonic photon is given by (Odžak and Milošević, 2009; Odžak and Milošević, 2011)

$$W_n^{qq'} = \frac{1}{2\pi} \left(\frac{n\omega}{c} \right)^3 \left| \int_0^T \frac{dt}{T} e^{in\omega t} \hat{e}_{\vec{k}}^* \cdot \vec{d}^{qq'}(t) \right|^2, \quad (6)$$

where the time-dependent dipole $\vec{d}^{qq'}$ was given by Eq. (17) in the above-cited paper. By $\hat{e}_{\vec{k}}$ we denote the polarization vector of the emitted harmonic. As in the case of HATI one can observe interference minima in the molecular HHG spectra. Using the examples of the N_2 ($3\sigma_g$) and O_2 ($1\pi_g$) molecules, we will analyze these interference minima as well as conditions for theirs location in the HHG spectra. The returning electron wave packet recombines into the molecular

orbital ($3\sigma_g$ for N_2 or $1\pi_g$ for O_2) which is a linear combination of even and odd atomic orbitals (see the next section). The corresponding partial recombination amplitudes interfere destructively for the emitted harmonic order, which is the solution of the corresponding nonlinear equation (Odžak and Milošević, 2009).

It can be shown that our matrix element is proportional to

$$\vec{K}^q(\vec{k}_{st}, t) \cdot \vec{R}_0 = \begin{cases} (2j+1)\pi & \text{for } s_{a\lambda} = +1 \\ 2j\pi & \text{for } s_{a\lambda} = -1 \end{cases}, \quad (7)$$

where \vec{K}^q is given by Eq. (B5) in paper published by Odžak and Milošević (2009) and j is an integer. Using (B5) and (C2) in the above-mentioned reference we finally obtain the following condition for the interference minima (Odžak and Milošević, 2009) for $s_{a\lambda} = +1$

$$n_{\min}^{(u,+1)} = \frac{I_p}{\omega} + \frac{(2j+1)^2 \pi^2}{2\omega R_0^2 \cos^2 \theta_L}, \quad j = 0, 1, \dots \quad (8)$$

while for $s_{a\lambda} = -1$ we have

$$n_{\min}^{(u,-1)} = \frac{I_p}{\omega} + \frac{2j^2 \pi^2}{\omega R_0^2 \cos^2 \theta_L}, \quad j = 0, 1, \dots \quad (9)$$

RESULTS AND DISCUSSION

As examples we will consider the N_2 , H_2 , O_2 , and Ar_2 molecules. For the N_2 (H_2) molecule, the initial HOMO is $3\sigma_g$ ($1\sigma_g$) so that the factor $(-1)^{m_a} = +1$ in Eq. (2a). Twelve atomic orbitals with $m_a=0$ will be taken into account: $a=1s, 1s', 2s, 2s', 3s, 3s', 2p, 2p', 3d, 3d', 3d'',$ and $4f$ ($a=1s, 1s', 2s, 2s', 3s, 2p, 2p', 3p, 3d, 3d',$ and $4f$). Therefore, for s states we have $s_{a\lambda}=1$, while for p states it is $s_{a\lambda}=-1$, etc. The HOMO of the O_2 molecule is $1\pi_g$, so that $(-1)^{m_a} = -1$. We choose five atomic orbitals having $m_a=1$: $a=2p, 2p', 2p'', 3d,$ and $4f$. For p and f states we have $s_{a\lambda}=-1$, while for d states it is $s_{a\lambda}=1$. For Ar_2 ($5\sigma_u$) we take ten atomic orbitals with $m_a=0$: $a=1s, 2s, 2s', 3s, 3s', 2p, 2p', 3p, 3p', 3d$. Now, for s and d states it is $s_{a\lambda}=-1$ (see Eq. 2b), while for p states we have $s_{a\lambda}=1$. Atomic orbitals which enter LCAO are the Slater-type orbitals obtained using the Hartree-Fock-Roothaan method (Atkins and Friedman, 2001; Levine, 2000). In our calculation we use the equilibrium internuclear distance for all molecular targets: $R_0=2.068$ a.u. (for N_2), $R_0=1.4$ a.u. (H_2), $R_0=2.282$ a.u. (O_2), and $R_0=7.2$ a.u. (Ar_2). Also, the next value of the ionization potential is taken into account: $I_p=15.58$ eV (for N_2), $I_p=16.18$ eV (H_2), $I_p=12.03$ eV (O_2), and $I_p=15.76$ eV (Ar_2).

In Figure 1 we present angle-resolved electron energy spectra for the Ar_2 molecule for three different molecular orientations with respect to laser polarization axis: $\theta_L=0^\circ, 45^\circ$ and 90° . Laser field is linearly polarized having intensity 1.35×10^{14} W/cm² and wavelength $\lambda=800$ nm. First of all, we can observe pronounced minima in the HATI spectra, particularly in the cutoff region, in accordance with Eq. (5). For chosen laser and molecular parameters we have minima for values $m=0, 1,$ and 2 in Eq. (5). These features are visible in the upper and middle panels of the figure.

Our theoretical approach allows us to connect the rescattering contribution for particular molecular orientation with the a th molecular constituent [see Eq. (36) in reference by Busuladžić, *et al.*, 2008]. For example, in the case of Ar_2

molecule with a large value of R_0 the p -state contribution becomes dominant and it can be shown that the corresponding rescattering $T^{(1)}$ -matrix contribution is proportional to $\cos\theta_L$, with the consequence that for $\theta_L=90^\circ$ the rescattering plateau is absent. This is illustrated by the bottom panel of Fig. 1. This is one example of how one can obtain information about the molecular symmetry by analyzing the angle- and energy-resolved HATI spectra (Milošević *et al.*, 2009).

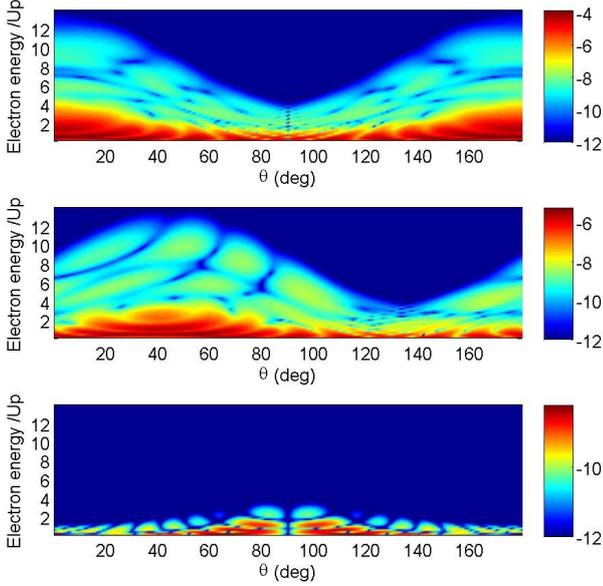


Figure 1: Logarithm of the differential ionization rate of Ar_2 , coded in false colors in the (E_{pf}, θ) plane, for three different orientations of the molecular axis with respect to the polarization vector of the laser field, from the top to the bottom panel: $\theta_L=0^\circ$, 45° , and 90° . Intensity of the linearly polarized laser field is $1.35 \times 10^{14} \text{ W/cm}^2$ and the wavelength is 800 nm. The electron kinetic energy E_{pf} is presented in units of U_p , where U_p is defined as the ponderomotive energy of the electron in the laser field. All HATI spectra are obtained using the dressed length-gauge modified MSFA.

It is important to stress that this novel two-source two-rescattering-centers interference has been observed in experiments with unaligned molecules (Okunishi, Itaya, Shimada, *et al.*, 2009; Kang, Quan, Wang, *et al.*, 2010). More precisely, the suppression remains visible in the orientation-averaged spectrum of O_2 but not of N_2 molecule. This is related with its ground state function symmetry (Okunishi, *et al.*, 2009). For parallel $\theta_L=0^\circ$ and perpendicular $\theta_L=90^\circ$ orientations, the high-energy plateau for O_2 is entirely absent (Busuladžić *et al.*, 2008), while for angles close to $\theta_L=0^\circ$ or $\theta_L=90^\circ$ it is few orders of magnitude lower than that of N_2 . The fact that the suppression remains visible in the orientation-averaged spectrum of O_2 but not of N_2 is due to the fact that for N_2 it is filled in by contributions from small and large angles. These contributions are absent or very low for O_2 . This effect is different from the suppression of ionization (direct ATI) that is well known to occur for O_2 (Grasbon, *et al.*, 2001).

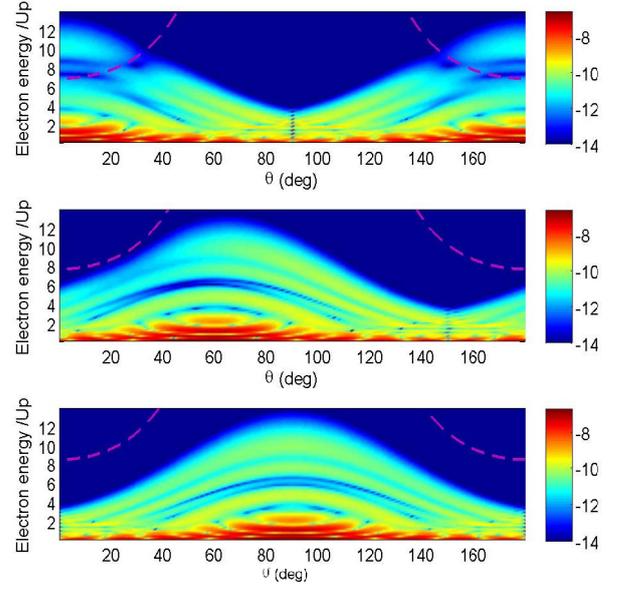


Figure 2: The same as in Fig 1, but now for H_2 molecule and for $\theta_L=0^\circ$, 60° , and 90° . The dashed pink curves are based on Eq. (5), (see the text).

In Fig. 2 we present angle-resolved energy spectra for the H_2 molecule for the following molecular orientations: $\theta_L=0^\circ$, 60° , and 90° . The laser parameters are the same as in the previous figure. The spectra for $\theta_L=0^\circ$ (top panel) and $\theta_L=90^\circ$ (bottom panel) are symmetric with respect to $\theta=\theta_L$ axis, while this symmetry is absent for $\theta_L=60^\circ$ (middle panel). Again, for parallel orientation: $\theta_L=0^\circ$ one can see the existence of minima that are absent in the atomic case (Busuladžić *et al.*, 2008; Milošević *et al.*, 2009). Now, this cannot be observed for larger values of θ_L . The reason for that is a small value of the internuclear distance between atomic centers in the hydrogen molecule. The dashed curves presented in all panels are based on Eq. (5). We can see in the middle and bottom panels that the curves go above the registered HATI spectra. In order to observe minima for larger angles for H_2 we have to increase intensity of the applied laser field. In Fig. 3 we present HATI spectrum of H_2 and perpendicular orientation ($\theta_L=90^\circ$) but now for the intensity $3.0 \times 10^{14} \text{ W/cm}^2$. Value of the wavelength is not changed. For this higher intensity the minima can be observed. Moreover, our condition for interference minima gives a perfect fit of the minima position. This can be explained in the following way. For $\theta_L=90^\circ$ the negative-parity atomic orbitals ($s_{a\lambda} = -1$) do not contribute to rescattering (Busuladžić *et al.*, 2008) and the condition (5) reduces to

$$E_{pf} \cos^2 \theta = \frac{\pi^2}{2R_0^2}, \quad (10)$$

which allows, in principle, to determine the internuclear separation.

Because of the small value of the internuclear separation for H_2 the suppression occurs at higher energies [see Eq. (10)]. In order to obtain the interference minima for perpendicular orientation we have to increase the intensity of the laser field.

Generally speaking, the spectra of H_2 are very similar to those of the N_2 molecule. This is because of the same type of symmetry of its HOMO. More precisely, the HOMO of N_2 is $3\sigma_g$, while the HOMO of H_2 molecule is $1\sigma_g$. Because of the different symmetry of the O_2 ground-state wave function, the corresponding spectra are very different from those of H_2 or N_2 . Also, we suppose that in the orientation averaged HATI spectra of H_2 the interference structure should be masked as it was the case for N_2 molecule (Okunishi, *et al.*, 2009).

More recently, we have developed molecular low-frequency approximation (MLFA) in order to simulate a molecular HATI experiment by ultrashort laser pulses. This new approach has enabled us to explain a new type of minima which are not due to two-source double-slit destructive interference. The MLFA theory is better approximation than the MISFA (Gazibegović-Busuladžić, Hasović, Busuladžić, *et al.*, 2011).

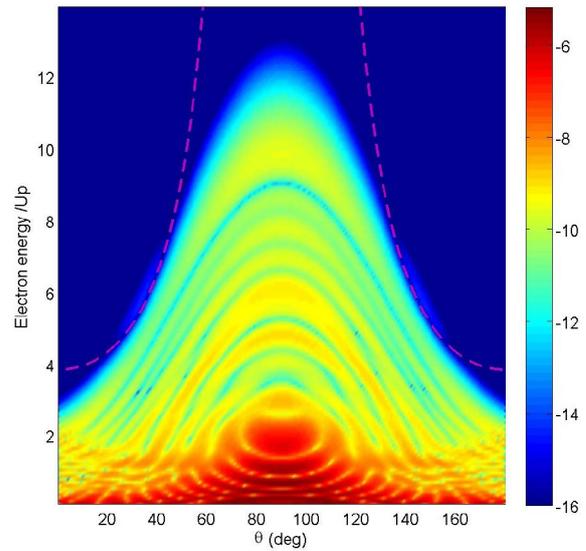


Figure 3: The same as in the bottom panel of Fig. 2, but for the intensity of $3.0 \times 10^{14} \text{ W/cm}^2$.

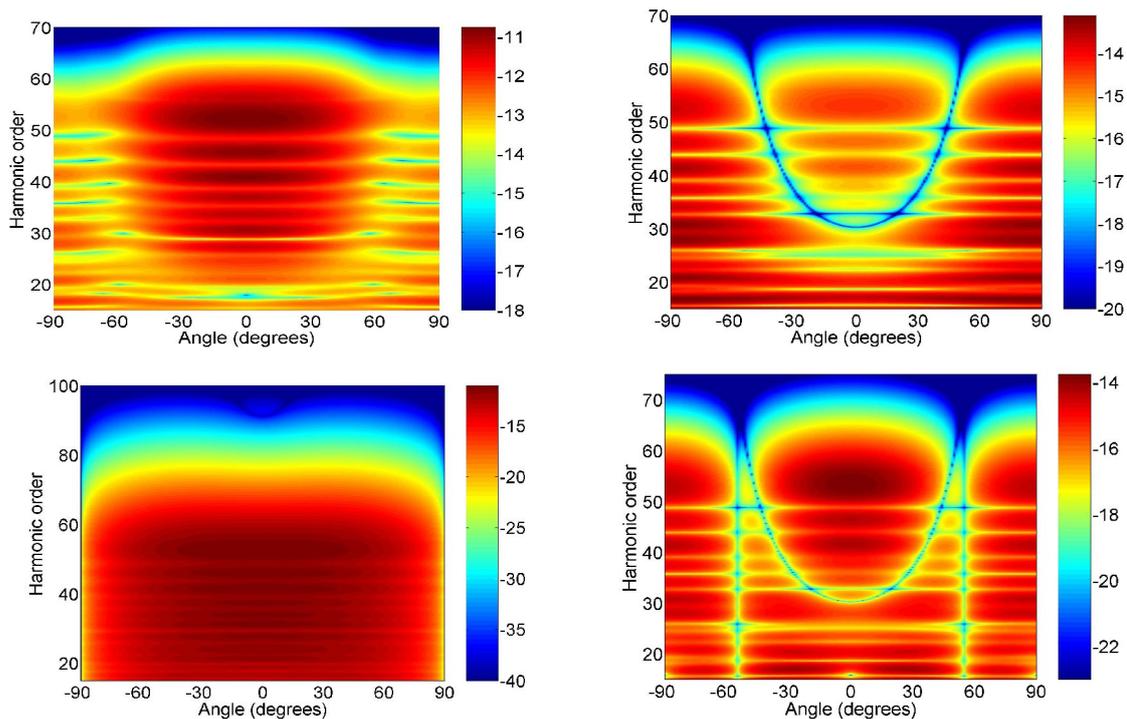


Figure 4: High-order harmonic spectra of the N_2 molecule obtained using a linearly polarized field having intensity $3.5 \times 10^{14} \text{ W/cm}^2$ and wavelength of 800 nm. Both components of the T -matrix element are used in calculations. Also, the final state is undressed. Upper left panel: Contributions of s , p , and d atomic orbitals within LCAO are included in calculated HHG spectrum, upper right: only taking s atomic orbitals, bottom left: only p orbitals and bottom right panel: only d orbitals.

Now, we will present our results for molecular HHG process. In Fig. 4 we present in false color the harmonic emission rate in the plane (θ_L, n) for N_2 molecule obtained using a linearly polarized laser field having the intensity $3.5 \times 10^{14} \text{ W/cm}^2$ and the wavelength $\lambda=800 \text{ nm}$. The angle θ_L is defined as angle between the internuclear axis and the laser

polarization axis. By n we denote the harmonic order. In all calculations the final state is undressed (Milošević, 2006). Clear two-center interference minima appear and these minima form a curve in the plane (θ_L, n) for all partial contributions which include only s , p or d atomic orbitals. These results are presented in the upper right, bottom left, and

bottom right panel, respectively. If we take only contributions of the components of the T -matrix element in the direction of the laser-field polarization we will have interference minima in accordance with formula (24) in work by Odžak and Milošević (2009). Corresponding results was presented in Fig. 3 (b) in the mentioned paper where one can observe minima in the harmonic spectrum. These minima are related with the relative contribution of even (s and d) and odd (p and f) atomic orbitals. The interference picture was completely different from the interference structure where we included only one type of orbitals. In the last case minima will appear in accordance with Eq. (8) for $j=0$ (s and d orbitals) and Eq. (9) for $j=1$ (p orbitals). These equations are special cases of Eq. (24) showed in paper by Odžak and Milošević (2009). This formula contains the ratio of the sum of the dipole matrix

elements with even and odd atomic orbitals whose linear combination forms the molecular orbital from which the high harmonics are emitted. We have shown that the destructive interference of even and odd partial recombination amplitudes is responsible for the observed minima (Odžak and Milošević, 2009). In the upper left panel of Fig. 4 the interference structure is blurred. Here, in our calculation we also include T -matrix element in the direction perpendicular to the laser polarization axis (Odžak and Milošević, 2010). This component has a big influence on the HHG spectrum of N_2 molecule that is on the interference structure appearing in the corresponding HHG spectrum. In other words, including perpendicular component of T -matrix element leads to washing out of clear interference minima structure (Odžak and Milošević, 2010; Odžak and Milošević, 2011).

Now, we are going to show HHG spectra of O_2 . Since the main contribution to the $1\pi_g$ HOMO of the O_2 molecule comes from the p atomic orbitals, we expect that the interference minima will appear for higher harmonic orders, i.e., higher laser intensities are needed to observe these minima (see the upper panel of Fig. 5). The laser intensity is $5.0 \times 10^{14} \text{ W/cm}^2$, which is higher than that used in experiment presented in Fig. 4. The wavelength is not changed. Again, only the combinations with the undressed final state lead to clear interference minima. In the total spectrum perpendicular component of T -matrix element was included.

Furthermore, these interference minima are very well described by Eq. (10) for $j=-1$ (bottom panel). In the total HHG spectrum of O_2 one can see that the influence of the perpendicular component of the T -matrix element is less pronounced and the interference structure is more clearly visible than in the N_2 case.

CONCLUSIONS

In this paper we have presented various numerical results for HATI and HHG of molecular systems characterized by different symmetry.

The results are obtained using our improved MSFA theory. We have predicted dramatic differences between the high-energy plateaus in the angle-resolved electron and photon spectra for different molecules. Also, the most noticeable feature of the molecular HATI and HHG spectra is the existence of minima that are absent in the atomic case. We have derived an analytical formula for their position for both

considered processes. Influence of internuclear distance as well as of different atomic orbitals on the position of the minima is considered.

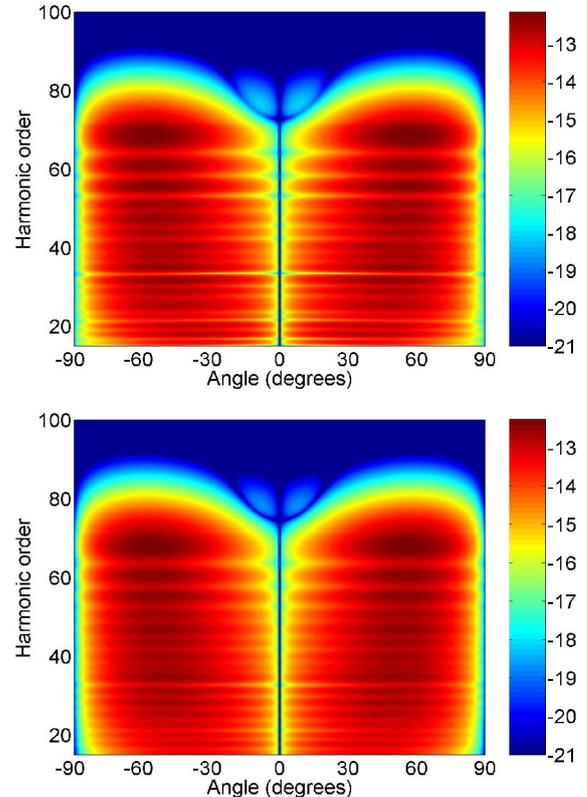


Figure 5. As in the previous figure, but now for O_2 and intensity of $5.0 \times 10^{14} \text{ W/cm}^2$. In the upper panel we use p , d , and f atomic orbitals, while in the bottom panel only p orbitals are taken into account.

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Summary/Sažetak

U ovome radu istražujemo procese jonizacije iznad praga višeg reda (eng. HATI) i generacije viših harmonika (eng. HHG) na dvoatomskim molekulama karakterisanih različitom simetrijom u jakom laserskom polju. Pri analizi je korištena modifikovana molekularna aproksimacija jakog polja (eng. MSFA). U radu smo predstavili rezultate za nekoliko molekula: N_2 , O_2 , H_2 i Ar_2 . Njihove najviše zaposjednute molekularne orbitale (eng. HOMO) su karakterisane $3\sigma_g$, $1\pi_g$, $1\sigma_g$ i $5\sigma_u$ simetrijom, respektivno. Analizirajući dobivene HATI i HHG spektre za različite orijentacije pomenutih molekula u odnosu na osu polarizacije laserskog polja, te za različite vrijednosti energije emitovanih elektrona i fotona, kao i odgovarajućeg ugla emisije, moguće je izvesti određene zaključke o samoj strukturi posmatranih molekula. Najznačajnija crta dobivenih molekularnih spektara su minimumi koji su odsutni atomskom slučaju.



Comparison of x-ray fluorescent analysis and cupellation method for determination of gold in gold jewellery alloy

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Article info

Received: 06/12/2011

Accepted: 25/01/2012

Keywords:

Gold alloys

Jewellery

X-ray fluorescent analysis

Cupellation

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Abstract: To make jewellery of gold, gold is alloyed with other metals. It is of great importance to accurately determine the total amount of pure gold in alloys used for making the jewellery and in jewellery made of gold, because it determines its value on the market. Several analytical methods are used for this purpose. This study was based on comparison of results of analysis of gold alloy for 14-carat jewellery obtained by non-destructive fluorescent analysis method and destructive cupellation method. The null hypothesis with 95 % confidence level on equivalence in measurement precision of percent by percent mass of gold in three very similar gold alloy samples in reproducibility conditions (three measurement series) for standard cupellation method and the method compared (validated), XRF method, has been confirmed. F-test did not confirm null hypothesis on precision equivalence for two mentioned analysis methods. There is a significant difference in variance values. However, the t-test was carried out, which verified the null hypothesis on equivalence between mean values of results achieved in two compared values. In order to confirm applicability of two methods, Z_{score} was calculated giving values of less than 2, using statistical data from inter-laboratory program with 62 participating laboratories applying cupellation method, and 60 laboratories applying XRF method for analysis of gold alloy used in production of 14-carat jewellery.

INTRODUCTION

Gold is a chemical element that plays an important role in many industry branches, primarily in industry of valuable jewellery. Over 80 % of all pure gold produced is used in manufacturing of various adornments, jewellery and money. Gold is the type of metal that is too soft for jewellery production, thus is alloyed with other metals, usually with silver, copper, zinc, nickel, palladium, iridium, etc. nickel and palladium are used for white gold alloys. Consequently gold jewellery is never made of gold only. Percentage of gold in jewellery alloys and jewellery itself is usually expressed in carats or degree of fineness (purity). According to these markers pure gold is defined as 24 carat gold. If an alloy is marked as 18-carat gold that means it contains 18 parts of gold and 6 parts of one metal or a number of other metals. The degree of gold fineness

describes the number of gold parts in 1000 parts of alloy. According to this mark, 18-carat gold is 750 fineness, which means that it has 750 parts of gold in 1000 parts of alloy, i.e. there is 75% of gold in alloy. Nowadays, jewellery available in the market is of 375; 585; 750; 915 and 999 fineness. It is very important to accurately determine the total amount of pure gold in alloys used for jewellery production and in jewellery made of gold, because their market worth is determined on that value.

There are several methods in jewellery industry dealing with quantitative determination of gold in alloys for jewellery production, that are based on determination of fineness or caratage of gold. Which method will be used depends on several factors, but most important one is measurement accuracy and precision of the respective method. In addition, the cost of measurement method and

device used for a specific analysis plays an important role in selecting the method of analysis.

