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The article are translated by authors and by Nikoleta Bašić, Radovan Urošević and Jelena Vukićević

SCOPE OF THE JOURNAL

It is the endeavour of the University of Pristina to acquaint the scientific world with its achievements. We would like to affirm the intellectual potential of this region as well as natural resources of the Balkans. We would like to put forward our attitude of principle that science is universal and we invite all scientist to cooperate wherever their scope of research may be. We are convinced that we shall contribute to the victory of science over barriers of all kinds erected throughout the Balkans.

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IN MEMORIAM

Dr GOJKO PASULJEVIĆ

(08.05.1931. - 23.12.1997.)



Prof. dr Gojko Pasuljević je rođen 08.05.1931. godine u Prizrenu gde je završio osnovno i srednje obrazovanje. Studirao je i 1957. godine diplomirao biologiju na Prirodno-matematičkom fakultetu u Beogradu.

Radio je kao profesor biologije u Učiteljskoj školi u Prizrenu, a oktobra 1969.

godine izabran je za asistenta na novootvorenoj Grupi za biologiju, tada Filozofskog fakulteta. Doktorsku disertaciju odbranio je 1973. godine na Prirodno-matematičkom fakultetu u Prištini. Njegova naučna aktivnost je bila usmerena na istraživanju herpetofaune Kosova i Metohije.

Posebna preokupacija prof. Pasuljevića bila je usmerena na proučavanju nekih biogeografski veoma

interesantnih elemenata faune Balkanskog poluostrva iz grupe reptila.

Rezultati prof. Pasuljevića u toj oblasti su od značaja jer je ukazao u kojoj je meri grupno variranje stvarni izraz divergentne evolucije i kakvu ulogu u mikroevolucionom procesu imaju prostorni izolacioni mehanizmi.

Savremena teorijska shvatanja o osnovnim mehanizmima mikroevolutivnog procesa-odnosno o faktorima endemične diferencijacije dobila su izvrsnu potvrdu u originalnim rezultatima o morfološkom varijabilitetu guštera *Ablepharus kitaibelii*.

Prof. Pasuljević je pripadao pionirskoj, prvoj generaciji osnivača i utemeljivača prvih fakulteta, a zatim i Univerziteta u Prištini. Čitav radni vek (36 godina) proveo je na ovom Univerzitetu i iza sebe ostavio 35 generacija studenata, profesora biologije.

Prof. Pasuljević će u našem sećanju ostati kao vredan, nenametljiv i skroman kolega i profesor.

D. Pejčinović

IN MEMORIAM

Prof. dr. Slobodan Glumac **redovni profesor u penziji (1930-1998)**



Kako to često biva, bolest se došunjala tiho i neprimetno, kao lahor, a razbuknula se u oluju koja neumitno donosi kraj. Tako je 16. januara 1998. godine otišao profesor Slobodan Glumac. Ali smrt nije mogla da odnese njegovo delo, ni da ukloni duboke tragove koje je ovaj izuzetan čovek ostavio u onim oblastima

koje su bile njegova ljubav i opredeljenje. Samo oni koji su imali sreću da ga poznaju znaju sa kojom lakoćom je rešavao i najsloženije izazove, sa kakvom lucidnošću je pronicao u biološke probleme i rasvetljavao ih. Poseban je bio doživljaj svaki razgovor sa njim, svaki javni nastup kada je visprenost njegovog uma vladala situacijom koristeći bolje i dublje razumevanje kao osnovu za izvanredne misaone obrte koji su razoružavali i najžešće sabesednike. Ti trenuci provedeni uz njega obogatili su živote svih onih koji su mogli da prepoznaju u njemu svetlo izuzetnosti i, zašto ne reći, genijalnosti.

Slobodan Glumac je rođen u Senju 1930. godine. Osnovnu školu je završio u Novom Sadu, srednju školu u Beogradu, gde je upisao Prirodno-matematički fakultet, studije biologije 1950. godine. Diplomirao je, radeći kao preparator Prirodnjačkog muzeja SRS, juna 1954. Po odsluženju vojnog roka, 1957. godine, još izuzetno mlad, uspešno je odbranio doktorsku disertaciju iz oblasti entomologije na Beogradskom Univerzitetu.

Uprkos početnim teškoćama u burnim posleratnim vremenima, za karijeru profesora Glumca se slobodno može reći da je bila meteorska. Zahvaljujući kvalitetima koji nisu mogli proći nezapaženo, uspeo je za kratko vreme da prođe sve stepenice u Univerzitet-skoj hijerarhiji. Prvo zaposlenje dobija još kao student 1952. godine kao preparator Prirodnjačkog muzeja SRS u Beogradu, gde je, odmah po diplomiranju postavljen za kustosa. Po odsluženju vojnog roka, na poziv prof. dr. Pavla Vukasovića, vraća se u Novi Sad gde je izabran za asistenta na novoosnovanom Poljoprivrednom fakultetu, 1958. godine za docenta, a godine 1962. na

istom fakultetu, za vanrednog profesora. Još kao docent, 1961. godine je od Nastavnog veća i Saveta tadašnjeg Filozofskog fakulteta, izabran za vršioca dužnosti i kasnije šefa Katedre novoosnovane studijske grupe za biologiju. Kao vanredni profesor Poljoprivrednog fakulteta 1963. godine prelazi na Filozofski fakultet na predmet Zoologija (Morfoloģija i sistematika beskičmenjaka). Iste godine je izabran i za direktora novoosnovanog Zavoda za biologiju. Ovu dužnost je vršio preko 9 godina (1963-1971.) do početka izgradnje novog objekta. Dve godine je bio jedan od prorektora Univerziteta u Novom Sadu. Njegovim doprinosom i zaslugom Institut za biologiju dobija zgradu i opremu kojom se i danas ponose saradnici Instituta. Za redovnog profesora je izabran 1969. godine. Predavao je studentima tri fakulteta u Novom Sadu i Prirodno-matematičkog fakulteta u Prištini, u okviru velikog broja predmeta na osnovnim i magistarskim studijama. Predavanja profesora Glumca pripadaju grupi onih koja se ne zaboravljaju. Njegova širina i znanje su mu omogućili lakoću izlaganja i najtežih sadržaja iz evolucije, predmeta koji je za njega predstavljao krunu bioloških studija. Svojim predavanjima je znao da podari filozofsku dimenziju razumevanja sveta i života. Uz to, njegov retorički dar, duhovitost i domišljatost davali su nezaboravan šarm svakom njegovom izlaganju.

Vodio je studente kroz izradu 32 diplomskih rada, bio mentor za 11 magistarskih radova i 7 doktorata. To je radio znalački, budeći kreativnost i dajući punu slobodu svakom svom saradniku, uz tanano usmeravanje ka pravim rešenjima kroz ideje koje su neprekidno isticale iz njega. Zato ti radovi imaju poseban kvalitet, a mnogi učenici zauvek nose prepoznatljivi pečat njegovog uticaja.

Obavljao je niz funkcija na Fakultetu i Univerzitetu. Od prodekana Filozofskog fakulteta, dekana Prirodno-matematičkog fakulteta, člana Univerzitet-skog Saveta, direktora Instituta za biologiju, do predsednika Društva biologa Vojvodine, potpredsednika Jugoslovenskog entomološkog društva, predsednika Društva biosistematičara Vojvodine i predsednika Unije