Nowadays, analytical methods used for quantitative gold analyses are the following: stone probe (Walchi and Vuilleumier, 1991; Eluere, 1986; Oddy, 1983) which is practically a non-destructive method used for determination of gold parts with 1-2 % deviation; cupellation method (ISO/ 11426: 1997), which is a destructive method, also used for determination of gold parts but with a deviation under 0,02 %, spectrometric methods, primarily inductively coupled plasma (Wu *et al.*, 2004; Juvonen *et al.*, 2002; Brill and Wiedemann, 1992) which is also a destructive method with deviation of 0,1 % but gives complete alloy analysis. Other, less accurate and less sensitive destructive spectroscopic methods – such as UV-VIS spectrophotometry (Balcerzak *et al.*, 2006; Chen *et al.*, 2006; Hu *et al.*, 2006; Zhao *et al.*, 2006; Gao *et al.*, 2005; Gangadharappa *et al.*, 2004; Melwanki *et al.*, 2002; Fujita *et al.*, 1999; Pal 1999; El-Zawawy *et al.*, 1995) atomic absorption spectrometry – flame and graphite furnace technique (Pyrzynska, 2005; Medved *et al.*, 2004; Petrović *et al.*, 2001) and, finally X-ray fluorescent analysis method (Jurado-Lopez *et al.*, 2006; Linke and Schreiner, 2000; Stankiewicz, 1998; Marucco and Stankiewicz, 1998) which is a non-destructive method with a deviation of 0,1 - 0,5 %, which is used for complete gold alloy analysis. Institute of Metrology B&H, in their precious metals quality control laboratory, determines fineness of gold in golden jewellery that is available on market in Bosnia and Herzegovina. The test method that is commonly used for such purposes is cupellation method or, so called, fire assay. By this method, the sample is melted at high temperature and dissolved in nitric acid, that destructs the sample. Consequently this method is not considered practical, since jewellery pieces are expensive. That is why an introduction of a new method was necessary; x-ray fluorescent analysis, which does not destroy samples and is precise enough to determine fineness of gold.

The aim of this study was to compare results of measurements of percent by mass of gold in golden alloys, used in jewellery production, measured by x-ray fluorescent analysis and cupellation method. Based on the results, we estimated the accuracy and precision of instruments for x-ray fluorescent analysis, excluding systematic error. For this purpose, two samples of 14-carat yellow gold were analyzed and in addition one sample, that was part of an inter-laboratory comparison, in which Institute of Metrology B&H participated, was analyzed.

EXPERIMENTAL

EXPERIMENTAL

Test equipment

To determine the percent by mass of gold present in golden jewellery alloy by X-ray fluorescent analysis, Oxford Instruments *CFI 900* spectrometer was used, with collimator 0,3 and “Multichannel proportionate counter filled with Xe” detector. The x-ray source was 50W (50kV and 1.0 mA); Tungsten anode tube. The instrument has a digital multichannel analyzer with automatic signal processing, including automatic correction parameters. Instrument is equipped with SmartLink Fundamental Parameters software and Statistic and Report Generator software.

Mass measurement was carried out on the analytical electronic balance, Sartorius AG, *LE224S*±0.1 mg. Laboratory furnace Nabertherm, *L 5/13 / B 170* with temperature range 30⁰C – 1300⁰C was used for scorification of samples. In addition, during the application of the cupellation method for determination of percent by mass of gold in samples the following equipment was used: cupels, plate rolling machine, sand bath, Kjeldahls flasks, and crucibles for assays.

Chemicals and reagents:

Silver of 99,998 % purity (*Alfa Aesar*, USA), was used for quartering gold alloys and everything was melted with lead of 99,9 % purity (*Sigma Aldrich*, Germany). Melted material was dissolved in a solution prepared from 65 % HNO₃, (*Fluka*, Germany). To prepare the blank, Austria gold of 99,998 % purity (*Ogussa*), was used. Redistilled water of 0.06 µS/cm conductivity was used in preparation of all solutions.

Analytical Quality Control

Quality assurance (QA) was achieved by: adequate apparatuses with the required measurement precision, chemicals and metals (Ag and Pb) of high degree of purity and series of certified reference materials (CRMs) by competent American manufacturer *X-calibur XRF service* listed in Table 1.

Table 1. Certified Reference Materials, *X-calibur XRF service*

CRM No	Content						
	Au (%)	Ag (%)	Cu (%)	Zn (%)	Ni (%)	In (%)	Pd (%)
14KY 84	58.43	7.63	29.23	4.71	-	-	-
14KY 820	58.34	4.91	30.33	6.42	-	-	-
14KY 270	58.36	7.26	28.64	5.74	-	-	-
14KY 290	58.39	12.82	24.50	4.29	-	-	-
14KY UA1	58.43	9.51	28.20	3.65	-	0.21	-
14KY VHF3	58.47	4.85	29.98	6.70	-	-	-
14KG 570	58.34	35.03	6.43	0.20	-	-	-

Samples

Two series of samples of analyzed: (a) two different samples of 14-carat yellow gold in form of metal plates; (b) a sample of 14-carat yellow gold that was a part of international inter-laboratory comparison program.

Analysis of Samples by Cupellation Method

Determination of percent by mass of gold in gold alloys by cupellation method was performed by standardized ISO 11426:1997 method. Despite the fact that cupellation is one of the oldest methods of gold fineness determination, it provides very accurate results, which makes it the most used method, provided that sample destruction is not a problem.

To determine percent by mass of gold in alloy by cupellation method, two different samples of gold alloy were used (585 fineness) and for each sample, a series of 10 analyses was performed under conditions assuring repeatability. For that purpose, samples of 0.22 – 0.23 g were weighed on an analytical balance with accuracy ± 0.1 mg. Samples were wrapped into lead foils, weighing

approximately 6 grams each. Pure silver (approximately 0,3 g) was added to each sample. The mass of silver was 2,5-3 times higher than mass of gold in alloy, depending on gold fineness. In the process of adding silver, attention was given to amount of gold already present in the alloy. The samples were compressed into tight balls and placed into preheated furnace cupels. The temperature in the furnace was maintained at $1065 \pm 1^\circ\text{C}$ for approximately 25 minutes under oxidizing conditions. Cupel surface absorbs alloying metals, whereas precious metals remain on the cupel surface in form of metal beads. After cooling to room temperature, beads were rolled with rolling machine into 0.12-0.15 mm thick strips, rolled again into cornets.

Separating gold from silver

As analyzed samples contained no other precious metals, the next step was separation of silver from gold. For this purpose, strips were dissolved in nitric acid, whereby the silver was dissolved, while the gold remained undissolved.

Cornet samples were immersed in 20 mL nitric acid (33 %) preheated in 100 mL Kjehldals flasks at a temperature below the boiling point (at least 5°C below), and brought to the boil. The solution was left to boil around 15 minutes, i.e. until the evolution of nitrous fumes had ceased. The solution was then decanted, cornets washed with redistilled water and 20 mL of nitric acid (49 %) was added. Gentle boiling was continued for 15 minutes. The procedure of dissolution with 49 % acid was repeated twice. The solution was decanted; pure gold cornets were washed in warm redistilled water (60°C - 70°C) and finally transferred into crucibles. They were annealed at 750°C around 5 minutes, cooled and weighed. Results showing percent by mass of gold in alloy are presented in promilles (‰) for two different samples in series of 10 repeated analysis each obtained by cupellation method are presented in Table 2.

Analysis of Samples by X-ray Fluorescent Analysis

To determine percent by mass of gold in alloys using x-ray fluorescent analysis method, the same samples of gold alloy, fineness 585, which were analyzed by cupellation method, were used here. Analyses were repeated ten times. It is a known fact that fluorescence intensity is proportional to mass part of all components present in the sample. Relying on that fact, the concentration of elements in samples was determined by comparing results of sample analysis with results obtained by previous analysis of compatible certified reference materials with known quantitative composition of metals. In this case, relevant *calibration files* were stored into the software of the instrument, which were obtained by measuring the fluorescence intensity for each metal in CRM and in these files a relation was established between the received signal (number of impulses per second) of analyzed sample and CRM signal.

Results showing percent by mass of gold in alloy were presented in promilles (‰) for two different samples and 10 repetitions using x-ray fluorescent analysis method are presented in Table 2.

The second batch analysis was conducted on a sample that was the testing sample of inter-laboratory comparison, i.e. inter-laboratory program of testing precious metals alloy. The program was organized by IAAO (*International Association of Assay Offices*) and HMC (Hallmarking Convention). Laboratory for Precious Metals of B&H Institute of Metrology took part in this program. The

program was identified as *Round Robin No. 22* and included analysis of two samples of 14-carat yellow gold (sample ID: RR-22) by methods of x-ray fluorescent analysis and cupellation. Analyses were repeated four times, in line with participation protocol of inter-laboratory comparison.

Analyses results, expressed as percent by mass of gold in alloy, presented in promilles (‰) are shown in Table 2.

RESULTS AND DISCUSSION

Analyzed results presenting percent by mass of gold in alloys used to make 14-carat jewellery by cupellation method and x-ray fluorescent analysis are shown in Table 2. We can conclude that there is little variation in results obtained by cupellation method for all three samples. The difference is shown on the first decimal place for results expressed in promilles. Results obtained by XRF method for all three samples vary to a part of promille.

Table 2. Results of percent by mass of gold in gold alloys for production of 14-carat jewellery obtained by cupellation method and x-ray fluorescent analysis method for 10 and 4 repetitions respectively, expressed in promilles (‰).

	IRM ¹ -1		IRM-2		ILC ²	
	KUP ³	XRF ⁴	KUP	XRF	KUP	XRF
	588.5	588.0	583.9	582.5	588.2	589.0
	588.8	585.3	583.0	584.2	587.6	582.4
	588.4	588.9	583.9	588.4	588.2	588.2
	588.6	587.1	583.5	585.1	587.7	589.9
<i>Au</i> (‰)	588.4	588.8	583.3	583.9		
	588.3	586.8	583.5	585.6		
	588.8	587.8	583.7	582.0		
	588.7	586.4	583.5	587.0		
	588.9	588.5	583.4	586.7		
	588.4	585.6	583.3	582.1		

¹Internal Reference Material; ²International Inter-laboratory comparisons; ³Cupellation Method; ⁴X-ray Fluorescent Analysis Method

For comparison of two analysis methods F- test and Student t-test were performed. To perform this tests the following condition were met: (a) Possession of the reference test method (cupellation method); (b) Multiple testing of at least one sample by the new method and reference method in terms of repeatability.

To calculate the F-test and t-test, the following parameters were previously calculated: mean value of series of measurement (\bar{X}) for each individual sample, standard deviation for a series of repeated measurements (s), pooled standard deviation (S_c). They are shown in Table 5.

Verification of the null hypothesis on absence of significant differences in methods precision

Statistical data, relevant for verification of the null hypothesis on equivalence in precision of measurement by the same method in three very similar test samples in comparable conditions (different analyses time) are presented in tables 3 and 4. All comparisons were performed with 95 % confidence level.

Table 3. Statistical parameters for reproducibility of cupellation method

	KUP1	KUP2	KUP3
No. of measurements	10	10	4
Standard deviation (S)	0.210	0.279	0.320
F1 ex (2/1)		1.76	
F2 ex (3/2)		1.32	
F3 ex (3/1)		2.32	
F _{tab} (95 %)	F1(9 ; 9) 3.18	F2(3 ; 9) 3.86	F3(3 ; 9) 3.86

Table 4. Statistical parameters for reproducibility of XRF method

	XRF1	XRF2	XRF3
No. of measurements	10	10	4
Standard deviation (S)	1.290	2.221	3.389
F1 ex (2/1)		2.96	
F2 ex (3/2)		2.32	
F3 ex (3/1)		6.90	
F _{tab} (95 %)	F1(9 ; 9) 3.18	F2(3 ; 9) 3.86	F3(3 ; 9) 3.86

The null hypothesis on equivalence in measurement precision with 95 % confidence level was tested in following cases: (a) Contents of gold, using one method (CUP) for three selected samples (three measurement series); (b) Contents of gold, using one method (XRF) for three selected samples (three measurement series).

One of the following hypotheses was to be confirmed: H_0 ; there is no significant difference in precision if $F_{tab} > F_{exp}$; H_1 ; there is significant difference in precision if $F_{tab} < F_{exp}$.

Experiments confirmed null hypothesis on equivalence in precision of measuring mass of gold in three very similar samples of gold alloy in conditions of reproducibility (three measurement series) by standard cupellation method. The null hypothesis on equivalence in precision of determining parts of gold in conditions of reproducibility, using comparison (validation) method of X-ray fluorescent analysis (XRF) was also confirmed. In one of the three measurement series there was $F_{tab} < F_{exp}$ (by comparison of the third and the first measurement batch variances), which can be attributed to the random error effect.

Verification of the null hypothesis on absence of significant difference in results means value for two methods

The results of analyses of percent by mass of gold in alloys obtained by utilizing two analysis methods, CUP and XRF, for three measurement series in repeatability conditions were compared.

F-test did not confirm the null hypothesis on precision equivalence for two mentioned analysis methods. There is significant difference in variance values. Increased variance values are obvious for XRF methods (for all measurement series), which indicates reduced precision in results obtained through application of this method.

Although the null hypothesis on equivalence for two compared methods was not confirmed, t-test was taken for verification of the null hypothesis on equivalence between mean values of results for two measurement series (of two analysis methods) in repeatability conditions.

Table 5. Values of relevant statistical parameters for comparison of two methods

N	IRM-1		IRM-2		ILC	
	10	10	10	10	4	4
\bar{X} (%)	588.6	587.3	583.5	584.6	587.9	587.4
S	0.210	1.290	0.279	2.221	0.320	3.389
Sc	0.92		1.58		2.40	
F _{exp} (95 %)	37.7		63.4		112.2	
F _{tab} (95 %)	3.18		3.18		9.28	
t _{exp} (95 %)	3.16		1.56		0.29	
t _{tab} (95 %)	2.10		2.10		2.45	

One of the following hypotheses was to be confirmed: H_0 ; there is no significant difference in mean values if $t_{tab} > t_{exp}$; H_1 ; there is significant difference in mean values if $t_{tab} < t_{exp}$.

The null hypothesis on equivalence between mean values of results achieved by two compared methods – cupellation method and XRF – has been confirmed.

In one of three measurement series there was $t_{tab} < t_{exp}$ (by comparison of the third and the first measurement batch values), which can be attributed to the random error effect.

By comparing t-values (t_{ex}) for all three samples with critical value (t_{tab}), obtained from table data for the Student's t distribution for n_1+n_2-2 degrees of freedom and 95 % confidence level, we can conclude that XRF method results in adequate precision. The method has been confirmed only for the alloy type used in making 14-carat yellow gold. For all other types of alloy, the same or similar procedure should be repeated in order to confirm that the method does not cause systematic error in relation to the relevant reference method.

ILC Results Analysis

Statistic interpretation of data from inter-laboratory program was performed by the organizer laboratory (*Swiss Assay Office*) in accordance with ISO 5725-5:1998. The following statistic parameters were calculated: Mean value (\bar{X}) of results for each laboratory individually and all participating laboratories, standard deviation (s) of results for each laboratory individually and all participating laboratories, population mean (μ) of the mean value of all results of participating laboratories, standard deviation of reproducibility (σ_{Repro}) of all participating laboratories results (*note: only laboratories whose results were within the interval of $\mu \pm 10 \cdot \sigma_{Repro}$ were considered*). Z-values for each participating laboratory were calculated from obtained statistical data shown in Table 6, according to ISO Guide 43-1- Proficiency testing by inter-laboratory comparisons, excluding all results which were outside acceptable interval.

$$Z_{SCORE} = \frac{\bar{X}_{LAB} - \mu}{\delta_{REPRO}}$$

The mentioned parameters were determined for x-ray fluorescent analysis method and cupellation method separately. Results of statistical analysis of data collected via *Round Robin No 22 program* were presented in Table 6. All presented data indicate that calculated Z_{score} values are

less than 2, meaning that laboratory results for both methods applied are satisfactory.

This indirectly confirmed the validation procedure applied for 14-carat yellow gold alloys.

Table 6. Analysis of ILC results

Parameters		KUP	XRF
No. of participating laboratories	p	62	60
Set value (%) ± standard deviation of reproducibility	$\mu \pm \sigma_{\text{Repro}}$	588.02±0.27	587.93±2.80
Mean value of precious metals laboratory (%)	\bar{X}	587.93	587.38
Z value of precious metals laboratory	Z_{score}	-0.35	-0.23

CONCLUSIONS

Analysis of gold alloy for 14-carat jewellery was performed via two distinct analysis methods, destructive standardized cupellation method and non-destructive XRF method.

The null hypothesis with 95% confidence level on equivalence in measurement precision of percent by mass of gold in three very similar gold alloy samples in reproducibility conditions (three measurement series) has been confirmed, for standard cupellation method and the method compared (validated), XRF method.

F-test did not confirm the null hypothesis on precision equivalence for two mentioned analysis methods. There is significant difference in variance values. Although the null hypothesis on equivalence for two compared methods was not verified, t-test was taken, verifying the null hypothesis on equivalence between mean values of results achieved in two compared values.

Satisfactory results of both methods in terms of the mentioned analysis were confirmed by calculating the Z_{score} , the value that was significantly below two (2), for statistical data from inter-laboratory program with 62 participating laboratories, applying cupellation method and 60 laboratories applying XRF method of analysis of gold alloy used in production of 14-carat jewellery.

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Summary/Sažetak

Preko 80 % od cjelokupne količine dobivenog čistog zlata koristi se za proizvodnju raznih ukrasa, nakita i novca. Zlato je metal koji je previše mekan da bi se kao takav koristio za izradu nakita, zbog čega se legira sa drugim metalima. Od velike je važnosti tačno odrediti ukupnu količinu čistog zlata u legurama za izradu nakita i u nakitu jer to određuje njihovu vrijednost na tržištu.

Poznato je više analitičkih metoda kako destruktivnih tako i nedestruktivnih za kvantitativnu analizu zlata. U ovom radu poređeni su rezultati analize legura zlata za 14-karatni nakit dobiveni nedestruktivnom metodom rendgenske fluorescentne analize i destruktivnom metodom kupelacije.

Potvrđena je nulta hipoteza uz 95 % nivoa povjerenja o jednakosti u preciznosti mjerenja masenog udjela zlata iz tri vrlo slična uzorka legure zlata u uslovima obnovljivosti (tri serije mjerenja), kako za standardnu metodu kupelacije, tako i za metodu koja se komparira (validira), metodu rendgenske fluorescentne analize.

F-testom nije potvrđena nulta hipoteza o jednakosti u preciznosti za dvije navedene metode analize. Postoji signifikantna razlika u vrijednostima varijansi. Iako nije potvrđena nulta hipoteza o jednakosti preciznosti za dvije metode koje se kompariraju, proveden je t-test kojim je potvrđena nulta hipoteza o jednakosti srednjih vrijednosti rezultata dobijenih po dvije komparirane metode.

Za potvrđivanje primjenjivosti dvije metode izračunata je vrijednost Z_{score} koja je bila znatno manja od dva (2), za statističke podatke iz interlaboratorijskog programa u kome su učestvovala 62 laboratorije sa primjenom metode kupelacije i 60 laboratorija primjenjujući XRF metodu analize legura zlata za izradu 14-karatnog nakita.



Electrochemical characteristics of welded joints on stainless steel in maritime atmosphere

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Article info

Received: 10/11/2011

Accepted: 26/01/2012

Keywords:

Stainless steel

Seawater

Welding

Corrosion

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Abstract: Maritime atmosphere represents the corrosion environment characterized by air saturated with chloride. Many different factors affect the quality of welded joint and the material around it. In case of welding of steel structures, those factors include selection of the welding process, an additional electrode material, and type of lining. Stainless steel is used for different equipment that is exposed to sea water. Connecting those parts together is done by welding method whose quality depends on a number of factors. Some of those factors are investigated in this study. Samples used in experiments are X5CrNi 18-10ASTMAISI304 stainless steel sheets of austenitic type. This sheet is welded in two different ways: manual arc welding in a protective atmosphere of argon and manual arc welding with covered rutile electrode. Corrosion characteristics have been investigated for three distinct zones: zone of welded joint itself, zone in the vicinity of welded joint and zone far from welded joint (basic material). Tests were performed in 0.9% and 3% NaCl solution, as well as in sea water samples from the area of Dubrovnik and Ploče (brackish water). Electrochemical study has been performed by means of potentiodynamic polarization between -0,150 V and 0,350V vs. saturated Ag/AgCl electrode. Results obtained for X5CrNi18-10 austenitic steel and its welded parts in different media at room temperature indicate some degree of self-passivation along with uniform corrosion processes. Based on the obtained results, we concluded that values of corrosion potential lie between 0.350V and -0.150V, depending on the environment in which each sample is probed. In the case of sample welded with dross, increase of corrosion rate does not follow increment of chloride concentration in the expected extent. Corrosion processes are mostly located on the ZUT-OM interface. For the majority of samples, welding in argon atmosphere proved to be a more acceptable way of processing metals from the aspect of corrosion resistance.

INTRODUCTION

Atmospheric corrosion is the most common form of corrosion, and it is defined as the degradation of materials exposed to air and pollution in the air. The most important factor of atmospheric corrosion is appearance of the damp in the form of rain, dew, condensation or high relative air humidity. Corrosion is enhanced by the appearance of dew

and condensation of moisture on the metal surface, especially if they are not followed by frequent washing rains which dilute or eliminate pollutants.

Sea atmosphere, characterized by the air saturated with chloride, represents corrosion environment at sea and near to sea. Sea atmosphere can be extended to a certain distance into continent depending of the topography and dominant wind direction. Depositing particles of sea salt on the metal

surface play an important role in atmospheric corrosion in sea atmosphere. The speed of deposition of NaCl is higher than 15mg/m² daily. Besides that, there are many different chemical loads which make the situation worse, on local level (urban centers, industry etc.). There are studies which examined the corrosion caused by the deposited particles of NaCl, KCl, Na₂SO₄, MgCl₂ i CaCl₂. These salts are also found in sea water and they were identified in sediment on the metal surface (Juraga, Alar, Šimunović, Stojanović, 2007). A thin film of dew, saturated with sea salt or acidic sulfates and acid chloride in an industrial atmosphere, is an aggressive electrolyte that causes corrosion. Wet areas cause condensation of damp on metal surfaces during the night.

Aerosols may occur in two ways: by ejection of particles from the sea surface (sea fog, wind-dispersed dust), or by physical and chemical processes in the atmosphere (secondary aerosols) (<http://www.euro-inox.org>). Stainless steels have become considerably more resistant to aggressive liquids with the growing contents of chromium and molybdenum

Welding is a technological process that forms a monolithic inseparable welded joints by establishing internal connections between particles (atoms, ions, molecules) through local or full heating or plastic deformation or through joint action of both heating and plastic deformation (Pejović, Tomić, Mičić M, Pavlović , 2009).

Electric arc occurs between the work piece and the electrode which can be expendable or inert electrode. In the case of arc welding with protective gas (GMA), the electrode is in the form of wire and metal bath is protected by an inert gas. In case of arc welding by opened arc with covered electrode (SMA), the protective gas is generated by burning the electrode coverings. Trough burning of the cover, dross is formed with a number of additional changes of the area which taken together protect the melt from oxidation. The choice of the electrode is dependable on the types of materials that will be welded and of the welding method. The protective gas is used for majority of welding methods to prevent contamination and oxidation of welded joints, especially for welding of stainless steel, which rapidly oxidized at high temperatures.

The composition of the welded joint included welded seam, zone of base metal with structural and other changes that occurred during the heating (heat-affected zone), and border part of the base metal that has not changed under the welding heat.

Many different factors affect the quality of the weld and materials around it, including the selection of the welding process, the amount and concentration of heat input, weldability of the base material, an additional electrode material, and type of covering, weld geometry and interaction of all these factors.

Heat-affected zone (ZUT) is part of basic material located next to zone of melting. Crystal structure and mechanical properties have been changed by amount of heat introduced by welding in zone of heat impact. Heat-affected zone depends on the heat input and it is usually tight circa 2-8mm. The structure of metal, voltage and thermal gradient change because of the influence of high temperatures in welding processes. Chemical inhomogeneity is often present. Properties of welded joint also depend on the way of welding. Various welding processes produce different microstructures of welded joint and different heat-affected zones. All this factors affect the corrosion behavior of

welded joints (Pejović, Tomić, Mičić, Pavlović, 2009.; <http://www.aston-inox.com>; Pejović B. Tomić, Mičić, 2007). During the welding, partial oxidation often occurs on the surface in the heat-affected zone which is manifested by heat tinting at high temperatures. These oxide films can considerably reduce the corrosion resistance of welded joints so it is necessary to either prevent their formation or remove them if they are formed after welding.

Research objectivities of the present work were: (a) To monitor the corrosion processes occurring on the parts of welded stainless steel; (b) To define types of corrosion attack in certain simulated corrosion conditions; (c) To define the zone in which it corrosion appears in certain corrosion conditions; and (d) To determine the corrosion rate.

EXPERIMENTAL

Material and methods

Samples of stainless steel X5CrNi18-10 ASTM AISI304 of austenitic type are used for the experiments. This sheet was welded in two ways: (a) Manual arc welding in a protective atmosphere of argon, by the electrodes ISO W 19 9 Lsi (Kulušić, Krstulović, Ivić, 2002); (b) Manual arc welding with covered rutile electrode E 19 9 LR 12 (www.pfst.hr/data/materijali/skripta%20Zastita%20materijala.doc). Working electrodes were made according to the sketch in Figure 1 (Kozica, Korać, Cacan, 2011).

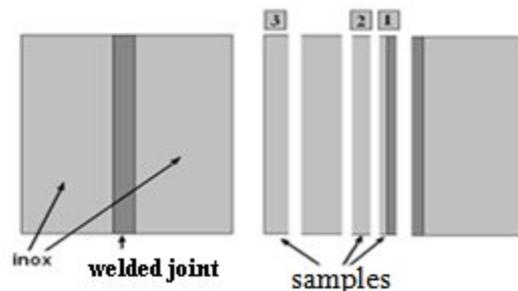


Figure 1: Sketch of the position of samples of working electrodes on the weld.

Sample 1 was cut out so that it includes the border of the weld and metal, sample 2 is a piece of metal close to the weld, and sample 3 was cut out in that way that metal area was 2.5 cm apart from welding. Samples of clean electrodes were also prepared. Dimensions of the electrodes were 2.5 mm × 2 mm. Investigation was done on Potentiostat/Galvanostat 263 A (Princeton Applied Research). Samples of the test material were used as the working electrodes.

As a reference electrode, platinum electrode was placed symmetrically opposed to the working electrode in order for achieving equal distribution of current flux.

All working electrodes were protected by Teflon tape before the start of experiment. The surface of working electrode exposed to solution was defined and the surface was mechanically treated with sand paper of different fineness, from 200 to 1000. Grease was removed from prepared surfaces with ethanol and acetone, and washed with distilled and re-distilled water. Next the surface was activated with a mixture of 30% H₂O₂ and concentrated H₂SO₄ (1:1, v/v) and then washed with distilled water and

re-distilled water. Immediately after the treatment of a surface, the electrode was placed in the prepared electrochemical cell. The corrosion characteristics of already mentioned samples in 0.9% and 3% NaCl solution, as well as in sea water from the area of Dubrovnik and Ploče, Croatia were analyzed. All measurements were conducted at 25±0.5°C.

RESULTS AND DISCUSSION

The values of corrosion potential, corrosion current and calculated corrosion rate were determined from voltammograms presented here (Figure 2 and 3).

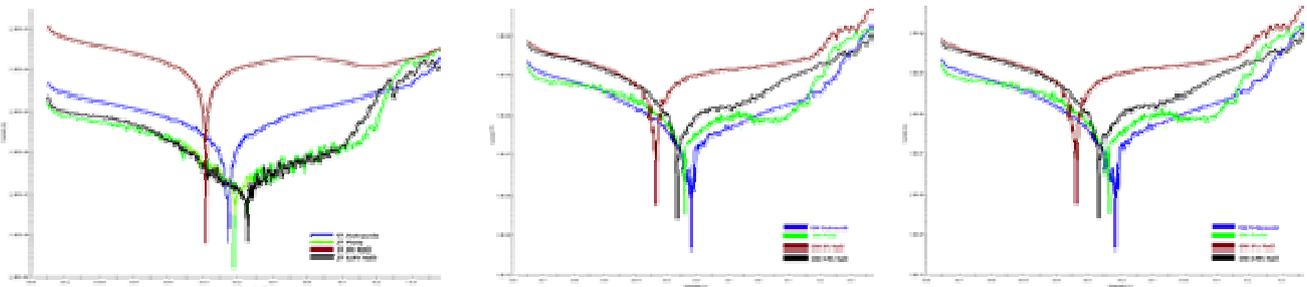


Figure 2. Voltammograms of samples after the welding with argon.

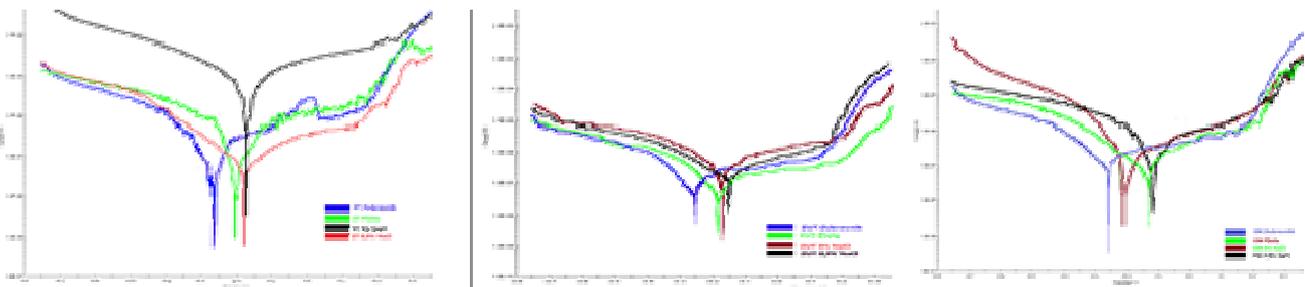


Figure 3. Voltammograms of samples after the welding with dross.

Corrosion potentials (Figure 4), Tafel constants (β_A and β_K) and polarization resistance can be determined from voltammograms obtained by potential-dynamic recordings in different mediums.

Corrosion rate was calculated using the formula:

$$v_{corr} [mm / god] = \frac{0,13 \cdot i_{corr} \cdot M(Fe)}{\rho(Fe) \cdot z} \cdot 25,4$$

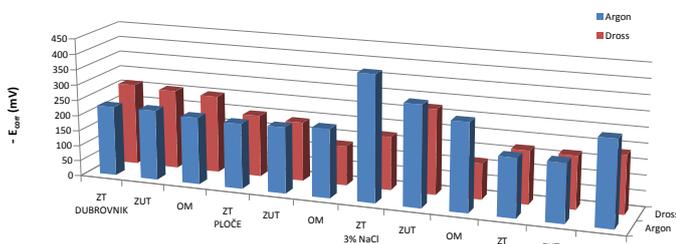


Figure 4. Corrosion potential depending on the sample and ways of welding in different corrosion environments.

Severity of the corrosion current (Figures 5 and 6) was calculated according to the formula:

$$i_{corr} = \frac{\beta_A \cdot \beta_K}{2,3 \cdot (\beta_A + \beta_K)} \cdot \frac{\Delta i}{\Delta E}$$

The highest corrosion instability was found in the sample with heat-affected zone (ZUT) in the case of welding by using dross.

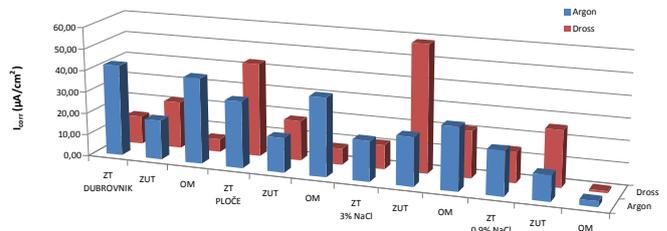


Figure 5. Corrosion current depending on the sample and ways of welding in different corrosion environments.

Expected change of corrosion rate is not present in the case of welding in argon atmosphere, but it can be concluded that melting zone (ZT) suffers heat impact approximately as heat-affected zone (ZUT). The basic material (OM) is generally spared of the corrosive degradation in the case of welding by using dross.

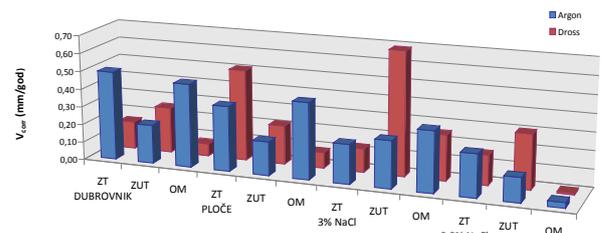


Figure 6. Corrosion rate depending on the sample and ways of welding in different corrosion environments.

Corrosion rate depending on the concentration of chloride ions

Increase in the concentration of chloride ions increases the corrosion rate, which is shown on Figure 7, while the influence of increasing concentrations of chloride is most notable in the sample that represents the base material.

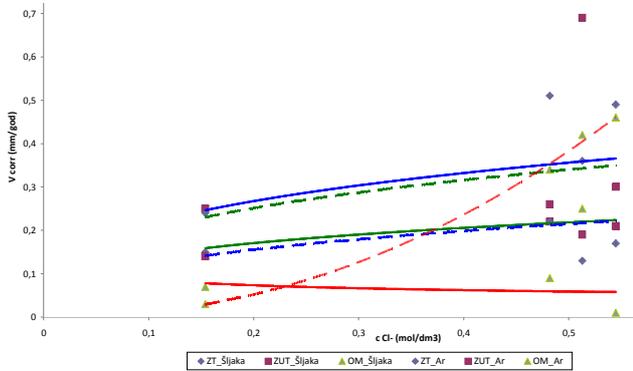


Figure 7. Corrosion rate depending on the concentration of chloride ions.

In the case of samples which are welded with dross, increase in concentration of chloride ions does not follow the expected increase of corrosion rate, so it can be concluded that corrosion in this case is affected by other ions present in water. A sample with heat-affected zone shows the strongest dependence of corrosion rate on chloride ions concentration. Steel plate Samples were tested to check the influence of sea water in coastal areas. Samples surface was mechanically treated with sand paper of different fineness, from 200 to 1000. Grease was removed from prepared surfaces with ethanol and acetone, then washed with distilled water. One sample was exposed to sea water that was in the form of finely dispersed aerosols. Spraying has been performed periodically during the period of four months. The second sample was submerged in 3% NaCl solution for a period of four months. Figures 8 and 9 show layouts of both samples before and after the effects of corrosive medium.

Staining and salt crystals have appeared during the spraying of the first sample with seawater aerosol in a period of 30 days. The next observed change was formation of small, hardly noticeable rust areas, with the characteristic brown-yellow color. The last detected change on metal was formation of small diameter dents and considerable expansion of rust (Figure 8).

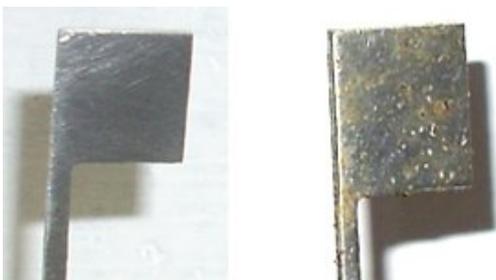


Figure 8. The steel samples sprayed with seawater aerosol.

Sample 2 was kept in the 3% NaCl solution for four months. Formation of coloration on the metal surface appeared first. After a while, the sediment of corrosion

products formed in the beaker where the sample was kept. Three months later, solution has become quite blurred, and any changes on the surface of the sample were difficult to detect. After removing the sample from the beaker, the surface was washed, with distilled water and wiped clean. The large holes on metal were observed that inevitably caused a large mass loss. It is noted that the edges were the most damaged parts, since they served as centers of corrosion (Figure 9).

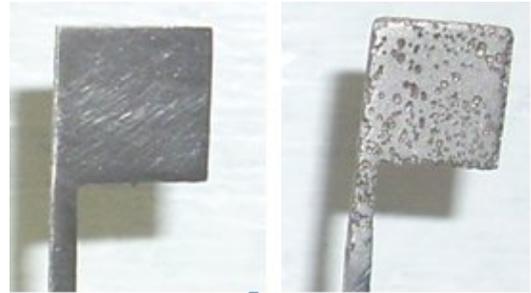


Figure 9. The steel samples submerged in 3% NaCl solution.

CONCLUSIONS

An electrochemical studies of austenitic steel X5CrNi18-10 and its welded parts in different media at room temperature, undoubtedly show that besides corrosive processes, self-passivation processes can occur.

Electrochemical behavior of welded material depends on the chemical stability and condition of the surface, as well as of the thickness and continuity of the formed passive film.

Based on the obtained results it is concluded that the ideal range of working potential varies from 0.350V to -0.150V, depending on the environment in which each sample is located.

Tafel diagrams were recorded in the range from -0.750V to 0.350V, which proved as acceptable because anode part voltamogram in this case is larger and enables making a conclusion about the ability of passivation of metals.

In the case of samples which were welded with dross, increase in concentration of chloride does not follow the expected increase of corrosion rate as expected, so it can be concluded that in this case corrosion affects other ions present in water as well.

Corrosion processes are mostly located on the border between ZUT-OM.

Welding in an atmosphere of argon for the majority of the samples proved as acceptable method of metal processing from the aspect of corrosion resistance.

Samples that represent a basic material, for both types of welding, show more positive corrosion potentials when compared with heat-influence zone and melt zone, also they show lower values of corrosion currents and higher polarization resistance.

The concentrations of chloride ions determined by Mohr method in brackish water from the port of Ploče and seawater from Dubrovnik amounts to 0.482mol/L and 0.513mol/L respectively. Corrosiveness of sea water is proved by the change of the surface sample 1. in experiment of the impact of seawater aerosols.

Corrosion rate increases with the increasing concentration of chloride ions, consequently the material decays faster.

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Summary/Sažetak

Morska atmosfera predstavlja korozionu sredinu koju karakteriše zrak zasićen hloridima. Kod zavarivanja čeličnih konstrukcija mnogo različitih faktora utiče na kvalitet vara i materijala oko njega, uključujući izbor procesa zavarivanja, dodatni materijal elektrode, vrsta obloge. Nehrdajući čelici se koriste za izradu instalacija i uređaja, koji se koriste u morskoj vodi. Spajanje dijelova takvih objekata izvodi se zavarivanjem na čiji kvalitet utiče valiki broj faktora, od kojih su neki istraživani u ovom radu. Za eksperimente su korišteni uzorci inox čeličnog lima X5CrNi18-10 AISI ASTM 304 austenitnog tipa. Ovaj lim je zavarivan na dva načina: ručnim elektrolučnim zavarivanjem u zaštitnoj atmosferi argona i, ručnim elektrolučnim zavarivanjem sa obloženom rutilnom elektrodom. Ispitivane su korozione osobine uzoraka vara, dijela do vara i osnovnog materijala u 0,9% i 3% rastvoru NaCl, kao i u morskoj vodi sa područja Dubrovnika i iz Ploča (bočata voda). Elektrohemijska ispitivanja uzoraka su izvršena potenciodinamičkom polarizacijom od -0,750V do 0,350V u odnosu na zasićenu Ag/AgCl elektrodu. Rezultati ovih ispitivanja austenitnog čelika X5CrNi18-10 i njegovih zavarenih dijelova u različitim medijima na sobnoj temperaturi pokazuju da, pored korozionih procesa, postoje i procesi samopasivacije. Na osnovu dobivenih rezultata se može vidjeti da se vrijednosti korozionih potencijala nalaze između -0,350V i -0,150V, zavisno od sredine u kojoj se pojedini uzorak nalazi. U slučaju uzorka koji je zavarivan sa šljakom porast koncentracije hlorida ne prati brzina korozije u očekivanoj mjeri. Korozijski procesu su pretežno locirani na granici ZUT-OM. Zavarivanje u atmosferi argona se kod većine uzoraka pokazalo kao prihvatljivijim načinom obrade metala s aspekta korozijske postojanosti.

Structure of blue copper proteins: electron-transfer kinetics of Cu(II/I) copper complex with macrocyclic ligand with N₂S₂ donor set

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Article info

Received: 09/01/2012
Accepted: 27/01/2012

Keywords:

Electron-transfer
Copper complexes
Blue copper proteins

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Abstract: In electron-transfer, the change in the oxidation state of the reactants is generally accompanied by structural changes, which influence the electron-transfer kinetics. Previous studies on the systems of Cu(II/I) complexes involving cyclic tetrathiaether ligands indicated that inversion of coordinated donor atoms may be a primary factor in controlling gated electron transfer. Complex formation and isomerization studies on [14]aneN₄ type complexes have demonstrated that coordinated N atoms are shown to invert since they must undergo a hydrogen abstraction prior to inversion. In the systems with [14]aneN_xS_{4-x} ligands, there is a choice of N or S inversion. This study has been conducted to determine the effect of inversion of coordinated N atoms on electron-transfer rates as a function of different concentrations of water as hydrogen ion acceptor existing in aprotic solvent (acetonitrile). Data on electron-transfer kinetics are presented here. Possible conformational changes and kinetics pathways for N-S mixed donor complexes are discussed.

INTRODUCTION

Copper proteins perform a variety of functions in biological systems including uptake, storage and release of electrons. The blue copper proteins are small proteins, with type 1 copper center close to the periphery of the protein. Based on structural work, the type 1 copper proteins, azurin and plastocyanin contain one copper ion which is strongly coordinated by the N^δ of two histidines and S^γ of cysteines, with elongated axial S (methionine) bond completing distorted tetrahedral environment (Figure 1).

A comparison of azurin (Cascella, Magistrato, Tavernelli, et al., 2006) with plastocyanin shows that the geometry is closer to a trigonal bipyramid, so azurin has weakly bound glutamine oxygen unlike plastocyanine. Active site in an enzyme is constrained by surrounding protein matrix to impose the distorted tetrahedral geometry that is normally favored by Cu(I) state resulting in a relatively high reduction potential of the type 1 copper sites, unique spectral properties and relatively high self-exchange rate constant. Number of studies attempted to explain this unique behavior of active metal center in blue copper proteins using complexes mimicking a structure and

geometry of the blue copper protein active site or computational methods.

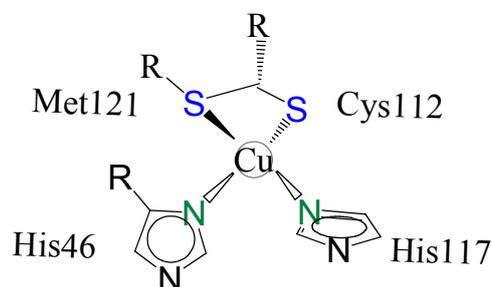
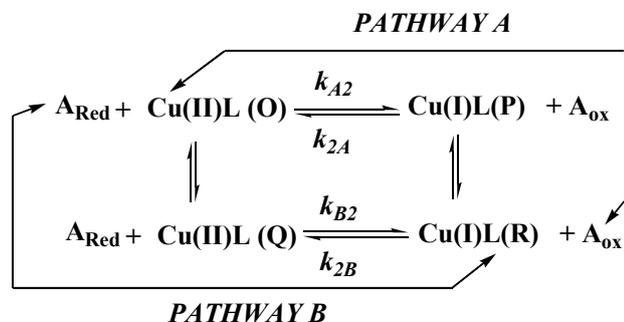


Figure 1. Structure of metal center in blue copper proteins.

Extensive studies on biomimetic complexes of copper (II/I) with tetrathiamacrocyclic ligands of different ring size attempted to elucidate this unique structure-function relationship. (Malkin and Malsmstrom, 1970; Randall, Gamelin, LaCroix, et al., 200; Valle, and Williams, 1968). The differences between the calculated self-exchange rate constants obtained from copper (II) reductions and copper (I) oxidations were several orders of magnitude. (Comba,

2000). To explain this behavior, a dual pathway square scheme was proposed which involves conformational changes of the reduced and oxidized form, preceded or followed by the electron-transfer. Comba, 2000, Solomon, Hare, and Gray, 1976; Gray, Malmstrom, and Williams, 2000). Dual-pathway square ET scheme mechanism was proposed to explain Cu(II/I) ET cross reactions (Scheme 1).



Scheme 1. Dual-pathway square scheme mechanism proposed for Cu(II/I) ET cross reactions (Dunn, Ochrymowycz, and Rorabacher, 1997).

Cu(II)L(A) and Cu(I)L(B) forms represent stable forms of two oxidation states, while Cu(II)L(Q) Cu(I)L(P) represent metastable intermediates with distorted geometry. A_{ox} and A_{red} are the oxidized and reduced forms of the counter reagent. Horizontal reactions symbolize electron transfer reactions, and vertical reactions conformational change processes. In the absence of conformational changes, electron transfer reactions will occur in a single step, resulting in specific rate constant for the two ET processes being equivalent. Thus, pathway A is preferred for the Cu(II)L reduction reaction, and Cu(I)L oxidation will follow Pathway A in the absence of conformation-limited behavior.

Conformational control in electron transfer kinetics of copper systems.(Comba,2000; Leggett, Dunn, Vande Linde, et al., 1993; Villeneuve, Schroeder, Ochrymowycz, et al.,1997) is highly dependable on donor atom inversion of ligands (N or S donors). Complex formation and isomerization studies on [14]ane N_4 type complexes have shown that coordinated N atoms are slow to invert since they must undergo a hydrogen ion abstraction prior to inversion, followed by donor atom rotation and reprotonation. By contrast, sulfur inversion requires sample rotation of the sulfur lone pair. In the systems with [14]ane N_xS_{4-x} ligands, (Figure 2), there is a choice of N or S inversion.

For the copper complex with [14]aneNS₃ ligand no nitrogen inversion is required for the conformational change from Cu(II)L to Cu(I)L. For other systems, with two nitrogen atoms each in the macrocycle, the different placement of the nitrogen is expected to cause unique electron-transfer kinetic behavior.

In this study, we focused on an investigation of the effect of the relative placement of nitrogen and sulfur atoms in the macrocyclic ring of [14]aneN₂S₂ ligand in copper (II/I) complexes (Figure 3) upon the electron-transfer rate constant as a function of water content acting as a proton acceptor in acetonitrile solution.

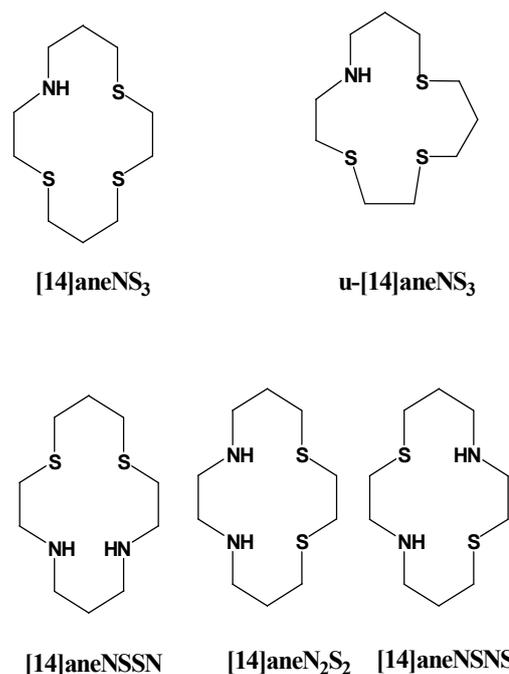


Figure 2. [14]ane N_xS_{4-x} ligands with different position of S and N atoms, resulting in distinguished kinetic behavior based on necessity of S and N donor atom inversion.

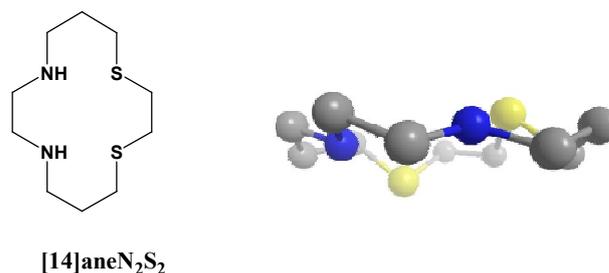


Figure 3. Structure of ligand with N and S donor sets obtained by using MM 2 force field energy minimization. Calculated steric energy was 15.13074 Kcal/mole. Blue balls represent N atoms, while yellow balls represent S atoms. Hydrogen atoms from structure were excluded because of clarity.

In the case of systems with one nitrogen donor atom, there is no need for the nitrogen to invert and, thus the water content in nonaqueous solution should have no effect on the kinetic behavior of these systems. For macrocycles containing two or more nitrogen donor atoms, the addition of a proton acceptor (water) might show changes in mechanistic behavior if one or more nitrogen atoms were required to invert. This is directly related on position of nitrogen atoms within macrocycle acting as a ligand in copper complex. Based on this line of reasoning, Cu (II/I) complexes with N₂S₂ macrocycle as a ligand studied in this work was expected to show different kinetic behavior reflecting the number of nitrogen required to invert during Cu(II/I) electron transfer. The electron-transfer kinetics of Cu(II/I) complexes with N₂S₂ ligands was investigated as a function of water content in acetonitrile utilizing cross reaction kinetics between the copper (II/I) complexes and appropriate counter reagents chosen on the basis of their formal potential and self-exchange rate constants.

EXPERIMENTAL

Materials

Reagents. Copper perchlorate was prepared by adding HClO_4 to CuCO_3 , as previously described. The product was first recrystallized as hydrate salts from water and then recrystallized from acetonitrile by evaporation to yield the acetonitrile-solvated salts.

Counter reagents. (S)-(1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]-eicosane)cobalt(III) perchlorate ($\text{Co}(\text{sep})\text{Cl}_3$), pentaammineisonicotinamideruthenium(II)perchlorate ($\text{Ru}(\text{NH}_3)_5(\text{isn})(\text{ClO}_4)_2$), tetraamminebipyridineruthenium(II) perchlorate ($[\text{Ru}(\text{NH}_3)_4(\text{bpy})](\text{ClO}_4)_2$) were prepared using standard and modified literature methods (Stanbury, Haas, and Taube, 1986).

Polyaminothiaether Ligand. Stock solutions of ligand were prepared by an extraction of formed unprotonated ligand by using dichloromethane in five repeated extractions. The neutral ligand was then dissolved in acetonitrile and the concentrations were determined spectrophotometrically.

Copper(II) Complexes formed with polyaminothiaether ligand. Solutions of the copper(II) complexes with $[\text{14}] \text{aneN}_2\text{S}_2$ ligand were prepared by adding an appropriate volume of copper(II) perchlorate solution of known concentration to the ligand solution where the ligand was in excess over copper(II) perchlorate.

Copper(I) Complexes. In acetonitrile, solutions were prepared by dissolving at least ten-fold excess of ligand in a previously standardized solution of copper(I) perchlorate in 0.1 M $\text{NaClO}_4/\text{CH}_3\text{CN}$ that had been purged with nitrogen. The concentration of the complex was assumed to be identical to that of the original copper(I) perchlorate.

Karl-Fischer Reagents. Karl-Fischer (KF) reagents were used for the determination of water in acetonitrile. The KF titrant (titer 1 mg/ml), as obtained from GFS Chemicals consisted of a solution of iodine in methanol and KF solvent contained pyridine, sulfur dioxide and methanol and served as a solvent for the sample.

All starting chemicals were obtained from Sigma Aldrich, USA.

Methods

Stopped-Flow Kinetic Measurements. The cross-reaction kinetic data for the reduction and oxidation of the copper complexes were collected by using a stopped-flow spectrophotometer. For the reactions in acetonitrile, a modified Durrum-Gibson stopped-flow spectrophotometer interfaced to an Insight 486 PC was used. All reactions were thermostated at 25 ± 0.2 °C using a Forma Scientific 2095 water bath.

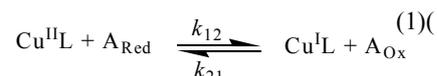
UV-visible Spectra. The general UV-visible spectra of the copper complexes were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. A Cary-17D dual-beam spectrophotometer thermostated at 25 ± 0.2 °C was used to perform all quantitative absorbance measurements.

Formal Potentials. Formal potentials of copper complexes and counter reagents were determined by cyclic voltammetry (CV) using a BAS-100 Electrochemical Analyzer. A three-electrode electrochemical cell was used with a 3 mm glassy carbon disk or silver wire working electrode, a Pt wire auxiliary electrode and a Ag/AgCl (3 M NaCl) reference electrode. The ionic strength was

maintained at 0.10 M using 0.10 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ or $\text{NaClO}_4 \cdot \text{CH}_3\text{CN}$. Ferriin ($E^\circ = 1.112$ V vs. SHE) was used as an internal standard in aqueous solutions, and ferrocene ($E^\circ = 0.400$ V vs. SHE) was used in acetonitrile solutions. Reference electrodes were stored in 3 M NaCl . The glassy carbon-working electrode was polished with Micropolish Alumina 2 and 3 prior to use.

Analysis of Electron-Transfer Kinetic Data

The major focus of this study was to determine the self exchange rate constant, k_{11} , for copper(II/I) complexes with mixed donor macrocycle. This was accomplished by measuring the electron-transfer kinetics of selected cross-reaction



Here, the terms A_{Red} and A_{Ox} represent the reduced and oxidized form of the counter reagent. These reactions can be described by the following rate equation:

$$-\frac{d[\text{Cu}^{\text{II}}\text{L}]}{dt} = k_{12}[\text{Cu}^{\text{II}}\text{L}][\text{A}_{\text{Red}}] - k_{21}[\text{Cu}^{\text{I}}\text{L}][\text{A}_{\text{Ox}}]$$

where k_{12} and k_{21} are second-order rate constants for the copper(II) complex reduction reaction and copper(I) complex oxidation reaction, respectively. For some of the systems studied, the data analysis could be simplified by doing experiments under pseudo-first order conditions. This was accomplished by using at least ten-fold excess of one of the reactants over the other, so that the concentration of the major reactant did not change significantly during the reaction. If the counter reagent is in excess, the observed pseudo-first order rate constant, k_{obs} , for $\text{Cu}^{\text{II}}\text{L}$ reduction can be defined as:

$$k_{\text{obs}} = k_{12}[\text{A}_{\text{Red}}]$$

so that the resulting pseudo-first-order rate equation is:

$$-\frac{d[\text{Cu}^{\text{II}}\text{L}]}{dt} = k_{\text{obs}}[\text{Cu}^{\text{II}}\text{L}]$$

presuming that the reduction proceeds to the completion. A similar relationship can be derived for $\text{Cu}^{\text{I}}\text{L}$ oxidation. The kinetic data obtained under these conditions were then fitted to the integrated first-order expression:

$$\ln \frac{A - A_{\text{eq}}}{A_0 - A} = -k_{\text{obs}} t$$

where A represents the absorbance of the reaction mixture at any time t , A_{eq} represents the absorbance of the reaction mixture at $t = \infty$ and A_0 represents the absorbance at $t = 0$.

If the reaction of interest was too fast to monitor by the stopped-flow method, then second-order conditions were employed and the kinetic data were fitted to the general reversible second-order rate expression.

RESULTS AND DISCUSSION

Physical Parameters for Copper(II) $[\text{14}] \text{aneN}_2\text{S}_2$

In the current study, cyclic voltammetric experiments were carried out in acetonitrile to determine the standard potentials of the copper complexes with $[\text{14}] \text{aneN}_2\text{S}_2$,

All potential values for the corresponding systems in aqueous and acetonitrile solution are listed in Table 1.

Table 1. Physical Parameters for Copper(II) complexes in acetonitrile and in water at 25 °C, $\mu = 0.10$ M (NaClO₄).

Complexed ligand	E ^f , V vs. Fc.	λ_{max} , nm	$10^{-3} \epsilon$, M ⁻¹ cm ⁻¹
[14]aneN ₂ S ₂ in acetonitrile	-0.363	370 ^a	8.2(1) ^a
[14]aneN ₂ S ₂ in water	0.04 ^b	337 ^a	7.6(1) ^a

^aKoenigbauer, 1986; ^bWesterby 1988.

Standard potential of Copper(II) [14]aneN₂S₂ is lower when compared with the standard potential of Cu(II/I)([14]aneNS₃). In general, the replacement of a sulfur atom with a nitrogen atom in the macrocyclic ligand lowers the Cu(II/I) potential as is observed for all these systems in both solvents (Westerby, Juntunen, and Leggett, et al., 1991). This phenomenon is due to the fact that the stability constants for the copper(II) cyclic polyamino polythiaethers showed an increase by five to six orders of magnitude (Westerby, Juntunen, Leggett, et al., 1991) with each additional substitution of a nitrogen atom for a sulfur donor atom. However, the calculated copper(I) stability constant values were found to be relatively constant with the majority having values of approximately 10^{15} M^{-1} .

The near-UV absorption peak exhibited by the copper-polyaminothiaether complexes shifts to higher energies when the sulfur atoms are replaced by nitrogens. If the maximum wavelengths of the absorption band for these systems are compared to the value of 390 nm for the Cu(II)([14]aneS₄) and 255 nm for the Cu(II)([14]aneN₄), it is clear that these observations are consistent with the assignment of this peak to the S→Cu(II) charge transfer band (Westerby, Juntunen, and Leggett, et al., 1991) and, therefore, as the number of sulfur donor atoms increases, the energy of the electron transfer decreases.

Electron-Transfer Kinetics of Cu(II/I)([14]aneN₂S₂).

The self-exchange rate constant values for Cu(II/I)([14]aneN₂S₂) as determined from reduction reactions, $k_{11(\text{Red})}$, cover a 9.3-fold range which is within the limits of experimental error (Table 2). The range of the $k_{11(\text{Ox})}$ values determined for the six oxidation reactions with two different oxidation reagents are within a 5.3-fold range (Table 3).

Since no increase in $k_{11(\text{Ox})}$ or $k_{11(\text{Red})}$ was observed as a function of water content in acetonitrile, we can conclude that the presence of a proton acceptor does not affect the electron-transfer rate. The mean value of $\log k_{11(\text{Red})} = 1.68$ is nearly three orders of magnitude larger than the mean values of $\log k_{11(\text{Ox})} = -1.17$. Based on this observation, we can conclude that the Cu(II/I)([14]aneN₂S₂) system shows the characteristic “square-scheme” behavior in which pathway A is preferred, that is, the value of $k_{11(\text{Red})}$ represents the self-exchange rate constant via Pathway A ($k_{11(\text{A})}$) while the values of $k_{11(\text{Ox})}$ represent the self-exchange rate constant for Pathway B.

The two stable conformations of copper(II) complexes are generally Conformer I and Conformer III (Figure 4).

Conformer I exists as a five-coordinate species, where the lone electron pairs on all sulfur atoms and the hydrogens on the nitrogen atoms are oriented in the same direction relative to the macrocyclic ring. In Conformer III, the lone electron pairs of sulfur atoms and/or the hydrogens attached

to nitrogen atoms that are bridged by one trimethylene group are oriented in one direction, while the hydrogens attached to the nitrogens and/ or the sulfur lone electron pairs bridged by the other trimethylene bridge are oriented in the opposite direction. Copper(I) complexes exist as distorted 4-coordinate tetrahedral complexes in Conformer V in which the direction of the lone electron pairs on the sulfurs and the hydrogens on the nitrogens alternating as one proceeds around the ring.

Table 2. Mean cross-reaction rate constant and self-exchange rate constants calculated for Cu(II)([14]aneN₂S₂) with selected counter reagents in acetonitrile at 25°C, $\mu = 0.10$ M (NaClO₄).

Counter Reagent	% H ₂ O (w/w)	$k_{12}(\text{or } k_{21})$ M ⁻¹ s ⁻¹	k_{11} M ⁻¹ s ⁻¹	log k_{11}
Reductions				
Co ^{II} (sep)	0.007	1.3 (5) × 10 ³	12.95	1.11
	0.010	3.0 (12) × 10 ³	70.80	1.85
		2.9 (6) × 10 ³	66.17	1.82
	0.10	2.7 (16) × 10 ³	57.22	1.76
		1.9 (9) × 10 ³	28.01	1.45
	1.0	3.9 (3) × 10 ³	120.91	2.08

Table 3. Mean cross-reaction rate constant and self-exchange rate constants calculated for Cu(II)([14]aneN₂S₂) with selected counter reagents in acetonitrile at 25°C, $\mu = 0.10$ M (NaClO₄).

Counter Reagent	% H ₂ O (w/w)	$k_{12}(\text{or } k_{21})$ M ⁻¹ s ⁻¹	k_{11} M ⁻¹ s ⁻¹	log k_{11}
Reductions				
Ru ^{III} (NH ₃) ₄ (bpy)	0.010	0.6 (2) × 10 ⁶	0.027	-1.57
	0.10	1.5 (10) × 10 ⁶	0.209	-0.68
	1.0	1.3 (4) × 10 ⁶	0.137	-0.87
Ru ^{III} (NH ₃) ₅ (isn)	0.010	0.8 (5) × 10 ⁵	0.023	-1.64
	0.10	1.9 (9) × 10 ⁵	0.123	-0.91
	1.0	1.2 (5) × 10 ⁵	0.046	-1.34

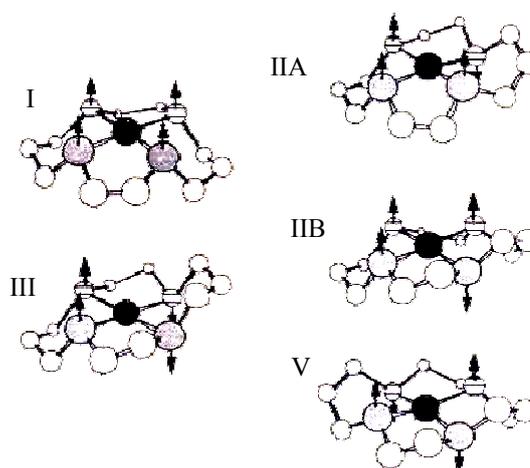


Figure 4. Schematic representation of the five conformers for the copper complexes formed with [14]aneN₂S₂ ligand. The solid circle represents the copper atom, the shaded circles represent nitrogen atoms, the striped circles represent sulfur atoms, and the open circles represent carbon atoms. Hydrogen atoms have been omitted for clarity. The arrows represent the orientation of the hydrogen atom attached to nitrogen or the unshared electron pair on sulfur relative to the macrocyclic ring. Conformers I and III are stable forms for Cu(II) complexes and Conformer V is a stable form Cu(I). In converting from Conformer I or III to Conformer V either Conformer IIA or IIB must be accessed as an intermediate. These two intermediate conformers differ only in the fact that one sulfur donor atom is oriented in a unique direction relative to the “plane” of the macrocyclic ring in Conformer IIA while in Conformer IIB it is a nitrogen donor atom that is oriented in the unique direction.

If Cu(II)([14]aneN₂S₂) exists in Conformer I, one nitrogen hydrogen and one sulfur lone electron pair must invert. If the Cu(II) complex is in Conformer III, the inversion of only the two sulfur donor atoms is necessary (**Figure 4**). Since no increase in the $k_{11(\text{Red})}$ values was observed as a function of water content in acetonitrile, we presume that the dominant form of the Cu(II) complex is Conformer III.

Previous studies (Koenigbauer, 1986; Westerby, 1988) of Cu(II/I)([14]aneN₂S₂) system showed kinetic behavior in aqueous solution at different pH values. For the oxidations conducted at low pH (1.0 to 2.5), the k_{11} values are much smaller than those obtained in acetonitrile solution. At higher pH (5.45 and 5.60), Koenigbauer observed two reactions, where the faster reaction was pseudo-first-order and the slower one was truly first-order. The k_{11} value for the faster reaction is approximately 2000 times higher than that for the oxidation at lower pH. The slower reaction appears to represent "gated" oxidation with the average k_{obs} value calculated to be $2.47 \times 10^{-3} \text{ s}^{-1}$. The self-exchange rate constant obtained for the oxidation at high pH (5.3) is in agreement with the $k_{11(\text{Ox})}$ values obtained in acetonitrile. Since $k_{11(\text{Ox})}$ decreases significantly with decreasing pH, we can assume that inversion of at least one nitrogen is involved in the conformational change. At very low pH, the concentration of hydrogen ion is high and deprotonation of coordinated nitrogen becomes difficult. The result is a very slow nitrogen inversion. However, at high pH, conformational change becomes the rate limiting-step and gated behavior is observed where the conformational change (R→P) controls the rate of the oxidation of reaction. Thus, the system is not following Pathway B, but a more complex scheme involving a number of metastable conformers Galijasević, Krylova, Koenigbauer, et al.,(2003).

CONCLUSIONS

Electron-Transfer Kinetics of Cu(II/I)([14]aneN₂S₂) followed square scheme mechanism but for current system is a free from significant donor atom inversion barriers. By controlling the amount of water in aprotic solvent, any dependence on proton acceptance and need for donor inversion would significantly affect the self-exchange rate constant values for reduction and oxidation reactions. For Cu(II) complex with [14]aneN₂S₂ ligand in the acetonitrile, the only possible conformation was Conformer III, where the inversion of only the two sulfur donor atoms is necessary that does not depend on hydrogen extraction. Thus, the position of donor sets in this type of ligand significantly directs electron-transfer process and in general overall complex geometry.

ACKNOWLEDGEMENT

Experimental work has been done on Wayne State University, MI, USA and supported by the US NSF under Grant CHE-98179.

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Summary/Sažetak

U elektron transfer procesu, promjena oksidacionog stanja reaktanata je generalno praćena strukturalnim promjenama, koje direktno uslovljavaju kinetiku posmatranih reakcija. Ranije studije na Cu(II/I) kompleksima sa cikličnim tetraoeter ligandima su pokazale da inverzija koordiniranih donorskih atoma u kompleksu je vjerovatno osnovni faktor u kontrolisanom tzv. "gated" elektronskom transferu. Studije formiranja Cu(II/I) kompleksa i izomeracije sa [14]aneN₄ tipovima kompleksa su pokazale da dolazi do inverzije koordiniranih N atoma zbog abstrakcije vodikovih atoma. U sistemima sa [14]aneN_xS_{4-x} ligandima, postoji mogućnost inverzije N ili S atoma. Cilj ovog istraživanja je bilo određivanje inverzije N atoma i efekat iste strukturne promjene na konstante brzine elektron transfera ali u funkciji niskih koncentracija vode u aprotičnom rastvaraču (acetonitril). Rezultati koji opisuju elektron transfer kinetiku i moguće konformacijske promjene kompleksa Cu(II/I) te kinetički mehanizam za ligande sa N-S donor atomima su predstavljeni i objašnjeni u ovom radu.



Determination of mercury in the urine by atomic absorption spectrometry - cold vapor technique

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Article info

Received: 01/02/2012

Accepted: 21/02/2012

Keywords:

Mercury,
urine
AASCVT

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Abstract: Urine is a liquid waste product of the body. Substances that are ingested and fail to be absorbed are excreted, solid waste through the intestines, the urine through the kidney and ureter and another fluid from the body through perspiration. Determination of mercury content of urine is not included in routine examinations, but mercury can be present in urine at concentrations that could have serious effects on human health. Urine donors were selected in regard to their occupations, age, lifestyle habits, and different diet, with special reference to dental professionals, consumers of marine food and smokers, as a group of subjects that could have a higher concentration of this metal. To determine the mercury content in urine, atomic absorption spectrometry – a technique of cold vapor method was used. The total content of mercury in 76 analyzed urine samples was in the range of 0.12 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentrations of mercury in some donors. In contrast, the other analyzed factors that theoretically can affect the levels of mercury in urine,

INTRODUCTION

Determination of Hg in urine and blood is of a great importance and it was recommended as a method for biomonitoring of exposure to this type of xenobiotics both in nature and in the workplace (Gazewski et al., 2007). Mercury and its compounds are used in agriculture, pharmaceutical and chemical industry, in production of measuring instruments, etc. The most important sources of occupational exposure to mercury are factories for the production of chlorine, using mercury electrodes in production processes, and handling of amalgam fillings by dental staff in dental offices. Exposure can occur through direct skin contact with mercury or mercury compounds or through inhalation of mercury vapor. The primary pathway of exposure is through the respiratory tract, i.e. about 80 % of inhaled mercury is absorbed in the lungs (Trzcinka-Ochocka et al., 2007). For the assessment of occupational exposure to mercury, based on levels of mercury in urine, there are biological limits (BEI). In Poland, the current BEI value of exposure to inorganic or metal mercury is 35 mg/g creatinine (CIOP/PIP, 2003). In Germany, the biological tolerance value (BAT) to the Commission for investigating

health hazards of chemical compounds for the urine workspace is 100 mg/L (DFG, 2004), while the value of 35 mg/g creatinine for BEI was adopted by American Conference of Governmental Industrial Hygienists (ACGIH) in 2004 (ACGIH, 2004). Apart from occupational exposure, mercury can get into the human body through the food chain, and by inhalation of toxic mercury vapor which get in the atmosphere by different sources. When it comes to the food chain, special case represent marine organisms, especially fish, which fall into the category of essential foods of human diet, and in which mercury appears in one of more toxic states, in the form of methyl mercury (Taljaard and Staden, 1999). All forms of mercury have toxic effects on most human organs, especially kidneys. Mercury falls into the category of heavy metals and has an exceptional ability to bioaccumulate in the body. Therefore, mercury has a long-term stay in the body and causes specific effects on human health. The most important forms of mercury are elemental mercury, inorganic and organic mercury compounds. All three forms have different toxicity, their effects are manifested by various symptoms, and all three forms can be found in the atmosphere, the aquatic environment, soil and plant material. Mercury is

deposited in the kidneys, liver, small intestine wall, muscles, spleen, heart and lungs, penetrates less in the central nervous system and deposits in the cerebral gray mass. Therefore it is essential to gain a knowledge of "normal" levels of Hg in order to assess its concentration in body fluids and secretions (Gazewski *et al.*, 2007). Research has shown that in healthy people who are not subject to any forms of mercury compounds, levels of mercury in blood and urine should not exceed the value of 5 mg L^{-1} , while values of 30 mg L^{-1} in blood and 50 mg L^{-1} in urine are showing long-term intoxication (Taljaard and Staden, 1999). Mercury who has entered the human body can be determined by analyzing the samples of hair, blood and urine and also indicates the period of exposure to mercury (Blaurock-Busch, 2009). As the mercury in these samples is present in trace amounts, well-sensitive measurement technique for its determination should be applied. For the determination of mercury in urine samples, which were analysed in this work, we used the method of atomic absorption spectrometry - cold vapor technique. In this method, long-term mineralization of urine samples is not required because the total Hg concentrations can be measured after the addition of saturated KMnO_4 and acid to the urine sample. The donors were selected in regard to their different occupations, ages, habits, and different diet with special emphasis on the dental staff, consumers of marine foods and smokers, as a target groups that could eventually have elevated concentrations of metals in the urine. The content of mercury in urine of all donors ranged from 0.12 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam filling and urinary concentration of mercury in individual donors. That was not a case in other in other groups when other analyzed factors were taken into account.

EXPERIMENTAL

Sampling

Seventy six urine samples were collected from people of different age, place of residence, occupation, and with a different diet, health problems and lifestyle habits. All the participants of the study filled questionnaire designed to identify possible sources of mercury exposure. Information collected included demographics (e.g., sex, age, address), information about potential sources of mercury (e.g., diet, type of employment, amalgam fillings, whether the respondent consumed cigarette or not and how much per day, health problems).

Determination of Hg in urine samples

The determination of mercury in urine, based on the method of Piotrowski *et al.* (Piotrowski *et al.*, 1973; Gazewski *et al.*, 2007), was carried out by cold vapor atomic absorption spectrometry (Spectraa-10, Varian). The method allows to determine the total Hg concentration after overnight mineralization of urine samples by potassium permanganate in sulphuric acid solution at room temperature. The excess of oxidants was reduced by hydroxylamine hydrochloride solution. Ionic mercury, Hg (II), from digested urine was converted into Hg^0 by reaction with stannous (II) chloride and then vaporized. The vaporized Hg was determined by absorbance measurement at the absorption Hg wavelength of 253.7 nm.

In order to determine the mercury in urine: 10 % SnCl_2 and 10 % (v/v) HNO_3 solutions and 1 mg/mL solution of mercury were used. Using technique of cold vapor, the

sample flow was set to 6.2 mL/min while the flow of reducer (SnCl_2) and 10 % HNO_3 was 0.90 mL/min. The instrument was previously calibrated with standard solutions. The value of relative standard deviation was 4 %. For the quantitative determination of mercury in samples calibration curve method was used.

Analytical quality control of results

In order to verify the analytical quality control of results, the urine spiking experiments were performed and recovery factors were calculated. The accuracy of the method was confirmed on the basis of satisfactory values of recovery factors (96-105 %). The limit of quantification for total mercury in urine, based on six standard deviations of the blank, was $0.2 \text{ } \mu\text{g/L}$ ($n = 10$) ($6 \times \text{SDB}$).

RESULTS AND DISCUSSION

The data shows the analysis results for mercury content in urine, depending on various factors that could affect the final content of mercury accumulated in the human body. The main parameters that could cause the elevated concentrations of this metal are: the number of teeth with amalgam filling, fish consumption, use of tobacco, the workplace and residence environment. The content of mercury in urine samples taken from 76 donors was compared with available literature data (Lie *et al.*, 1982; Yamamura, 1990; Ulukapi *et al.*, 1994; Khordi – Mood *et al.*, 2001). All urine donors were residents of Sarajevo Canton.

Total mercury content in urine of all donors, aged 12 to 75 years, ranged from 0.12 to 12.24 ng/mL. The maximum allowable concentration of mercury (that was not pathophysiological) during the eight-hour exposure was 0.1 mmol/L and 20.06 ng/mL (Đurić *et al.*, 2008). Thus, in all of our analyzed samples mercury content did not exceed the quoted predefined value.

Out of 76 donors of urine, 32.89 % were male and 67.11 % female. The concentration of mercury in male donors ranged from 0.12 to 5.28 ng/mL, while the female population showed mercury content from 0.17 to 12.24 ng/mL.

The value of 60.52 % of donors had dental amalgam fillings. Concentrations of mercury ranged from 0.26 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentration of mercury in individual donors (Table 1).

Table 1. The contents of mercury in individual urine donors with amalgam fillings.

Number of urine donors	Number of teeth with amalgam fillings	Interval of Hg concentrations in urine (ng/mL)
4	1	0.34 – 1.20
8	2	0.46 – 2.70
6	3	0.52 – 5.28
3	7	0.50 – 6.65
4	8	0.50 – 12.24

A study conducted in Iran (Khordi – Mood *et al.*, 2001) also shows and explains the increase in concentration of mercury in urine after tested children received the amalgam fillings (value of Hg: 3.83 - 5.14 mg/L).

Research regarding the population of children with dental amalgam fillings shows the results of analysis of urinary concentration of mercury in children in Turkey after the amalgam restorations (Ulukapi et al., 1994). Mercury content ranged from 0.34 to 1.7 mg/L.

Twenty nine or 38.15 %, of urine donors were smokers. The content of mercury in urine ranged from 0.12 to 2.65 ng/mL. Some of the urine donors, also smokers, had a small number of teeth with amalgam fillings (from 1 to 3). Generally, one can say that in this population had low mercury content in urine. So, we did not found a significant correlation between the daily number of consumed cigarettes and the urinary concentration of mercury in individual donors (Table 2).

Table 2. The contents of mercury in individual urine donors (smokers).

	Number of urine donors	Interval of Hg concentrations (ng/mL)	Mean concentrations of Hg (ng/mL)
Consumers of 5 to 20 cigarettes per day	16	0.33 – 1.91	0.79
Consumers of 20 to 40 cigarettes per day	12	0.12 – 2.65	0.65
Consumers of 40 to 60 cigarettes per day	1	1.20	1.20

High percent, (80.26 %) of all donors were consumers of marine products, especially fish. Comparing the content of mercury in urine in freshwater fish consumers, as well as people who do not consume marine products, with a content of mercury in urine of marine products consumers we concluded that no correlation between a level of mercury in urine and consumption of marine products could be derived.

One of the target groups of tests was one where donors are occupationally exposed to mercury. The dental staff of School of Dentistry at University of Sarajevo, that include dentists and dental nurses was tested. Dental staff in their practice works with dental amalgam fillings on a daily base. The results of analysis of mercury content, with a total of 15 urine donors from this group were compared with the results of mercury with other donors and significant variation in the content of mercury in urine were not observed. Concentrations of mercury ranged from 0.50 to 1.55 ng/mL in doctors' samples, while the mercury content in the urine provided by dental nurses was even lower and ranged from 0.50 to 0.78 ng/mL. For future studies more comprehensive studies with a higher number of donors from dental offices would certainly give better picture of levels of mercury exposure.

Research done in Norway (Lie et al., 1982), where the respondent populations living in highly industrialized areas and one living in an industrially undeveloped area were tested, reveals significantly higher urinary mercury concentrations especially in donors living in more industrial region (mean Hg 7.4 µg/L). A similar level of mercury as in our samples (mean Hg 2.8 µg/L) was noted in the study

population which was not occupationally exposed to mercury in Japan (Yamamura, 1990).

CONCLUSIONS

Total mercury content in urine of all 76 donors was determined by atomic absorption spectrometric method - cold vapor technique.

The content of mercury in the urine of all donors aged 12 to 75 years ranged from 0.12 to 12.24 ng/mL. The maximum allowable concentrations of mercury in eight-hour exposure was 0.1 mmol/L or 20.06 ng/mL. Thus, in either our sample analyzed mercury content did not exceed the said defined value.

Higher values of total mercury concentrations in urine were noted in the female donors (0.17 to 12.24 ng/mL), while in male donors those values were comparing it with the total concentration of mercury in urine (0.12 to 5.28 ng/mL) for all donors.

The percent of 60.52 of all donors had dental amalgam fillings. Concentrations of mercury ranged from 0.26 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentration of mercury in individual donors.

Twenty nine (38.15 %) urine donors were smokers. Mercury content ranged from 0.12 to 2.65 ng/mL. Some of urine donors (also smokers) had a small number of teeth with amalgam fillings (from 1 to 3). There was no significant correlation between the daily number of cigarettes consumed and the urinary concentration of mercury in individual donors.

With 80.26 % of donors who consume marine products, especially fish, elevated concentrations of mercury in urine were not detected in relation to the donors who consume freshwater fish.

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Summary/Sažetak

Urin je produkt otpada iz čovječijeg organizma. Tvari koje su unesene u organizam i ne uspiju se apsorbovati izlučuju se, čvrsti otpad putem crijeva, tekući preko bubrega i mokraćovoda, a jedan dio tečnosti iz organizma izađe kroz znoj. Određivanje sadržaja žive u urinu ne spada u rutinske analize, ali živa može da bude prisutna u urinu u koncentracijama koje mogu da indiciraju prisustvo ovog teškog metala u čovječijem organizmu što za posljedicu može imati ozbiljne efekte na ljudsko zdravlje. Odabrani su donatori urina različitih zanimanja, starosne dobi, životnih navika, te različite prehrane, sa posebnim osvrtom na stomatološko osoblje, konzumente morskih namirnica i pušače, kao ciljane grupe ispitanika koje bi eventualno mogle da imaju povišenu koncentraciju ovog metala u urinu. Za određivanje sadržaja žive u uzorcima urina korištena je metoda atomske apsorpcione spektrometrije – tehnika hladnih para. Sadržaj žive u urinu, kod svih donatora urina, se kretao u rasponu od 0,12 do 12,24 ng/mL. Uočena je pozitivna korelacija između broja amalgamiranih zuba i urinarne koncentracije žive kod pojedinih donatora, za razliku od ostalih analiziranih faktora, koji mogu uticati na povišen sadržaj žive u urinu, gdje to nije bio slučaj.



Total phenolic content and antioxidant activity of ethanolic extracts of *Aesculus hippocastanum* L.

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Article info

Received: 22/02/2012
Accepted: 14/03/2012

Keywords:

Aesculus hippocastanum L.
Antioxidant activity
Phenolic compounds
DPPH

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Abstract: *Aesculus hippocastanum* L. (horse chestnut) belongs to the genus *Aesculus*, the most widespread genus of the Hippocastanaceae family, and it is native to the countries of the Balkan Peninsula. Different parts of the plant were used for the treatment of many diseases. Total phenolic content of ethanolic extracts of bark of twigs and fruit and fruit itself was evaluated by Folin-Ciocalteu method while antioxidant activity was tested using DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenging method. Preliminary investigation of chemical composition was done by TLC and aesculin was detected in samples of bark of twigs. Results for content of total phenolics were expressed as gallic acid (mg GAE/mL) and aesculin (mg AE/mL) equivalents, respectively. Among the tested samples, the highest amounts of total phenolics were detected in all bark extracts, 763.53-1048.00 mg AE/mL, while samples of pulp had the lowest content of these compounds, 43.41-66.15 mg AE/mL.

All bark extracts showed higher antioxidant activity than aesculin which was used as a standard, while extract of pulp mixed with bark showed significantly lower antioxidant potential.

INTRODUCTION

Aesculus hippocastanum (horse chestnut) is a large deciduous, rapidly-growing tree that can reach a height of 36 meters. It is native to the countries of the Balkan Peninsula, but because of its large, showy flower clusters the tree is cultivated worldwide for its beauty. Flowers are white or pink with a small red spot.

While the common name for the tree is horse chestnut, it is also known as buckeye, and like other buckeyes, is a member of the Hippocastanaceae family, rather than the chestnut family (*Castanea*). Historically, the seed extract was used as a treatment for many ailments, including rheumatism, rectal complaints, bladder and gastrointestinal disorders, fever (first written account in 1720), hemorrhoids (as early as 1886) and leg cramps. Currently, horse chestnut seed extract is widely used in Europe for chronic venous insufficiency, hemorrhoids, post-operative edema, and topically for clearing skin conditions.

To date, more than 210 compounds of different classes have been isolated and identified from the genus *Aesculus* (Zhang *et al.*, 2010). The primary active constituent found in horse chestnut seed extract is aescin (Sirtori, 2001, Jiang *et al.*, 2011). Aescin is actually a mixture of triterpene saponins present in two forms, α and β , which are distinguished by their water solubility and melting points. Other constituents include bioflavonoids (quercetin and kaempferol), (Dudek-Makuch and Matlawska, 2011) proanthocyanidin A2 (an antioxidant), and the coumarins fraxin and aesculin (Stanić *et al.* 1999).

It is evident that the popularity of herbal medicine, as for natural or industrial formulations of nutritional supplements, is at its top, from both the points of view of consumers and researchers. With such a huge interest, the scientific role of researchers is particularly devoted to acquire more information about composition, structures and activity effects, in relation to physiological benefits and metabolic processes of these products.

A close examination of the recent literature indicates some interests in horse-chestnut products. Therefore, it has been a discover healthy benefits for human consumption of various products obtained and derived from *A. hippocastanum* L. (Baraldi *et al.*, 2007, Küçük Kurt *et al.*, 2010).

Except medicinal importance, *A. hippocastanum* was studied as a possible biomonitor of the heavy metal pollution (Yilmaz *et al.*, 2006).

EXPERIMENTAL

Material and methods

The plant material of *A. hippocastanum* L. was collected in fall 2010 from three different locations in Sarajevo, 1-Sutjeska; 2-Ilidža; 3-Pofalici. For preparation of ethanolic extracts 10 g of bark of young twigs (BT) and fruits (BF), bark of fruit with pulp (BF+P) and a pulp itself (P) were infused into 100 mL of hot ethanol for 10 days, filtered and stored into sterile bottles.

Preliminary investigation

Preliminary investigation of extracts composition were done by thin layer chromatography in ethyl acetate:methanol:water (17:3:1) system. Detection of sample components was done using Folin-Ciocalteu and DPPH reagents, and UV light. Aesculin was used as a standard.

Total phenolic content

Total phenolic content were determined spectrophotometrically according to the Folin-Ciocalteu method, using gallic acid and aesculin as standards and expressing the results as gallic acid (mg GAE/mL) and aesculin (mg AE/mL) equivalents. Data presented are average of three measurements.

Antioxidant activity

The antioxidant activity of ethanolic extracts was evaluated using the DPPH radical-scavenging method, which is based on the reduction of stable 1,1-diphenyl-2-picrylhydrazyl radical (Brand-Williams *et al.*, 1995).

DPPH• is a stable free radical compound with characteristic absorption at wavelength of 517 nm. Antioxidants upon interactions with DPPH neutralize its free radical character and the colour of the reaction mixture changes from purple to yellow.

The radical solution was freshly prepared daily, stored in a flask covered with aluminium foil, and kept in the dark at 4 C between measurements. A portion of the sample solution (100 µL) was mixed with 1 mL of 5.25×10^{-5} M DPPH• in ethanol. Decreasing of absorbance of tested samples was monitored every 60 seconds for 30 min at 517 nm on Perkin-Elmer Lambda 25 UV/Vis spectrophotometer. The radical-scavenging activity of the tested samples, expressed as percentage inhibition of DPPH•, were calculated according to the formula (Yen and Duh, 1994),

$$IC_{50}(\%) = [(A_0 - A_t) / A_0] \times 100 \quad (1)$$

where A_0 and A_t are the absorbance values of the blank sample and the test sample, at particular times, respectively. Percent of inhibition after 30 min was plotted against concentration and the equation for the line was used to obtain the IC_{50} value. A lower IC_{50} value indicates greater antioxidant activity. All determinations were performed in triplicate. Aesculin was used as a positive probe.

RESULTS AND DISCUSSION

Preliminary investigation was done by thin layer chromatography (TLC) which has proved its worth as a simple, inexpensive method for the chemical and biological screening of plant extracts.

Detection of phenolic compounds was done by spraying TLC plates with Folin-Ciocalteu reagent (Stahl, 1969). Positive detections were blue spots on white background (Fig. 1). The TLC plate with samples is developed with the elution solvent and dried. It is then sprayed with a DPPH solution. The plate is examined in daylight. Active (free-radical scavenging) compounds appear as yellow-white spots against a purple background (Marston, 2011).

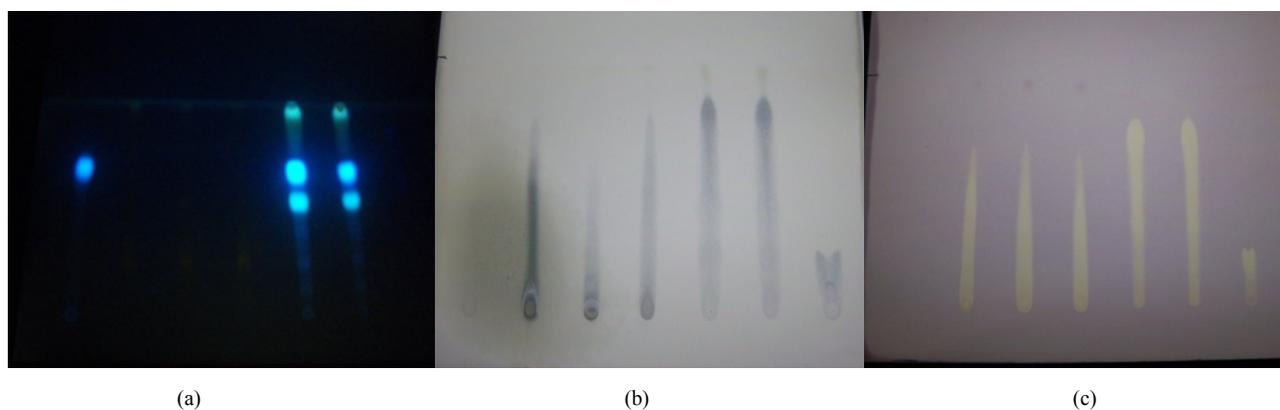


Figure 1: Thin layer chromatograms of bark extracts with different detection. (a) UV 365nm, (b) Folin-Ciocalteu reagent, (c) DPPH solution.

Presence of phenolic compounds is confirmed as a specifically blue colored spots detected with Folin-Ciocalteu reagent. Yellow spots detected with DPPH reagent indicate presence of compounds with antioxidant activity (Figure 1). Aescin (A) was used as standard which

was identified in bark of twigs extracts, as well as gallic acid (GA) that is most common phenolic compound found in the plants.

Among the tested samples, the highest amounts of total phenolic were detected in all bark extracts (763.53 mg EE/mL for 2-BT to 1048.00 mg EE/mL for 3-BF), while samples of pulp had the lowest content of these compounds

43.41 mg EE/mL 1-P. Generally, data obtained as aesculin equivalents are higher than those obtained as gallic acid equivalents (Table 1).

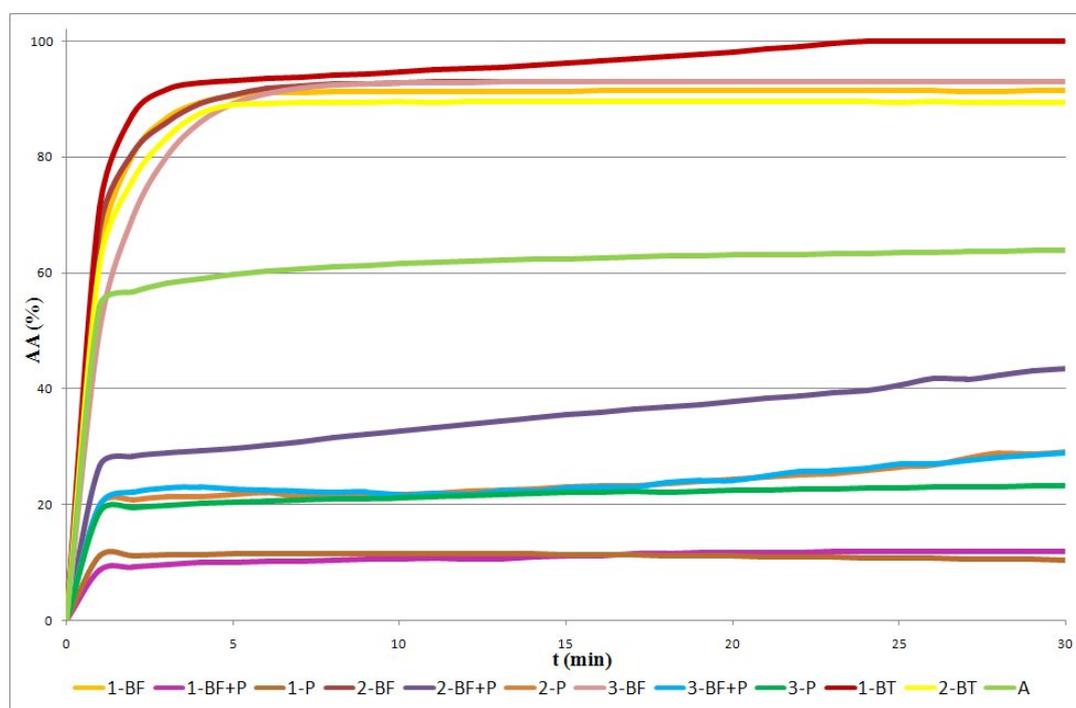


Figure 2: Reaction progress of reduction of stable DPPH radical by Horse chestnut samples.

It is well known that bark of the chestnut are rich in tannin (Barreira *et al.*, 2008) and these phenolic compounds might account for the high values obtained, while in the extract of pulp the content of total phenolics was quite low.

Table 1: The total phenolic content and related antioxidant activity.

Sample	Total phenolic		DPPH
	[mg (GAE)/mL]	[mg (EE)/mL]	IC ₅₀ (mg/mL)
1-BF	178.45 ± 24.36	862.31 ± 117.71	0.14 ± 0.02
1-BT	202.71 ± 23.39	979.53 ± 113.01	0.28 ± 0.01
1-P	8.80 ± 0.58	43.41 ± 3.05	12.94 ± 0.64
1-P+BF	12.10 ± 0.17	64.87 ± 0.82	2.09 ± 0.05
2-BF	183.77 ± 20.36	888.00 ± 98.36	0.18 ± 0.01
2-BT	158.01 ± 27.76	763.53 ± 114.80	0.16 ± 0.02
2-P	12.36 ± 0.67	66.15 ± 3.60	4.38 ± 0.28
2-P+BF	14.75 ± 0.81	78.97 ± 4.33	3.87 ± 0.08
3-BF	216.97 ± 29.37	1048.00 ± 141.94	0.32 ± 0.02
3-P	10.68 ± 1.24	57.24 ± 6.66	7.38 ± 0.59
3-P+BF	14.12 ± 1.79	74.83 ± 8.26	6.26 ± 0.16
Aesculin	-	-	0.82 ± 0.06

(1) Location -1- Sutjeska; 2-Ilidža; 3- Pofalići;
Part of plant; BF- bark of fruit; BT - bark of twigs; P- pulp

DPPH radical scavenging method was used to evaluate free radical scavenging ability of ethanolic extracts of different parts of *A. hippocastanum*. Figure 2 shows very high rate of DPPH inhibition of all bark samples (90-100%) in concentration of 1 mg/mL. Samples of pulp and bark of fruit mixed with pulp had much lower inhibition of DPPH (10-40%), in comparison with aesculin as standard which

reach the 64% in same concentration. These results are in agreement with antioxidant activity of *A. hippocastanum* from Turkey, where bark extract were rich in phenolic compounds with high correlation to its high antioxidant capacity (Celep *et al.*, 2010).

CONCLUSIONS

Antioxidant activity of plant extracts are mainly attributed to the active compounds present in them. Phenolic compounds have been considered as powerful antioxidants. In general, our results showed that *A. hippocastanum* bark extracts were rich in phenolics and they possess a considerable antioxidant potential, although strong correlation is not confirmed.

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Summary/Sažetak

Aesculus hippocastanum L. (divlji kesten) pripada rodu *Aesculus*, najrasprostranjenijem rodu u familiji Hippocastanaceae i raste u zemljama Balkanskog poluostrva. Gotovo svi dijelovi biljke koriste se za tretman različitih bolesti. Sadržaj ukupnih fenola u etanolnim ekstraktima kore mladih grančica i ploda kao i u samom plodu određen je Folin-Ciocalteu metodom, dok je antioksidativna aktivnost određena DPPH metodom. Preliminarna ispitivanja hemijskog sastava vršena su hromatografijom na tankom sloju, a eskulin je detektovan u uzorcima kore grančica.

Rezultati za sadržaj ukupnih fenola izraženi su kao ekvivalenti galne kiseline (mg GAE/mL) i eskulina (mg AE/mL). Među ispitivanim uzorcima najveći sadržaj ukupnih fenola imaju uzorci kore (763.53- 1048.00 mg AE/mL), dok su uzorci ploda imali najmanji sadržaj ovih spojeva, 43.41-66.15 mg AE/mL.

Svi ekstrakti kore pokazuju bolju antioksidativnu aktivnost od eskulina koji je korišten kao standard, dok su uzorci ploda pomiješani sa korom pokazali značajno manju antioksidativnu sposobnost.



Spectrophotometric analysis of total ascorbic acid content in various fruits and vegetables

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Article info

Received: 20/03/2012

Accepted: 26/03/2012

Keywords:

Total ascorbic acid
2,4-Dinitrophenylhydrazine
Spectrophotometric method
Fruits and vegetables

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Abstract: Total ascorbic acid (ascorbic acid + dehydroascorbic acid) has been determined in twenty-one different samples of fruits and vegetables by spectrophotometric method. This method is based on the oxidation of ascorbic acid to dehydroascorbic acid by bromine water in the presence of acetic acid. After coupling with 2,4-dinitrophenylhydrazine (DNPH) a red complex was produced and absorbance of that complex was spectrophotometrically measured at 521 nm. A linear concentration range for standard solutions of ascorbic acid was obtained up to 10 $\mu\text{g mL}^{-1}$, with a correlation coefficient of 0.9929. The contents of ascorbic acid were found between 9 and 49 mg/100 g of fresh fruits, also 3 and 90 mg/100 g of fresh vegetables. The interferences of glucose, fructose and sucrose were also investigated. The limit of detection of ascorbic acid was found to be 0.01 $\mu\text{g mL}^{-1}$ (3σ from 10 measurements of ascorbic acid concentration of 3 $\mu\text{g mL}^{-1}$), and limit of quantification of ascorbic acid was 0.017 $\mu\text{g mL}^{-1}$. A relative standard deviation was 2.4 % ($n = 10$, $c = 7 \mu\text{g mL}^{-1}$). The content of total ascorbic acid in twenty-one different samples of fruits and vegetables was compared with results of spectrophotometric method and literature values.

INTRODUCTION

Vitamin C (L-Ascorbic acid) is water-soluble vitamin with strong reducing action and it is an important co-enzyme for internal hydroxylation reaction. Vitamin C is found in both reduced form (ascorbic acid) and oxidized form (dehydroascorbic acid). It is widely used food additive with many functional roles, many of those are based upon its oxidation-reduction properties. Functional roles include its use as: a nutrition food additive, antioxidant, reducing agent, stabilizer, modifier, colour stabilizer (Eitenmiller *et al.*, 2008). The desire to develop methods with ideal characteristics have resulted a large number of procedures with varying applicability. For the determination of ascorbic acid in food

the method should apply for both, ascorbic acid and dehydroascorbic acid, to give a total value of vitamin C (Ball, 1994). Many analytical techniques are mentioned in the literature for the determination of vitamin C in different matrices, such as: titrimetric (Verma *et al.*, 1996), fluorimetric (Xia, 2003), spectrophotometric (Rahman *et al.*, 2006.; Sataya *et al.*, 1998), high-performance liquid chromatography (Nyyssönen *et al.*, 2000), enzymatic (Casella *et al.*, 2006), etc. In this work we used spectrophotometric determination of total ascorbic acid based on coupling with acidic DNPH in twenty-one different samples of fruits and vegetables. DNPH procedure is one of the most simple, accurate and applicable method for determination of total ascorbic acid in fresh food, such as fruits and vegetables.

EXPERIMENTAL

Reagents

Metaphosphoric acid - acetic acid

Fifteen grams of solid metaphosphoric acid were dissolved in mixture of 40 mL glacial acetic acid and 450 mL of distilled water, in a 500 mL volumetric flask. The solution was filtered and collected.

2, 4-dinitrophenylhydrazine solution and thiourea solution

2 g of 2, 4-dinitrophenylhydrazine and 4 g thiourea were dissolved in 100 mL 4,5M H₂SO₄.

Standard vitamin C (Ascorbic acid) solution

A stock solution of 500 ppm of vitamin C was prepared daily.

Samples

Investigated samples were twenty-one different kind of fruits and vegetables obtained from local markets: Black currant, rose hip, parsley, sea buckthorn, date, pepper, orange, red currant, strawberry, red grapefruit, lemon, mandarin, potato, tomato, carrot, banana, cranberry, blueberry, apple, blackberry, cucumber.

Sample preparation

Five grams of sample were homogenized with 25 mL of metaphosphoric acid - acetic acid solution, and it was quantitatively transferred into a 50 mL volumetric flask and shaken gently to homogenize solution. Then it was diluted up to the mark by the metaphosphoric acid - acetic acid solution. The obtained solution is filtered and centrifuged at 4000 rpm for 15 minutes, after what the supernatant solution is used for spectrophotometric determination (Perkin Elmer spectrophotometer Lambda 25) of vitamin C content in 21 samples of different fruits and vegetables.

Estimation of Vitamin C

Procedure: 0,23 mL of 3% bromine water were added into 4 mL of centrifuged sample solution to oxidize the ascorbic acid to dehydroascorbic acid and after that 0,13 mL of 10 % thiourea to remove the excess of bromine. Then 1 ml of 2, 4-DNPH solution was added to form osazone. All standards, samples and blank solution were kept at 37 °C temperature for 3 hours in a thermostatic bath. After it all were cooled in ice bath for 30 minutes and treated with 5 mL chilled 85 % H₂SO₄, with constant stirring. As a result, a colored solution's absorbance was taken at 521 nm.

Reactions

Ascorbic acid is oxidized to dehydroascorbic acid by adding bromine water. After that L-dehydroascorbic acid reacts with 2,4-DNPH and produces an osazone, which treated with 85 % H₂SO₄ forms red colored solution. A typical calibration plot was made and used to determine the concentration of ascorbic acid in the investigated samples.

RESULTS AND DISCUSSION

Absorption maximum of ascorbic acid

To determine the absorption maximum, standard solutions of ascorbic acid in concentration of 3 mg mL⁻¹ were prepared. Spectrum of 2,4-DNPH solution was

measured according to this procedure, in the wavelength interval 490-530 nm (Fig. 1).

Calibration curve

After determination of the λ_{\max} of colored complex (521 nm) using a Perkin Elmer spectrophotometer, the absorbances of all standards (converted to colored complex) were taken to construct a calibration curve. The calibration curve was constructed by plotting the concentration versus the corresponding absorbance (Fig. 2). The limit of detection (LOD) of ascorbic acid is 0.01 μ g/mL (3σ of 10 measurements of standard solution of ascorbic acid, concentration of 3 mg/mL). The limit of quantification (LOQ) of ascorbic acid is 0.017 μ g/mL. The relative standard deviation was 2.4 % for 10 measurements of standard solution of ascorbic acid concentration of 7 μ g/mL.

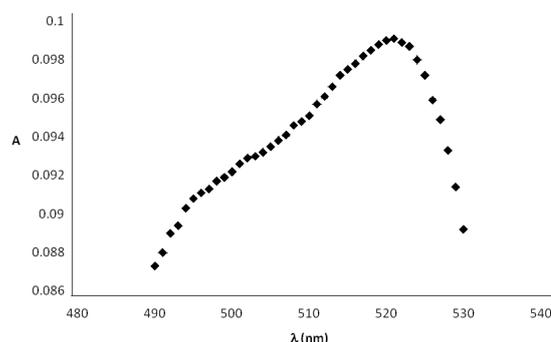


Figure 1. Absorption maximum

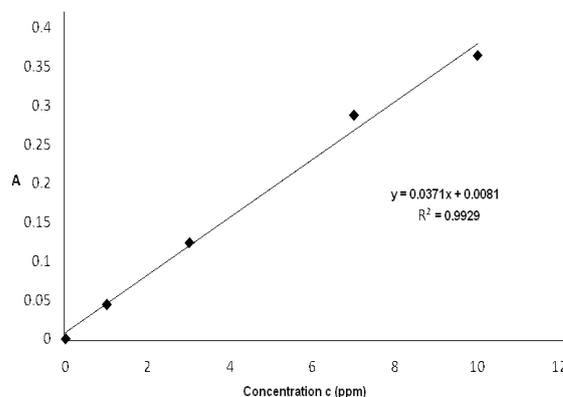


Figure 2: Calibration curve for determination of vitamin C

Interferences of fructose, glucose and sucrose

Using this method can interfere compounds that can provide products with 2, 4-DNPH. Interferences of fructose, glucose and sucrose on total ascorbic acid determination were examined over the absorption spectrum of 2, 4-DNPH sugar complex, under the same conditions as those for standard solutions and samples. Concentration of investigated interferences were 5 μ g/mL.

It has been determined that fructose and sucrose have no response in the interval of 490-530 nm, while glucose had 15 times lower absorption than ascorbic acid under the same conditions and concentration.

Determination of vitamin C in samples

Samples of different fruits and vegetables were prepared according to previously written procedure. Results of total content of AA in the investigated samples obtained by

spectrophotometric and spectrofluorimetric (Čopra - Janićijević *et al.*, 2011) methods as well as literature value are shown in Table 1. Spectrofluorimetric method was based on the condensation reaction between AA and *o*-phenylenediamine (OPDA) in the absence of the oxidant.

The highest content of total ascorbic acid obtained by spectrophotometric method was found in samples of: black currant (184.36 $\mu\text{g mL}^{-1}$), rose hip (168.44 $\mu\text{g mL}^{-1}$), and parsley (90.53 $\mu\text{g mL}^{-1}$). The lowest content of total ascorbic acid was found in samples of: blackberries (5.18 $\mu\text{g mL}^{-1}$) and cucumber (3.64 $\mu\text{g mL}^{-1}$).

Table 1: Content of total ascorbic acid (AA) in the investigated samples

Samples	Spectrophotometric method ^a (AA mg/ 100g)	Spectrofluorimetric method ^a (AA mg/ 100g)	Literature value (AA mg/ 100g)
Black currant	184.36 ± 0.37	25.28 ± 0.26	181 - 215
Rose hip	168.44 ± 0.94	59.56 ± 0.26	426 - 2500
Parsley	90.53 ± 0.61	41.32 ± 0.22	133 - 150
Sea buckthorn	64.60 ± 0.56	37.6 ± 0.67	114 - 1550
Date	60.34 ± 0.37	2.63 ± 0.32	0.4 - 3
Pepper	50.27 ± 0.41	50.54 ± 0.17	44.9 - 80
Orange	49.42 ± 0.33	39.76 ± 0.29	38.9 - 53.2
Red currant	39.94 ± 0.55	20.99 ± 0.37	41 - 81
Strawberry	33.33 ± 0.98	24.32 ± 0.08	41.2 - 60
Red grapefruit	21.43 ± 0.62	28.7 ± 0.30	4 - 34.4
Lemon	21.23 ± 0.15	31.08 ± 0.26	25 - 53
Mandarin	19.90 ± 0.46	57.44 ± 0.22	20 - 26.7
Potato	19.58 ± 0.09	20.89 ± 0.14	5 - 20
Tomato	15.90 ± 0.68	25.51 ± 0.29	12.7 - 39
Carrot	14.93 ± 0.23	17.81 ± 0.24	5.9 - 15
Banana	13.10 ± 0.72	20.19 ± 0.40	8.7 - 18
Cranberry	12.05 ± 0.89	12.18 ± 0.47	10 - 13.3
Blueberry	9.77 ± 0.85	7.13 ± 0.27	2.5 - 16.4
Apple	9.55 ± 0.82	8.21 ± 0.17	4.6 - 6
Blackberry	5.18 ± 0.33	7.73 ± 0.35	3.1 - 7
Cucumber	3.64 ± 0.28	7.68 ± 0.37	2.8 - 4

^a Average of three determinations ± SD

Agreement for spectrophotometric and spectrofluorimetric methods were the best for the investigated samples of pepper, potato, cranberry and apple. The biggest differences of obtained results between two methods and literature value was for the investigated sample of date. The reason could be that date consists a lot of glucose which could interfere. As ascorbic acid is largely similar to the glucose by structure, some of the glucose may be extracted from the sample. Glucose may also form the colored complex with DNPH as ascorbic acid.

Also the differences between obtained results and literature value for some investigated samples may also be explained on the basis that the ascorbic acid concentration vary with conditions such as temperature and the storage

period on preservation. Vitamin C content slowly decreases with temperature and storage period of vegetables. Rhman et al has published that the initial concentration of ascorbic acid were decrease by 76% at 5 °C and 64% at - 10°C during two months storage time (Rhman *et al.*, 2007).

From the Table 1 we can see that most results obtained by spectrophotometric method are well comparable with results of spectrofluorimetric method and literature values.

CONCLUSIONS

Spectrophotometric method for determination of total ascorbic acid in fruits and vegetables with 2,4-DNPH is a simple and reliable method. Comparison of results obtained by spectrophotometric method is in a good agreement with results obtained by spectrofluorimetric method and literature values.

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Summary/Sažetak

Sadržaj ukupne askorbinske kiseline (askorbinska kiselina + dehidroaskorbinska kiselina) je određen u dvadeset i jednom uzorku voća i povrća spektrofotometrijskom metodom. Metoda se zasniva na oksidaciji askorbinske kiseline do dehidroaskorbinske kiseline bromnom vodom u prisustvu acetatne kiseline. Nakon kuplovanja sa 2, 4-dinitrofenilhidrazinom (DNFH), stvara se kompleks crvene boje čija se apsorbansa spektrofotometrijski mjeri na 521 nm. Dobiveno je linearno područje za standardne rastvore askorbinske kiseline do 10 $\mu\text{g/mL}$ s koeficijentom korelacije od 0,9929. Sadržaj askorbinske kiseline se kretao između 9 i 49 mg/100 g svježeg voća i između 3 i 90 mg/100 g svježeg povrća. Ispitan je uticaj mogućih interferenci kao što su glukoza, fruktoza i saharoza. Granica detekcije askorbinske kiseline je 0.01 $\mu\text{g/mL}$ (3σ od 10 mjerenja standardnog rastvora askorbinske kiseline koncentracije 3 $\mu\text{g/mL}$), dok je granica kvantifikacije askorbinske kiseline 0.017 $\mu\text{g/mL}$. Relativna standardna devijacija (RSD) je 2.4 % ($n = 10$, $c = 7\mu\text{g/mL}$). Sadržaj ukupne askorbinske kiseline u ispitivanom dvadeset i jednom uzorku voća i povrća poređen je s rezultatima dobijenim spektrofluorimetrijskom metodom kao i sa literaturnim vrijednostima.



Integrated knowledge of physics and chemistry: case of Physical Chemistry course

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Article info

Received: 09/04/2012

Accepted: 14/05/2012

Keywords:

Bologna Process

Integrated knowledge of chemistry and physics

Physical chemistry

Longitudinal research

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Abstract: One of the major achievements of the learning process is acquisition of integrated knowledge. This paper presents the first results of the degree of knowledge of the second year chemistry students in subjects relevant to the objects of physical chemistry. Data was collected using questionnaires and tests given out to students of chemistry in the academic year 2010/2011. The first results obtained show a weak and insufficient integration of knowledge in general chemistry, general physics and mathematics required for further subject courses such as physical chemistry. The negative difference in the number of points on the pretest and posttest (the results are lower for 80% of questions on the posttest) was detected, although the test was repeated after the end of the winter semester and completion of Physical chemistry course. This poor performance on tests can be an indicator of a number of difficulties in the learning process, which are identified through this research in attempt to find correct solution for this problem.

INTRODUCTION

Knowledge integration is a complex process starting with a first steps encompassing knowledge accumulation, consolidation and formation of a stable structure. This process subsequently leads to the main issue of long-term quality of acquired knowledge and its use in the process of learning (Taber, 2003b; Taber 2004; Taber 2007). Therefore, the significant role of teachers and the teaching process is to help students to establish a successful transition and the connection to prior knowledge, and to develop different skills that are the result of the new doctrine, which must activate prior learning (Taber, 2007).

One should always keep in mind that the integrated knowledge is characteristic of modern and contemporary approach to world trends that are governed with competitive and collaborative relationships, the exchange of information and culture of support and trust (Ruan et al.,

2012). According to the theory of knowledge, „know how“ approach to use the right quantum of integrated knowledge is an imperative especially in the system where knowledge is a key resource for creating competitive advantage (Wang & Farn, 2012). These findings confirm the assumption that it should be the dominant feature of university education and the goal worth striving for.

Integration of physics and chemistry knowledge is expected event not only as a result of historical events but, as many believe, as a logical path since fundamentals of chemistry are the foundations of physics too. Rightly Keith Taber (2003a) points out that the current division of natural science is largely a result of historical accident - it could probably be completely different. Certain boundaries and divisions between these sciences are almost inexistent there - but there are areas of special interest that must be studied as integrated (Hewitt et al., 2007) and in that manner should

be implemented in the educational process and in the study of chemistry.

However, some research shows that students generally do not have a habit of taking into account the relevant concepts in physics when learning chemistry (Taber, 2003b). Keith Taber (2008) also showed that if the students are expected to apply knowledge of physics as they study chemistry, they would consider it as unnecessary task. Some studies have shown that the integration of concepts in chemistry and physics is one of the most challenging aspects of learning outcomes (Taber, 2008). The same investigator, in his studies of integrated knowledge of chemistry and physics noted that if the questions are posed in the context of chemistry, physics students often do not know the answer, but if asked to explain it from physicist point of view using the concepts they learned in physics, they will give correct answer. Taber (2008) concludes that it is not surprising that some students are sorting their knowledge grouped into categories according to the of the relevant subject curricula.

Researchers agree that in realization of integrated knowledge in education process teacher has a significant role (Aikenhead, 2003; Taber, 2008). The teacher is the one who decides how and how not students integrate their knowledge of chemistry and physics. On the other hand, some researchers believe that the national tests (as well as international tests that assess knowledge and its integration), mainly containing multiple-choice questions require only a recall of specific information. Thus, instructor has to focus on approach that helps students to memorize facts, without having a chance to develop their critical thinking skills (Liu *et al.*, 2008). Even a teaching staff face the difficulties in the area of acquisition and integration of conceptual knowledge (Emereole, 2009).

Students often have problems of a conceptual nature (Izatt *et al.*, 1996). One study conducted at the University of Alabama (USA), showed that the engineering students should have better knowledge of mathematics, in order to study chemistry and physics as integrated science. Very common case of learning difficulties is use of SI units (Pitt, 2003), that we also observed when testing our students. The problem of units conversion, the use of mathematical operations with exponents, knowledge of the functional relationship between the physical units are some of the major problems caused by lack of knowledge inherited from early education (Zejnilagić-Hajrić *et al.*, 2010; Nuić *et al.*, 2011).

Students rely heavily on an algorithmic approach in problem solving which involves the use of the memorized set of procedures that is contrary to the conceptual problem solving, which involves understanding the concept and find solutions, without using stored procedures. Algorithmic way of solving problems in chemistry is not in accordance with scientific research and intellectual development of students (Cracolice *et al.*, 2008). Besides using an integrated approach in teaching science increases motivation for learning, but also improves student achievement, as the tests that assess the integration of knowledge, as well as the traditional tests showed (Frampton, 2009).

This paper presents the first results of the degree of knowledge of the second year chemistry students in subjects relevant to the objects of physical chemistry.

RESEARCH METHODOLOGY

Research aim

The effect of prerequisite knowledge courses such as General Chemistry, General Physics and Calculus on success in Physical Chemistry I and II class was examined in this study. The main goal was to determine a level of acquired and integrated knowledge and its subsequent effect on active participation in learning process that ultimately determines student success on final exams.

Participants

Research participants were second year chemistry students (2010/2011). Number of students who participated in research varied from 45 to 35 thus research data are presented in percentages. Seventy percent of students were enrolled in general chemistry major while 30% of them in chemistry education major. Out of total number, 22% of students have repeatedly attended Physical Chemistry I course. Total of 85% of students passed all first year required exams, but 5.5% of them did not pass General Physics exam.

Research questions

Main research question:

Q-1 In what extent second year chemistry students integrate relevant prior chemistry, physics and mathematics knowledge acquired in high school and during the first year of study?

Q-2 What are the learning difficulties that students encounter during lectures and what factors affect the level of integrated knowledge relevant for Physical Chemistry course?

Research instruments

Research instruments designed for this study, were two questionnaires (Q1 and Q2) and Integrated Physics and Chemistry knowledge test. These tests are designed in such way so the pretest (T1) and posttest (T2) results are used to record changes of student knowledge in Physical Chemistry I. Parameters for measuring changes in the achieved knowledge were gain and loss factors.

Q1 and T1 were applied prior to Physical Chemistry I class in the winter semester of the academic 2010/2011, and Q2 and T2 are applied at the end of the winter semester, after completion of Physical Chemistry I teaching, learning and exam taking. The instruments of research are attached.

Test dealing with knowledge integration in mathematics, physics and chemistry consisted of 20 questions with following structure: 8 math questions (3 differential and integral calculus questions, one linear function question and 4 computing questions), 4 questions in chemistry and 8 questions dealing with physics and chemistry together. Each correct answer was worth 1 point (20 points for the entire test). Passing threshold was set to be 55%, or 11 points.

RESULTS

Our results based on the Q1 answers show that students mainly use recommended syllabus literature (49%), lecture notes (41%), and PowerPoint presentations (10%). Physical Chemistry textbook recommended by syllabus was used by 82% of students (67% used a photocopied textbook) while 3% of students did not use any resources for exam preparation. Significant number of students, approximately 33% to 40% uses study materials taken from their senior colleagues for both General Chemistry and Physics courses.

This indicates a passive approach towards preparation and development of study skills.

The largest number of students received grade 8 (C) in General Chemistry I, while in General Chemistry II average grade was 7 (D). In Physics I, Physics II, Calculus I and Calculus II classes, the largest number of students achieved grade 6 (E).

The largest numbers of students quite objectively estimated their own knowledge that is in a good agreement with received grades. Interest in chemistry studies confirmed 40% of students assessing it as high. Over 82% of students have no plans to change their study subject (chemistry) but more than 75% of students, intend to switch from chemistry education major to general chemistry major. An interesting answer is that 80% of students would recommend chemistry studies to their friends or relatives, and even 22% of students stated that they have close family members who already has a degree in chemistry.

The Q2 showed that students rarely behave as an active partner in the teaching process. Only 4% of students had direct contact with the teacher, while in the case of communication between student - teaching assistant results were significantly better (40%), but still unsatisfactory. Students consider the absence of oral exams (according to the Bologna principles study exams are taken mainly in writing, with quizzes and tests) as a reason for lack of direct communication with an instructor. The written form (test) exam are preferred by only 26% of students and more than 50% believe that students should have an oral exam, while 59% of students suggested that a combination of written and oral exams would be the best way of knowledge assessment.

Student questionnaire responses indicate that the deriving and solving mathematical equation in terms of chemical problem explanation was a main source of difficulties in understanding new material. We observed that students have significant difficulty in applying knowledge of differential and integral calculus (the subject of Calculus I and Calculus II courses in the first year of study). According to the data (Figure 1) 51% of students are having difficulties just in the domain of integration of knowledge (explaining, performing logical conclusion, examples of problem solving). At the same time, multiple choice questions were the easiest to answer, but explaining and defending chosen answer was again a weak point for majority of students.

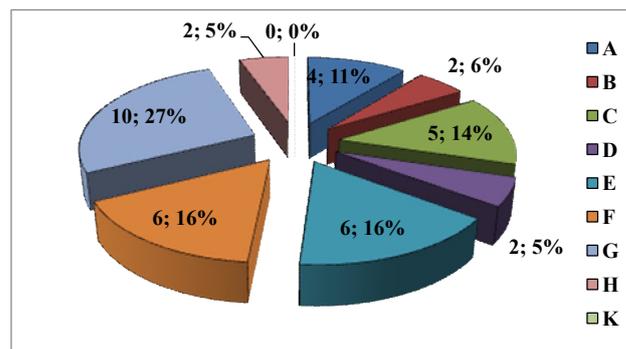


Figure 1. Distribution of student responses according to the type of difficulty encountered in a learning process.

A = Definitions of different terms and values, B = Describing occurrence, C = Explanation, D = Comparison, E = Problem solving, F = Giving a new example, G = Deriving an equation, H = Giving logical conclusion, and K = Multiple-choice questions

In response to one of the questions dealing with the content of courses by complexity, the students cited three concepts: chemical potential, state functions in physics and partial molar volumes. Such responses are not surprising since previous knowledge, especially in mathematics, is necessary for understanding these complex concepts.

The results of the T1 and T2 are presented in Figure 2.

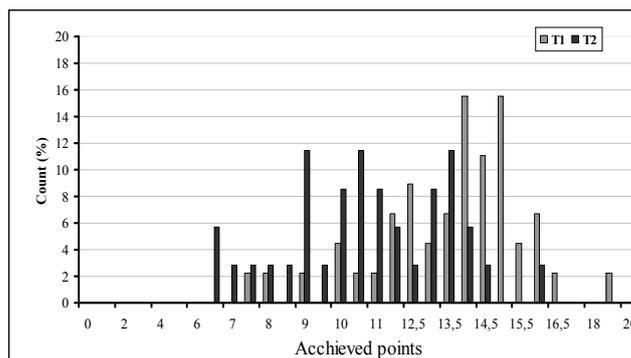


Figure 2. Distribution of number of students according to achieved results in tests (T1 i T2).

T1 = Pretest, T2 = Posttest

The average number of points per student is 12.8 points on the pretest, and 9.5 points on the posttest. Gain and loss factors that represent difference between a number of points achieved on test 2 when compared to test 1 are represented in Table 1. It is obvious that the gain factor was achieved only for four questions out of twenty. Statistical data of T1 and T2 results are presented in Table 2.

Table 1. Gain/loss factor distributed according to question number of T1 and T2.

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
gain									2			8			32		2			
loss	66	26	32	15	9	30	24	40		8	10		3	16		6		23	20	56

Table 2. Statistical analysis results for T1 and T2.

Test	N	Mean	Median	Mod	Max	Min	Variance	St.dev.	Total points	Total points (%)
T1	45	13.5	14	15	19	7.5	5.1	2.3	608.5	67.6
T2	35	11	11	11	16	6.5	5.9	2.4	385.5	55.1

With the passing threshold set as 11 points, the average number of points on the pretest was greater than the passing threshold, and on posttest the average number of points was equal to the number of required points for the pass which was unexpected for us.

On the pretest the difference between the minimum and maximum number of points was 11.5, and 9.5 on posttest. Total sum of points at T1 was 67.5% while on T2 was 50.1%. According to the number of obtained points students can be divided into three groups: (a) Group I consists out of students who achieved a score of 0-10 points; (b) Group II consists out of students who achieved a score of 11-15 points.; (c) Group III consists out of students who achieved the score of 16-20 points.

The largest number of students on both tests is in Group II. When T2 was analyzed, a decrease in Group II and Group III was observed, while a significant increase in Group I was observed (Figure 3).

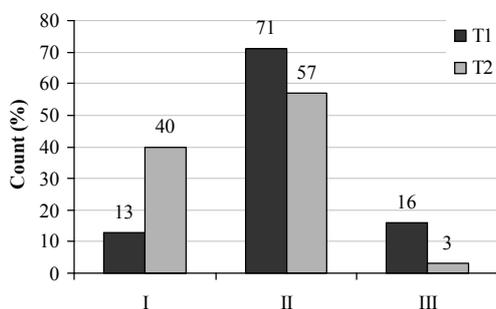


Figure 3. Students' test score distribution per group. T1 = Pretest, T2 = Posttest

On the pretest, a total of 87% of students have had scores above the passing threshold, and on the posttest that number dropped to 60% of students, showing the negative factor of achievement (Figure 4).

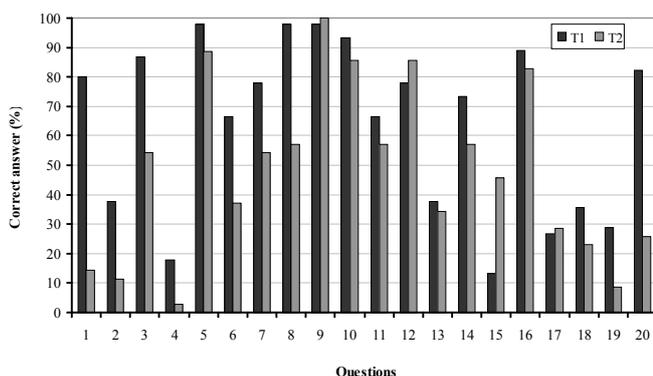


Figure 4. Correct answers distribution for T1 questions 1 to 20. T1 = Pretest, T2 = Posttest

The lowest score questions were those relating to the fundamental concepts and prior knowledge such as knowledge of basic mathematical functions, knowledge of the SI units of measurement and the procedure for conversion of larger to smaller units and *vice versa*, as well as explanations of the chemical concept problems.

DISCUSSION

A large number of independent variables in the questionnaires and the first data collected during the study have helped to gain insight into the many reasons why students showed poor results, not only on T2 but also on the

exams (Physical chemistry I and II). Some of the reasons are different programs of secondary education. Most students had completed high school (50%), followed by nursing school (30%) and various technical schools (20%). Four years of chemistry through high school have had 75% of students. The number of years having physics and mathematics as a subject in high school education is less encouraging, 40% of students did not have physics subject in all grades of high school, while in the case of mathematics this percentage is higher (45%). Applications and implementation of curricula of the three basic subjects' matters (mathematics, physics and chemistry) relevant for chemistry study are different in different types of secondary schools and in different parts of the country. Such circumstances may arise as a significant cause for both low prior and actual (university) level knowledge of chemistry students. As an indication of lack of preparedness of students for the chemistry study can be considered lack of elementary knowledge in mathematics and physics, such as use of SI units and conversion factors (the problem of understanding the small and large numbers and decimal exponents in the SI system of units). In addition, a large number of class and contact hours plus five hours of weekly help sessions, open email communications with a teaching staff should have helped in achieving better scores.

At the University of Sarajevo, additional two weeks help classes were officially introduced as a mean of additional help, for all students who failed to pass the final exam. In the case of Physical Chemistry I and II course, students showed no interest in additional help lectures although they stated in surveys that they have difficulty solving computational problems or understanding particular concepts.

Additionally, poor teaching conditions including insufficient or outdated lab equipment, large number of students in class, lab or quiz sessions (not compatible with the Bologna principles of organization of teaching) show how numerous are factors that cause the poor efficiency of the teaching/learning process in the case of the analyzed test group of students. Lack of basic textbooks, insufficient number or no copies of textbooks in the library, poor Internet connections and not enough places for internet communication, the obsolescence of existing computer equipment, overloaded teachers and assistants are all additional, but not less important factors that affect the quality of teaching and the outcomes of teaching and learning.

When all these factors are put together, it is obvious that a number of changes in accordance with current education trends have to be implemented in education process if the higher quality learning outcomes are to be expected.

CONCLUSIONS

(1) The data obtained in this study showed that the integration of mathematics, chemistry and physics acquired, necessary for further studies especially in cases of physical chemistry, is poor.

(2) Some factors such as uncoordinated curricula and poor teaching conditions, student -instructor ratio, students' lack of motivation, poor secondary education quality, and insufficiently rigorous enrollment selection, could be reasons for such results.

It is evident that the results of longitudinal studies can help to evaluate the curricula subjects and find new solutions tailored to the active role of students, which is outlined in the documents of the Bologna process.

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Appendix 1

QUESTIONNAIRE 1

1. Your major is:
 General Chemistry _____ Chemistry Education _____
2. Type of high school you completed is:
 a) High school b) Technical school _____ c) Nursing school
 d) Other _____
3. Number of high school years in which you had Mathematics class:
 a) zero b) one c) two d) three e) four
4. Number of high school years you had Physics class:
 a) zero b) one c) two d) three e) four
5. Number of high school years I have had chemistry class:
 a) zero b) one c) two d) three e) four
6. I am taking Physical Chemistry I class:
 a) first time
 b) second time
 c) third time
 d) I am enrolled in first academic year for a second time, but I am taking Physical Chemistry second year course
7. Estimate your interest in Chemistry studies:
 a) no interested at all b) weakly interested c) satisfactory interested d) very interested e) extremely interested
8. I completed the first year of a study with:
 a) Passed all exams
 b) Failed on one exam (course name _____)
 c) Failed on two exams (courses name _____, _____)
 d) Failed on more than two exams (courses name: _____)
-
9. My achieved grades in following courses are:
 a) General Chemistry I grade: A(10); B (9); C(8); D(7); E (6), F(fail)
 b) General Chemistry II grade: A(10); B (9); C(8); D(7); E (6), F(fail)
 c) General Physics I grade: A(10); B (9); C(8); D(7); E (6), F(fail)
 d) General Physics II grade: A(10); B (9); C(8); D(7); E (6), F(fail)
 e) Calculus I grade: A(10); B (9); C (8); D(7); E (6), F(fail)
 f) Calculus II grade: A(10); B (9); C(8); D(7); E (6), F(fail)
10. During the first year of my study, I was using the most:
 a) lecture notes b) recommended textbooks c) materials found on internet
 d) Other sources (which ones: _____)
11. Are you planning to change the major: yes no maybe
12. Among your close family members, who has a degree in chemistry?
 a) one of my parents b) both parents c) siblings ____ d) close relatives: ____ e) no one
14. Would you recommend the chemistry study at the Department of Chemistry to your family members or friends?
 yes no
- In the following questions (15-17), circle the number corresponding to the meanings below:
 1 - very dissatisfied; 2 - somewhat satisfied;
 3 - no opinion; 4 - satisfied; 5 - very satisfied*
15. What is the level of your satisfaction with acquired knowledge in General Chemistry?
 1 2 3 4 5
16. What is the level of your satisfaction with acquired knowledge in General Physics?
 1 2 3 4 5
17. What is the level of your satisfaction with acquired knowledge in Mathematics?
 1 2 3 4 5

Appendix 2

QUESTIONNAIRE 2

1. How often during one semester you use consultation offered by your teacher?

- a) never b) 1-2 times c) rarely d) often e) very often

2. How often during one semester you use consultation offered by your teacher's assistant?

- a) never b) 1-2 times c) rarely d) often e) very often

3. For study and exam preparation in Physical Chemistry I, you used the following sources:

- a) your own, recommended by the teacher textbook, problem solving workbook
b) photocopied, recommended by the teacher textbook, problem solving workbook
c) recommended by the teacher textbook, problem solving workbook borrowed from your school library
d) recommended by the teacher textbook, problem solving workbook borrowed from National University Library
e) books borrowed from your colleagues
f) books borrowed from your teacher's assistant
g) books borrowed from your teacher
h) none of the above
i) other _____

4. The exam taking method you prefer is:

- a) Written only b) Oral only c) Both, written and oral

Explain your answer:

5. Type of my difficulty encountered in a learning process is mostly:

- a) Definitions of different terms and values,
b) Describing occurrences,
c) Explanation,
d) Comparison,
e) Problem solving,
f) Giving a new example,
g) Deriving an equation,
h) Giving logical conclusion,
k) Multiple-choice questions.

6. Your intent to continue your study in Chemistry is:

yes no undecided

7. If your answer to question six was NOT or UNDECIDED, can you, please, list at least two reasons why, and what would be your alternative field of study (in case you would continue undergraduate study at all)

1. _____
2. _____
3. _____

8. Please write down your suggestions for improvement in acquiring better knowledge in Physical Chemistry I and II

Appendix 3

TEST OF KNOWLEDGE INTEGRATION IN MATHEMATICS, PHYSICS AND CHEMISTRY

Problems

1. Calculate: $\int x dx =$
2. Calculate: $\int \frac{dx}{x^2} =$
3. Write down first derivative of the function: $y = 2x^4 + x^2 + 5$
4. How are determined parameters a and b of the function: $y = ax + b$?
5. Calculate: $2 + 2 : 2 =$
6. What is the logarithm of 10^{-14} to base 10?
7. Calculate square root of 3.6×10^{-11} .
8. Round off the following numbers to two decimal places according to the rounding rules:
 1.258 _____, 1.253 _____, 1.255 _____
9. Write the chemical equilibrium equation for the following reaction: $N_2 + 3H_2 = 2 NH_3$
10. What volume, under standard conditions, occupies 1 mol of some gas?
11. Convert: $1 \text{ mol dm}^{-3} =$ _____ mol cm^{-3}
12. Convert: _____ $\text{mg cm}^{-3} = 2 \text{ g dm}^{-3}$
13. Write the value of gas constant and Avogadro's number using SI units
 $R =$ _____ $N_A =$ _____
14. Where will water boil sooner, On Mount Everest or mountain of Bjelašnica and why?
15. Explain the difference between one molal and one molar solutions?
16. If a dissolution process of a salt is exothermic process, what change of temperature is expected to be seen in calorimeter?
17. Explain the effect of catalyst on the rate of chemical reaction.
18. Gas is expanding isobarically at 105280 Pa. If the gas volume change was $0,5 \text{ dm}^3$, the value of work done by gas is:
a) 52.64 b) 52.6 J c) 52.6 W d) 52.64 J
Round off numbers!
19. When will hydrogen atom emit violet light?
20. What is a photon?

Summary/Sažetak

U procesu učenja jedno od važnijih postignuća su integrirana znanja. U ovom radu su predstavljeni prvi rezultati analize stupnja integriranih znanja studenata druge godine hemije iz predmeta relevantnih za oblast fizikalne hemije. Set podataka je prikupljen na osnovu upitnika i testova koje su studenti hemije rješavali u akademskoj 2010/2011. godini. Prvi dobijeni rezultati pokazuju slabo i nedovoljno integriranje znanja iz opće hemije, opće fizike i matematike, potrebnih za oblast fizikalne hemije. Negativna razlika u broju postignutih bodova na ulaznom i ponovljenom testu (dobijeni rezultati su slabiji za 80% pitanja na ponovljenom testu), iako je ponovljeni test realiziran nakon nastave održane u zimskom semestru iz fizikalne hemije. Ovako slabi rezultati studenata mogu biti pokazatelj određenih poteškoća u procesu učenja, koje su kroz ovo istraživanje identificirane s ciljem da se traže rješenja za njihovo ublažavanje.

MEĐUNARODNA GODINA HEMIJE – IYC 2011

Hemija – naš život, naša budućnost

Sve poznate tvari – plinovite, tečne i čvrste, sastoje se od hemijskih elemenata, ili spojeva načinjenih od tih elemenata. Shvaćanje čovječanstva o prirodi koja nas okružuje zasnovano je našem znanju hemije. Uistinu, svi životni procesi su kontrolirani hemijskim reakcijama.

Zbog svega navedenog, Međunarodna unija za čistu i primijenjenu hemiju IUPAC (International Union of Pure and Applied Chemistry) i UNESCO (United Nations Educational, Scientific and Cultural Organization) smatrali su da je potrebno obilježiti dostignuća hemije, i njezin doprinos dobrobiti čovječanstva na međunarodnoj razini, i odlučili su 2011. godinu proglasiti Međunarodnom godinom hemije IYC 2011. IUPAC je prepoznao da su brojne naučne discipline popularizirane proglašavanjem Međunarodne godine posvećene njihovom polju izučavanja. Na osnovu toga je započet koncept obilježavanja Međunarodne godine hemije 2011, koji je uspješno realiziran.

O ideji o obilježavanju Međunarodne godine hemije prvi put se razgovaralo 2006. godine, tokom aprilskog sastanka IUPAC-ovog izvršnog komiteta. Nakon toga je slijedilo odobrenje IUPAC-a u augustu 2007, UNESCO je dao podršku u aprilu 2008, a deklaracija UN-a donešena u decembru 2008. godine.

Tokom Međunarodne godine hemije, planirane su različite aktivnosti sa sljedećim ciljevima:

1. Istaknuti značaj hemije u javnosti i povećati razumijevanje hemije u smislu svjetskih potreba
2. Povećati interes mladih za hemiju
3. Pokrenuti entuzijazam za kreativnu budućnost hemije
4. Obilježiti ulogu žena u hemiji, i važnih povijesnih događaja u hemiji, uključujući obilježavanje stogodišnjice dodjeljivanja Nobelove nagrade za hemiju Mariji Sklodowskoj-Curie.

Obavljeni su razgovori između utjecajnih hemičara i predstavnika društva o budućem obliku hemije za održivost u kontekstu hemijskih postignuća

Ovdje je potrebno naglasiti ciljeve Ujedinjenih nacija za ovaj milenij:

- Cilj 1: Iskorijeniti ekstremno siromaštvo i glad
 - Cilj 2: Osigurati univerzalno osnovno obrazovanje za sve
 - Cilj 3: Promovirati jednakost spolova i istaknuti utjecaj žena
 - Cilj 4: Smanjiti smrtnost djece
 - Cilj 5: Poboljšati zdravlje majki
 - Cilj 6: Borba protiv HIV-a/AIDS-a, malarije i drugih bolesti
-

Cilj 7: Osigurati održivost okoliša

Cilj 8: Razviti globalno partnerstvo za razvoj

Hemija je vitalna za postizanje ovih ciljeva!

Organizatori su povezali ljude koje su željeli obilježiti Međunarodnu godinu hemije 2011. u jednu mrežu (IYC 2011 Network), i na taj način održavali međusobne kontakte. Participanti su tokom cijele godine predlagali ideje aktivnosti koje su, nakon odobranja organizatora, mogle biti realizirane, i nakon toga objavljene na web stranici spomenute mreže.

Kako je već navedeno, IUPAC i UNESCO su organizatori obilježavanja Međunarodne godine hemije. Partneri u ovim aktivnostima su i sljedeće organizacije i udruženja:

- Ujedinjene nacije (UN)
- Federacija hemijskih društava FACS, FASC, FLAQ, EuCheMS
- Nacionalna udruženja hemičara
- Industrija
- Nevladine organizacije (NGO)
- Obrazovne i istraživačke institucije
- Pojedinci

Obilježavanjem Međunarodne godine hemije željelo se postići sljedeće:

- Istaknuti prirodu, ljepotu i značaj – kako ekonomski, tako i značaj za okoliš – hemije u modernom svijetu.
- Efektivna upotreba medija da bi se poboljšao profil hemije, onako kako je vide učenici, stanovništvo i političari.
- Zajednički rad za postizanje ovih ciljeva.

Međunarodna godina hemije je prilika koja nam se neko vrijeme neće opet ukazati...

Ključni događaji prilikom obilježavanja Međunarodne godine hemije su bili, prije svega: Ceremonija otvaranja, Svjetski kongres IUPAC-a i Ceremonija zatvaranja

Ceremonija otvaranja

održana 27 - 28. Januara, 2011. u Parizu (Francuska), pod pokroviteljstvom UN-a, UNESCO-a i IUPAC-a, na temu: „Hemija i ciljevi Ujedinjenih nacija za novi milenij“.

Svjetski kongres IUPAC-a pod nazivom "Hemijske inovacije koje povezuju Sjevernu i Južnu Ameriku i svijet", održan od 30. Jula – 7. Augusta 2011 u San Juanu, Puerto Rico.

Ceremonija zatvaranja – pod pokroviteljstvom hemijske i farmaceutske industrije, održana 1. Decembra 2011, Brussels, Belgija

Ovo je bila prilika za izlaganje učesnika sa najviših nivoa iz svih sektora.

Ostali ključni događaji koji su se održali:

- **Pacificchem 2010** – 15. – 20. decembar 2010 – Honolulu, Hawaii, USA
- **Hemija – ključ afričke budućnosti**, Kongres Federacije afričkih hemijskih društava (FASC) 16 – 21. januar 2011, Johannesburg, Južna Afrika
- **CHEMRAWN** – Simpozij o biogorivima, Septembar 2011., Kuala Lumpur, Malezija

Neki primjeri realiziranih aktivnosti u sklopu obilježavanja Međunarodne godine hemije 2011:

- Afrička konferencija – Izazovi u prirodnim naukama, obrazovanju i stvaranju kapaciteta povezanih sa SAICM (Strategijski pristup Ujedinjenih nacija međunarodnom hemijskom menadžmentu). Ključni događaj održan je u Etiopiji.
- Naučni projekt o klimatskim promjenama za podršku poučavanju i strateška diskusija koju vode RSC & ACS (Royal Society of Chemistry & American Chemical Society)
- Brojni nacionalni prijedlozi za komemorativne poštanske marke, otvorene dane i posebne proslave, kao npr. Madame Curie na Sorbonni/L'Oreal nagrada za žene u nauci
- Obilježavanje hemijskih događaja

Zatim su realizirani još neki primjeri aktivnosti u sklopu obilježavanja IYC 2011:

- Oživljavanje postojećih nacionalnih i regionalnih aktivnosti
 - Društveno umrežavanje (Facebook, YouTube) o pitanjima vezanim za hemiju
 - Video klipovi (postojeći i novi) koji promoviraju doprinose hemije
 - Osiguravanje stručnog znanja kroz program “pitaj naučnika”
 - Obrazovni resursi – igre vezane za hemiju, Australski hemijski kviz, video materijali poznatih naučnika, sudionici na “sajmovima znanja”
 - Globalni eksperiment za djecu
-

Treba istaći da je realiziran i globalni eksperiment za djecu i mlade:

- Učenici, đaci i studenti iz svih krajeva svijeta (iz osnovnih i srednjih škola, fakulteta) su mjerili, prikupljali uzorke ili podatke, kao što su uzorci vode i mjerili pH vrijednost, i slali u zajedničku bazu podataka.
- Teme vezane za Međunarodnu godinu hemije: hemija i održivost su, između ostalog, bile fokusirane na zalihe pitke vode.

Dakle, IYC 2011 Međunarodna godina hemije je prilika da se naglasi da je naše shvaćanje fundamentalne prirode našeg svijeta utemeljeno na hemiji. Molekularne transformacije su bazne za proizvodnju hrane, lijekova, goriva i raznih materijala – u biti svih proizvedenih i ekstrahiranih produkata. Stoga ćemo se osloniti na ovu nauku da bismo održali održivi, zajednički okoliš za cijelu Zemlju.

IYC 2011 je bila jedinstvena prilika za svakoga, iz svih krajeva svijeta, da obilježi središnje doprinose hemije.

Na osnovu predloška od organizatora obilježavanja Međunarodne godine hemije (IYC 2011) UNESCO i IUPAC priredila prof.dr. Meliha Zejnilagić-Hajrić, oficijelni predstavnik i kontakt osoba za Prirodno-matematički fakultet Univerziteta u Sarajevu.

DRAFT ppt provided by the IYC Outreach Committee

Preuzeto i obrađeno sa mreže za obilježavanje IYC 2011

<http://www.chemistry2011.org/>

Contact person and official representative of Faculty of Science, University of Sarajevo in IYC 2011 event: Prof. dr. Meliha Zejnilagić-Hajrić

OBILJEŽAVANJE MEĐUNARODNE GODINE HEMIJE 2011 NA PRIRODNO-MATEMATIČKOM FAKULTETU UNIVERZITETA U SARAJEVU

O ODRŽANOM SIMPOZIJU POD NAZIVOM „HEMIJA – JUČER, DANAS, SUTRA“

Hemija je nauka koja se bavi izučavanjem svojstava tvari, kao i načina i uzroka njihovog stupanja u međusobne hemijske reakcije. Hemija je najživotnija nauka jer promjene koje ona proučava se dešavaju stalno, različitom brzinom, u mikro i makro svijetu. U nama i oko nas odigravaju se milioni raznih procesa i promjena, koje nastojimo da upoznamo i shvatimo. Zbog toga se danas gotovo u svakoj struci izučava ova nauka.

Međutim, često se zaboravlja koliki je svakodnevni značaj hemije. Nezamislivo je kako bi naš život izgledao bez dostignuća iz područja hemije, kao što su antibiotici, novi lijekovi, pesticidi, umjetna vlakna, sintetičke boje, novi materijali posebnih svojstava, deterdženti i drugi proizvodi. Zbog značaja hemije i njenog utjecaja na razvoj čovječanstva, slobodno možemo reći: Da nema hemije i njene primjene, mi bismo bili i goli, i bos, gladni i bolesni.

Prirodno-matematički fakultet kao najstarija visokoškolska institucija u Bosni i Hercegovini na kojoj se izučava hemija i pripremaju kadrovi iz hemijskih nauka, organizirala je simpozij pod nazivom „**Hemija, jučer, danas, sutra**“, koji je uspješno održan 9. i 10. decembra 2011. godine, u prostorijama Odsjeka za hemiju.

Ovaj simpozij je jedna od aktivnosti koju je Odsjek za hemiju realizirao u svrhu obilježavanja Međunarodne godine hemije 2011., koja je kao takva proglašena od strane krovnih svjetskih organizacija UNESCO (United Nations Educational, Scientific and Cultural Organization) i IUPAC (International Union of Pure and Applied Chemistry).

Na simpoziju se istakao značaj hemije na svjetskoj razini ali i njezina važnost za bosansko-hercegovačko društvo, koje se nastoji uključiti u moderne evropske integracije.

Simpozij je održan u dva dijela – prvi dio bio je namijenjen svim zainteresiranima, dok su drugog dana održane radionice za nastavnike hemije u osnovnim i srednjim školama, kao i za studente hemije.

U prvom dijelu simpozija održana su prigodna predavanja od strane članova Odsjeka za hemiju. Radno predsjedništvo je djelovalo u sljedećem sastavu: Prof. dr. Meliha

Zejniliagić-Hajrić, Prof. dr. Milka Maksimović, Doc. dr. Mustafa Memić, Doc. dr. Fehim Korać.

Zastupljene su bile sljedeće teme:

- O obilježavanju Međunarodne godine hemije (Prof. dr. Meliha Zejniliagić-Hajrić)
- Nobelova nagrada za hemiju 2011. (Doc. dr. Sanja Ćavar)
- Istorijat Odsjeka za hemiju na Univerzitetu u Sarajevu (Prof. dr. Meliha Zejniliagić-Hajrić)
- Prigodan govor o akademiku Prof.dr. Mladenu Deželiću (Doc. dr. Marija Janković i Prof. dr. Milka Maksimović)
- Odsjek za hemiju danas i sutra (Doc. dr. Mustafa Memić)
- Glasnik hemičara i tehnologa Bosne i Hercegovine i Udruženje hemičara i tehnologa Kantona Sarajevo (Doc. dr. Fehim Korać)
- Predstavljanje Grupe za istraživanje nastave hemije i fizike GINHF/CPERG (Ines Nuić, MA)
- Obraćanje gostiju (Prof. dr. Azra Jaganjac i Doc. dr. Anita Martinović)

Doc.dr. Marija Janković je pripremila tekst za ovu priliku koji je prezentirala prof.dr. Milka Maksimović, o akademiku Mladenu Deželiću, jednom od osnivača Odsjeka za hemiju na Univerzitetu u Sarajevu, koji je jedan od zaslužnih i za utemeljivanje Akademije nauka i umjetnosti BiH. (Planirano imenovanje Hemijskog amfiteatra imenom „Amfiteatar Mladena Deželića“ odgođeno je zbog objektivnih razloga do daljnjeg).

Na simpoziju je bilo prisutno 60 učesnika (nastavno osoblje Prirodno-matematičkog fakulteta, gosti i studenti hemije).

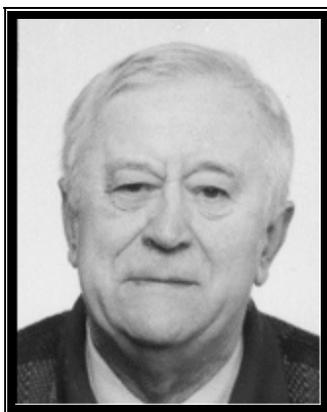
Drugi dan simpozija organizirane su dvije radionice pod nazivom „Motivacijski pokusi“ pod vodstvom Dubravke Turčinović, prof. savjetnice iz Zagreba. Prvoj radionici prisustvovalo je 34 polaznika (nastavnici hemije osnovnih škola i studenti hemije II i III godine studija), i organizatori radionice: Prof.dr. Meliha Zejniliagić-Hajrić, Ines Nuić, Jelena Ostojić i Belma Zukić. Drugoj radionici, pored navedenih organizatora, prisustvovalo je 30 polaznika (nastavnici hemije srednjih škola i studenti IV godine i I godine II ciklusa studija hemije).

U sklopu radionice izvedeni su ogledi prikladni za pojašnjavanje sljedećih hemijskih koncepata na nivou osnovne i srednje škole, što nastavnici i studenti mogu primijeniti u svome radu i učenju:

- Taložne reakcije
- Vrenje vode u papirnatoj kugli
- Simulacija hemijske ravnoteže
- Hemijska reakcija
- Hemijska kinetika
- Promjene topline u hemijskoj reakciji
- Ionska veza (gorenje magnezija)
- Kovalentna veza (gorenje zemnog plina)
- Izrada modela molekula
- Polarnost molekula

Učesnici koji su aktivno učestvovali u radu simpozija dobit će certifikate, prilikom pomenutog imenovanja Hemijskog amfiteatra na Odsjeku za hemiju Prirodno-matematičkog fakulteta u Sarajevu.

IN MEMORIAM



Zdravko Pujić *(1932-2006)*

Akademik Zdravko Pujić posjedovao je čudesnu riječ i darovitost da se iskaže tečnom, pitkom rječju. Njom je oduševljavao svoje studente sjajnim predavanjima, njom je plijenio pažnju svojih sugovornika, kolega i prijatelja i njom je šarmirao. Svojom nadahnutom riječju bio je u stanju objasniti i najkompliciranije kemijsko otkriće, tako, da su ga mogli razumijeti svi, čak i oni koji nisu napisali niti jednu kemijsku formulu. Prof. dr. Zdravko Pujić-Puja bio je talentirani kemičar, zaljubljenik u kemiju. Kazivao je "Kemija prati čovjeka od rođenja do smrti, bez nje nema ni života ni smrti." Ali, oni koji su ga poznavali, znali su, da je bio čovjek i prijatelj, često je Puja čovjek zasjenio Puju kemičara.

Častan, osjetljiv a nezloban, dobronamjieran i pun skrupula, spadao je u ljude koji su bili bolji prema drugima nego prema sebi. Svi su ga voljeli jer su njegovi nervi, iz svih čula, izgleda vodili pravo u srce. Iz srca je gledao svijet i zato bio sposoban da začudi, obraduje i rastuži. Uvijek je odgovarao na pitanje koje je postavljao život, zato je bila fascinirajuća njegova snaga da nadvlada infarkt srca, mozga, uremičku komu, da se vrati i da do posljednjeg daha u mirovini u svom kabinetu na svojoj katedri za biohemiju PMF-a okuplja sagovornike iz raznih branši.

Mogli ste danima razgovarati s njim a da ne saznate da govorite sa uglednim znanstvanikom-Akademikom. Ta njegova osobina da bude običan, jednostavan, topao čovjek

uljevalo je osjećaj sigurnosti malom čovjeku da će im "njihov Puja" u svakom trenutku pomoći, naći krevet u prebukiranoj bolnici, mjesto za upis djeteta u popunjenom razredu, priskočiti pri životnim tegobama. A i samom život nije bio baš uvijek lagodan.

Rođen 17. ožujka 1932. godine u Bijaću od oca Ivana i majke Anke, rođene Rajković. Državnu je realnu gimnaziju završio u Banja Luci (1950.god.). Studij kemije završio na Filozofskom fakultetu u Sarajevu 1957. godine. Bio je zaposlen u Zavodu za industrijska istraživanja BiH u Odjelu za fizikalnu kemiju. 1959. godine izabran je za asistenta za biohemiju na Katedri za fiziologiju i biokemiju i u Centru za primjenu radioizotopa medicinskog fakulteta u Sarajevu. Doktorsku disertaciju iz oblasti kemijskih znanosti obranio na Prirodno-matematičkom fakultetu Univerziteta u Sarajevu. 1964.g. Na Institutu za nuklearne nauke Boris Kidrič Vinča završio je školu za rad sa radioizotopima i primjenu nuklearne energije (1961.). Biran je za docenta u odsjeku za kemiju Prirodno-matematičkog fakulteta. 1974. g. unaprijeđen u vanrednog profesora za biokemiju i 1978.g. izabran za redovnog profesora. Participirao je na postdiplomskim studijama na Prirodno-matematičkom, Medicinskom, Farmaceutskom fakultetu u Sarajevu i Tehnološkom fakultetu u Banja Luci. Osnovne oblasti istraživanja bili su biokemija, radiokemija i kemijsko educiranje. Tijekom radnog vijeka objavio je ili referirao na znanstvenim skupovima više od stotinu naslova. Ima prijavljenja tri patenta u patentnom uredu ex-Jugoslavije. Rukovodio je izradom 120 diplomskih radova inženjera kemije. Bio je mentor u 8 magistarskih radova i tri doktorske disertacije. Koautor je dva srednjoškolska udžbenika. Od bitnijih funkcija bio biran: prorektor Univerziteta (1977.-1981.g.), predsjednik Društva kemičara i tehnologa BiH (1986.), predsjednik Pokreta za nauku mladima BiH (1978.), predsjednik Sekcije za odgoj i obrazovanje HKD "Napredak", član Središnjice HKD "Napredak". Od bitnijih priznanja nosilac je: Šesto-aprilske nagrade grada Sarajeva, Orden rada sa zlatnim vijencem i spomen – plakete grada Sarajeva. Redovan je član HDZU i ANU BiH.

Bio je poseban, osebujan čovjek, intelektualac. Njegov doprinos kemiji na ovim područjima je djelo za pamćenje.

Dr. Marija Janković

Preuzeto iz Radovi Hrvatskog društva za znanost i umjetnost 2007, IX, 269-270.

IN MEMORIAM



Velida Vatrenjak-Velagić *(1945-2003)*

Velida Vatrenjak-Velagić rođena je 1945. godine u Sarajevu i cijeli svoj životni vijek provela je u rodnom gradu. Osnovnu i srednju školu (klasičnu gimnaziju) pohađala je u Sarajevu. Svoju ljubav prema hemiji potvrdila je diplomom 1969. godine na Odsjeku za hemiju Prirodno-matematičkog fakulteta Univerziteta u Sarajevu te doktorskom disertacijom 1985. na Prirodoslovno-matematičkom fakultetu Sveučilišta u Zagrebu.

Svoj prvi radni odnos zasniva u Trgovinskoj školi u Sarajevu kao srednjoškolski profesor. 1970. godine pridružuje se stručnjacima na Hemijskom institutu Prirodno-matematičkog fakulteta u Sarajevu, kao asistent – pripravnik, i tu ostaje do 1972. godine. Od 1972. do 1990. radila je kao asistent na Katedri za analitičku hemiju Prirodno-matematičkog fakulteta u Sarajevu. Kasnije, u svojstvu docenta, vanrednog i na kraju redovnog profesora svoje znanje je prenosila mladima na dodiplomskom i postdiplomskom studiju u Odsjeku za hemiju Prirodno-matematičkog fakulteta. Vodila je nastavu iz predmeta: Analitička kontrola kvaliteta, Hemija životne sredine, Transport i sudbina metala V i VI grupe PSE u okolišu i Kontrola kvaliteta u analitičkom laboratoriju. Takođe, u okviru postdiplomskog studija obavljala je nastavu i na Odsjeku za biologiju PMF-a u Sarajevu te na Poljoprivredno-prehrambenom fakultetu.

Tokom svoje dugogodišnje karijere dala je svoj veliki doprinos kao: prodekan za finansije PMF-a, predstavnik PMF-a u Upravnom odboru PMF-a, ISO/REMCO-pridruženi član, ekspert u Stručno-savjetodavnom odboru Regionalnog Centra za Srednju i Istočnu

Evropu (BiH odjel), član TC-Environment, predsjednik WG 2-Air u okviru BiH, član UNESCO-Associated School Project, član Savjeta za zaštitu okoliša Vlade Kantona Sarajevo, podpredsjednica Upravnog odbora FONDEKO Svijet, član Upravnog odbora SUS BiH, član Društva hemičara i tehnologa Kantona Sarajevo, član Bošnjačkog udruženja inženjera i tehničara Kulturnog društva Muslimana "Preporod", član NGO Speleododo. U periodu rata u BiH bila je pripadnik Armije BiH.

Za ilustraciju sklonosti i potrebe da se posveti radu sa mladim naraštajima, studentima navodimo da je bila inicijator i koordinator na nivou BiH za organizaciju i vođenje takmičenja Mladih istraživača iz oblasti zaštite okoline.

Bila je mentor brojnih diplomskih, magistarskih i doktorskih radova, rukovođila je izradom velikog broja naučnih tema i projekata.

Velida Vatrenjak-Velagić je aktivno učestvovala u nizu naučnih skupova (kongresima, simpozijima) u domovini i inozemstvu, držala je predavanja iz oblasti popularizacije hemije, zaštite okoline, analitičke hemije. Autorica je više udžbenika iz oblasti hemije i hemije okoliša.

Velida Vatrenjak Velagić će biti zapamćena po svojoj čestitosti, hvale vrijednoj borbi za očuvanje životne sredine, kao neko ko se svojski borio za mlade naraštaje te po iznimno plodnom naučno-istraživačkom radu u oblasti analitičke hemije. Svojim je radom ostavila neizbrisiv trag u bosanskohercegovačkoj nauci, a njezina nesebična potpora kolegama, ustrajnost, entuzijazam i težnja perfekciji ostat će kao nit vođilja svima koji nastavljaju njen naučni put.

IN MEMORIAM



Dragutin Murko ***(1930-1999)***

Murko Dragutin, rođen je 1930. godine u Sarajevu, gdje je pohađao osnovnu školu i gimnaziju. Na Matematičko-prirodoslovnom odjelu Filozofskog fakulteta u Zagrebu studirao je hemiju, a studij je okončao diplomiranjem na Filozofskom fakultetu Univerziteta u Sarajevu. Njegov interes za drvo, zaštitu, impregnaciju drveta započinje sa prvim stalnim zaposlenjem u Zavodu za drvo-industrijska istraživanja u Zagrebu, gdje je ujedno obavljao i dužnost sekretara Centra za zaštitu drveta i Centra za industriju tanina. 1956. godine prelazi u Sarajevo, gdje je radio u preduzećima Energoinvest, Jugoinspekt, Farmes, da bi 1961. bio izabran za asistenta na Institutu za hemiju Medicinskog fakulteta Univerziteta u Sarajevu a 1964. godine izabran je za asistenta na Prirodno-matematičkom fakultetu. Učestvovao je u izvođenju nastave iz hemijskih predmeta na prekvalifikacionim (aplikacionim) i postdiplomskim studijama. Suradivao je na Ekonomskom, Šumarskom, Poljoprivrednom, Građevinskom, Mašinskom, Farmaceutskom i Medicinskom fakultetu, te u preduzećima koja su se bavila impregnacijom drveta. Ostavio je značajan trag u organizacijama društva inženjera i tehničara BiH gdje je obnašao niz odgovornih funkcija (predsjednik, dopredsjednik, generalni sekretar i sl.) za što je primio i odgovarajuća priznanja – dva ordena rada, diplome zaslužnog i počasnog člana. Dobitnik je zlatne plakete Univerziteta u Sarajevu, zlatnih plaketa Civilne zaštite YU, Vatrogasnog saveza, ITJ, Pokreta Nauka mladima, itd.

Bio je saradnik niza tehničkih, školskih, pedagoških, medicinskih i dr. muzeja u inozemstvu i član inicijativnih odbora za osnivanje istih u BiH. Bio je potpredsjednik Društva Zemaljskog muzeja u BiH, član Odbora za historiju nauka i odbora za historiju medicine, pri Akademiji nauka i umjetnosti Bosne i Hercegovine, saradnik Centara (zavoda) za povijest prirodnih znanosti i medicinskih znanosti HAZU Zagreb i dr.

Murko Dragutin je bio stručni savjetnik Zavoda za zaštitu kulturne i prirodne baštine BiH i je vršio nadzor i nad radovima na obnovi i zaštiti drvenih objekata sarajevske Bašćaršije.

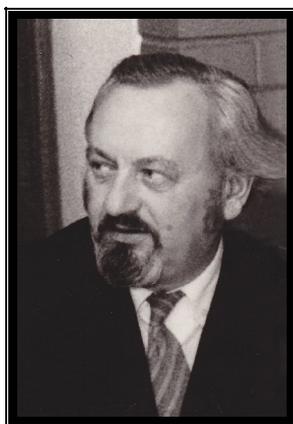
Dragutin Murko je aktivno sudjelovao na naučnim skupovima (kongresima, simpozijima) u domovini i inozemstvu, držao preko 150 predavanja iz oblasti popularizacije hemije, zaštite okoline, iz područja zaštite drveta, recikliranja otpada, kao i predavanja o znamenitim naučnicima-hemičarima i stručnjacima srodnih struka (farmaceutima, liječarima, metalurzima, rudarima i sl.) o istim područjima je pisao u raznim naučnim časopisima: *Priroda*, *Narodna tehnika*, *Biološki list*, *Kemija u industriji*, *Zaštita materijala*, itd. Impozantni naučni opus obuhvata preko 250 naučnih publikacija.

Koautor je četiri udžbenika Organske kemije i dva iz područja kožarstva, namijenjenih srednjim školama, od kojih su neki imali i preko 10 izdanja. Autor je ili koautor nekoliko monografija objavljenih u inozemstvu. Njegova iznimna sklonost ka popularizaciji nauke se ogleda i u činjenici da je snimio preko 100 naučnih emisija »Radio škole« za radio Sarajevo. Najzapaženije područje popularizacije nauke svakako su bile TV-emisije (filmovi) za koje je pisao scenario i vršio stručni nadzor i savjetovanje prilikom snimanja. Po njegovim scenarijima je napravljeno preko 60 kratkometražnih naučno popularnih TV filmova, kao i preko 100 kraćih TV prikaza iz istog područja (hemija, farmacija, tehnologija, minerali, ljekovito bilje,....).

Teme i filmovi o koži su prevedeni na strane jezike i plasirani na starano tržište. Protekli rat je proveo u Sarajevu sa porodicom i aktivno učestvovao u radu Prirodno-matematičkog fakulteta u teškim ratnim uslovima. Volja za rad ga nije napuštala ni kada je već bio teško narušenog zdravlja. I tada je nalazio satisfakciju u radu i pisanju naučnih članaka.

Svojom blagošću, susretljivošću i zavidnom nivou u naučno-istraživačkom radu ostavio je neizbrisivi doprinos ne samo u Bosni i Hercegovini nego i u širem regionu.

IN MEMORIAM



Tibor Ribar ***(1928-2008)***

Kao mladi profesor pripravnik, Tibor Ribar je došao u Sarajevo iz Sente, po Konkursu za mjesto asistenta na predmetu Fizička hemija, na Katedri za hemiju Filozofskog fakulteta u Sarajevu, 1958. godine. Od tada datira njegov naporni i uspješni rad i uspon u karijeri kroz i preko zapreka koje je postavljalo vrijeme i stepen razvijenosti hemije u Bosni i Hercegovini i Sarajevu, početkom druge polovine XX vijeka. Tek oformljen studij hemije na Filozofskom fakultetu u Sarajevu, skoro sve hemijske discipline, u današnjem smislu riječi, u prafazi razvoja, bez laboratorija, infrastrukture, literature, hemikalija, instrumentacije, pribora, nisu pokolebale mladog asistenta Tibora Ribara. Nešto ranije na isti predmet bio je izabran prof. dr Tibor Škerlak u nastavničko zvanje, pod čijim rukovodstvom, ali i vlastitom inicijativom, asistent Ribar daje ogromni doprinos afirmaciji fizičke hemije u univerzitetskoj nastavi i nauci BiH. Formira laboratorije, uvodi eksperimentalne vježbe za studente, provjerava ih, piše skripta, razvija i modernizuje početne nivoe, prati literaturu i primjenjuje savremena dostignuća u nastavu hemije u Sarajevu. Pri tome, Tibor Ribar ne zanemaruje ni vlastiti razvoj i napredovanje. Nakon odbrane doktorske teze biva izabran u zvanje docenta,

1964. godine, vanrednog profesora 1972., a redovnog profesora, 1982. godine, u kojem zvanju je i penzionisan 1998. godine.

U velikom dijelu svog radnog vijeka prof. dr Tibor Ribar bio je posvećen nastavi Fizičke hemije za buduće profesore hemije na Prirodno-matematičkom fakultetu u Sarajevu. Na taj način dao je nemjerljiv doprinos nastavi hemije u srednjim školama Bosne i Hercegovine. Naravno, prof. Ribar nije zanemarivao ni nastavu i saradnju u nauci u nekim područjima Fizičke hemije u obuci studenata, budućih inženjera hemije za industriju i naučne ustanove, kao i za mnogo generacija studenata Farmaceutskog fakulteta u Sarajevu, odnosno, studenata Prehrambeno – tehnološkog fakultetu u Sarajevu.

Prof. Ribar je vodio veliki broj diplomskih i magistarskih i doktorskih radova, a u širokoj lepezi njegovog interesa ističu se veliki broj saradničkih i voditeljskih aktivnosti u realizaciji mnogih naučnih tema i projekata.

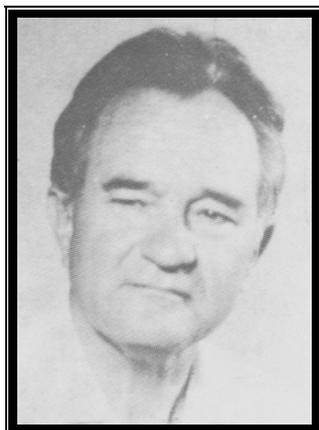
Tokom svog uspješnog radnog vijeka prof. Ribar objavio je veliki broj naučnih radova iz više područja Fizičke hemije (termodinamike rastvora, kinetike, homogene i heterogene katalize, itd.).

Prof. dr Tibor Ribar je obavljao niz značajnih i odgovornih funkcija na fakultetima sarajevskog univerziteta: bio je Šef Katedre za Fizičku hemiju, Šef Odsjeka za hemiju, član mnogih fakultetskih komisija i organa, Prodekan za nastavu Farmaceutskog fakulteta u dva mandata.

Na kraju ističem nešto što se u sjećanjima na profesora Ribara ne smije zanemarivati. Kao jedan od njegovih studenata i saradnika od prvih kontakata bio sam prijatno iznenađen njegovim znanjem, talentom u najširem smislu riječi i izrazitom skromnošću, što često ne ide zajedno. On je nenametljivo trošio svoj talenat i znanje pri rješavanju problema koji su stajali pred njim i saradnicima, a nikada nije isticao svoje zasluge. Ako ovome dodamo ranije ističani entuzijazam, moći ćemo, makar nedovoljno široko, sagledati zasluge prof. Ribara za razvoj hemije u Sarajevu i Bosni i Hercegovini i ostat će nam zadatak da se sa puno zahvalnosti sjećamo našeg Tibora Ribara.

Dr. Merzuk Cacan, profesor u penziji

IN MEMORIAM



Tibor Škerlak ***(1913-1992)***

Početak jula 1992. godine, kada je većina, slabo informisanih, Sarajlija mislila da će u avgustu moći „ići na more“, jedan snajperski hitac sa Grbavice ugasio je život prof. dr Tibora Škerlaka. Bilo je malo svjedoka tog događaja, ali je poznato da je bio upozoren da požuri pri prelasku raskrsnice tadašnjih ulica Bratstva-jedinstva i Vojvode Putnika, ali je on to popratio svojim, kao i uvijek, argumentovanim mišljenjem: „Ja sam suviše star da bi neko poželio da me ubije“. Nažalost, nije bio u pravu; zlikovcu se osamdesetogodišnji starac učinio opasnim po ideje njegovih nalogodavaca i finansijera. I bio je taj „pas rata“ u pravu: Tibor Škerlak je bio davno deklarisan aktivni antifašista. Ranih četrdesetih godina prošlog vijeka na ljubljanskim tavanima, u dubokoj ilegali, hemičar, tada već doktor nauka, Tibor Škerlak je prakticao hemiju u borbi sa italijanskim i njemačkim fašistima. Da nije tako rano ubijen (8.7.1992. godine) sigurno bi pomogao da se koristimo njegovim iskustvom i u borbi sa savremenim fašistima u periodu 1992. – 1995., a nažalost, i kasnije. Kao da je ubica sa Grbavice znao o kome se radilo kad mu se lik starca pojavio na nišanu.

Prof. dr Tibor Škerlak živio je u Sarajevu preko 35 godine. Došao je u proljeće 1954. godine iz Ljubljane, nakon izbora u zvanje vanrednog profesora Fizičke hemije na Katedri za Hemiju Filozofskog fakultet u Sarajevu. U zvanje redovnog profesora izabran je 1964. godine na Prirodno-matematičkom fakultetu u Sarajevu, a penzionisan je u tom zvanju 1984. godine. Njegov život i djelovanje u Sarajevu, a na fakultetu posebno, bio je, slikovito rečeno, ispunjen fizičkom hemijom. Ali, nije to bilo sve: Tibor Škerlak je bio generalno veoma obrazovan čovjek, širokih vidika, vlastitog intelektualnog pogleda na Svijet i događaje u njemu, aktivni učesnik u njima.

Pod mentorstvom prof. Škerlaka urađen je veliki broj diplomskih, magistarskih i doktorskih radova, rukovodio je izradom velikog broja naučnih tema i projekata. Bio je Šef Katedre za Fizičku hemiju, Šef Odsjeka za hemiju, Prodekan Prirodno-matematičkog fakulteta, Glavni i odgovorni urednik GLASNIKA hemičara i tehnologa Bosne i Hercegovine. Boravio je u više navrata u naučnim institucijama u razvijenim zemljama (SAD, Kanada, Velika Britanija, Nemačka), ali i u zemljama u razvoju (Zambija), gdje je prenosio svoje bogato naučno i pedagoško iskustvo na mlade kadrove u tim zemljama. Organizovao je prvi postdiplomski studij „Kinetika i kataliza“ na Prirodno-matematičkom fakultetu u Sarajevu, što je omogućilo, tada mladom, asistentskom kadru Odsjeka za hemiju da se razvija i napreduje do nastavničkih i naučnih zvanja.

Profesor Tibor Škerlak je objavio veliki broj naučnih radova, primjenjujući uvijek veoma stroge kriterije, kako prema svojim tako i tuđim rezultatima naučnog rada. Pri kraju radnog vijeka i iz penzionerskog statusa sarađivao je u naučnoj i stručnoj problematici velikih privrednih organizacija i njihovih instituta („Energoinvest“, „UNIS“, „Zrak“) čije je kadrove vodio kroz lavirint nauke i prakse, bivajući mentorom njihovim kadrovima.

Za ilustraciju sklonosti i potrebe da se posveti pedagoškom radu sa studentima hemije navodimo citat iz Prijave na Konkurs za izbor u nastavničko zvanje 1954. godine. Prof. Škerlak kaže: „ Za mjesto nastavnika na vašem fakultetu interesujem se, prije svega ... jer naročito volim pedagoški rad ...“. O ovome svjedoče mnogi uspješni hemičari kojima je prof. Škerlak bio nastavnik, a o njegovim, istina, strogim ali pravednim i korektnim metodama nastave i ispita pravi sud se donosio tek nakon završetka studija hemije.

Na kraju ovog teksta, koji ne može obuhvatiti mnogo od životopisa prof. Škerlaka, ističem jednu misao iz Izvještaja Komisije za njegov izbor u zvanje redovnog profesora, 1964.

godine. Usput navodim članove te reprezentativne Komisije, ljude koji su obilježili univerzitetsku nastavu i nauku u svojim specijalnostima: prof. Dr. Mladen Deželić, prof.

Dr. Branko Galeb i prof. Dr. Panta Tutundžić, akademik. Oni su potpisali tu misao: „Dr. Ing. Tibor Škerlak, vanredni profesor Fizičke hemije ima sve kvalitete naučnog radnika. Njegovo zalaganje u struci, sklonost prema pedagoškom radu, poznavanje stranih jezika (čak 7, opaska izvan citata) i nastojanje da formira svoje studente u visokokvalitetne stručnjake, a svoje saradnike u naučne radnike, kvalificiraju ga za visokoškolskog nastavnika“. Ja ovome dodajem samo da je prof. Škerlak ostao takav do kraja svog radnog vijeka i nasilne smrti.

Kao jedan od velikog broja studenata i saradnika prof. Škerlaka, izražavam mu, u ime ostalih, zahvalnost za sve ono što je u nas ugradio i što se i danas baštini u hemiji BiH, a nastavit će se baštiniti i u budućnosti. Jer, njegovi studenti će još dugo biti nastavnici i naučnici na univerzitetima u našoj državi, ali i širom Svijeta.

Dr. Merzuk Cacan, profesor u penziji

IN MEMORIAM



Vera Đurkin ***(1931-2009)***

Vera Đurkin rođ. Marković, rođena je 1931. godine u Tuzli. U rodnom gradu završava osnovnu školu i gimnaziju sa ispitom zrelosti 1950. godine. Hemiju je diplomirala na Filozofskom fakultetu u Sarajevu 1956. godine, gdje je krajem iste godine izabrana za asistenta. Doktorat hemijskih nauka stekla je na Prirodno-matematičkom fakultetu u Sarajevu 1964. godine. Osim predavanja i vođenja nastave za predmet "Hemija za biologe" Vera Đurkin je ranije kao asisten i kasnije kao docent surađivala kod izvođenja laboratorijskih vježbi iz analitičke hemije: kvalitativne, kvantitativne i višeg kursa iz analitičke hemije.

Profesorica Vera Đurkin, već kao docent, vršila je niz značajnih dužnosti u društvenim i univerzitetskim te fakultetskim organizacijama: prodekan za nastavu PMF-a, član Upravnog odbora PMF-a, predsjednik Upravnog odbora Instituta za hemiju PMF-a, član Savjeta PMF-a, član Savjeta Instituta za hemiju PMF-a, član Savjeta Instituta za rudarska i hemijsko-tehnološka istraživanja u Tuzli, član Upravnog odbora Saveza hemičara i tehnologa BiH, član raznih komisija na Univerzitetu i PMF-u, te Odsjeku za hemiju.

Radi usavršavanja u struci školsku 1964.-1965. godinu provela je na specijalizaciji u Londonu kao stipendist UNESCO na Imperial koledžu gdje je specijalizirala neke instrumentacijske metode analitičke hemije.

U vezi sa pozitivnom ličnošću i bogatoj naučnoj i stručnoj aktivnosti na fakultetu prof. Đurkin mogao bi se navesti dugi niz činjenica: veliki opus objavljenih naučnih radova iz šireg opsega analitičke hemije, učešća na domaćim i međunarodnim skupovima, visoki kvalitet nastave u svim njenim oblicima koji je pružila svojim studentima, zdušno je pomagala studentima obrazloženjima, tumačenjem, uputama i demonstriranjem, veliki broj izvedenih diplomanada, sudjelovanje u naučno-istraživačkim projektima...

Vera Đurkin, kao osoba sa duboko usađenim osjećajem odgovornosti, pristupala je svakom poslu veoma savjesno, pa tako i profesorskoj dužnosti na fakultetu.

Pored značajnog doprinosa nauci, prof. Đurkin je bila svestrana osoba. Naime, kao atletičarka i košarkašica bila je učesnica Prvog prvenstva BiH u atletici, održanog 1946. godine. Bilo je to vrijeme oskudice, u kojem u sportu nije bilo nikakvih stimulansa, nije bilo čak ni staza za treniranje a najveća nagrada bilo je putovanje ili nova oprema.

Bila je ugledna i poštovana profesorica koja je svojim dugogodišnjim uspješnim radom dala značajan doprinos razvoju i promociji analitičke hemije u Bosni i Hercegovini.

INSTRUCTIONS FOR AUTHORS

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-

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d) Reference to a proceeding:

Seliskar, C. J., Heineman, W.R., Shi, Y., Slaterbeck, A.F., Aryal, S., Ridgway, T.H., Nevin, J.H. (1997). *New spectroelectrochemical sensor*, in Proceedings of 37th Conference of Analytical Chemistry in Energy and Technology, Gatlinburg, Tennessee, USA, p.p. 8-11.

e) Patents:

Healey, P.J., Wright, S.M., Viltro, L.J., (2004). *Method and apparatus for the selection of oral care chemistry*, The Procter & Gamble Company Intellectual Property Division, (No.US 2004/0018475 A1).

f) Chemical Abstracts:

Habeger, C. F., Linhart, R. V., Adair, J. H. (1995). Adhesion to model surfaces in a flow through system. *Chemical Abstracts*, CA 124:25135.

g) Standards:

ISO 4790:1992. (2008). *Glass-to-glass sealings - Determination of stresses*.

h) Websites:

Chemical Abstract Service, www.cas.org, (18/12/2010).

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Reporting analytical and spectral data

The following is the recommended style for analytical and spectral data presentation:

1. **Melting and boiling points:**

mp 163–165°C (lit. 166°C)

mp 180°C dec.

bp 98°C

Abbreviations: mp, melting point; bp, boiling point; lit., literature value; dec, decomposition.

2. **Specific Rotation:**

$[\alpha]^{23}_{\text{D}} -222$ (*c* 0.35, MeOH).

Abbreviations: α , specific rotation; D, the sodium D line or wavelength of light used for determination; the superscript number, temperature (°C) at which the determination was made; In parentheses: *c* stands for concentration; the number following *c* is the concentration in grams per 100 mL; followed by the solvent name or formula.

3. NMR Spectroscopy:

^1H NMR (500 MHz, DMSO- d_6) δ 0.85 (s, 3H, CH₃), 1.28–1.65 (m, 8H, 4'CH₂), 4.36–4.55 (m, 2H, H-1 and H-2), 7.41 (d, J 8.2 Hz, 1H, ArH), 7.76 (dd, J 6.0, 8.2 Hz, 1H, H-1'), 8.09 (br s, 1H, NH).

^{13}C NMR (125 MHz, CDCl₃) δ 12.0, 14.4, 23.7, 26.0, 30.2, 32.5, 40.6 (C-3), 47.4 (C-2'), 79.9, 82.1, 120.0 (C-7), 123.7 (C-5), 126.2 (C-4).

Abbreviations: δ , chemical shift in parts per million (ppm) downfield from the standard; J , coupling constant in hertz; multiplicities s, singlet; d, doublet; t, triplet; q, quartet; and br, broadened. Detailed peak assignments should not be made unless these are supported by definitive experiments such as isotopic labelling, DEPT, or two-dimensional NMR experiments.

4. IR Spectroscopy:

IR (KBr) ν 3236, 2957, 2924, 1666, 1528, 1348, 1097, 743 cm^{-1} .

Abbreviation: ν , wavenumber of maximum absorption peaks in reciprocal centimetres.

5. Mass Spectrometry:

MS m/z (relative intensity): 305 (M⁺H, 100), 128 (25).

HRMS–FAB (m/z): [M+H]⁺ calcd for C₂₁H₃₈N₄O₆, 442.2791; found, 442.2782.

Abbreviations: m/z , mass-to-charge ratio; M, molecular weight of the molecule itself; M⁺, molecular ion; HRMS, high-resolution mass spectrometry; FAB, fast atom bombardment.

6. UV-Visible Spectroscopy:

UV (CH₃OH) λ_{max} (log ϵ) 220 (3.10), 425 nm (3.26).

Abbreviations: λ_{max} , wavelength of maximum absorption in nanometres; ϵ , extinction coefficient.

7. Quantitative analysis:

Anal. calcd for C₁₇H₂₄N₂O₃: C 67.08, H 7.95, N 9.20. Found: C 66.82, H 7.83, N 9.16. All values are given in percentages.

8. Enzymes and catalytic proteins relevant data:

Papers reporting enzymes and catalytic proteins relevant data should include the identity of the enzymes/proteins, preparation and criteria of purity, assay conditions, methodology, activity, and any other information relevant to judging the reproducibility of the results¹. For more details check Beilstein Institut/STREND A (standards for reporting enzymology data) commission Web site (<http://www.strenda.org/documents.html>).

¹ For all other data presentation not mentioned above please contact Editor for instructions.

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The following list will be useful during the final checking of an article prior to sending it to the journal

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- Manuscript has been "spellchecked" and "grammar-checked",
- References are in the correct format for the journal,
- All references mentioned in the Reference list are cited in the text, and *vice versa*.

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Submissions should be directed to the Editor by e-mail: ***glasnik@pmf.unsa.ba***, or ***glasnikhtbh@gmail.com***. All manuscripts will be acknowledged on receipt (by e-mail) and given a reference number, which should be quoted in all subsequent correspondence.



Glasnik hemičara i
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Print ISSN: 0367-4444
Online ISSN: 2232-7266

Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

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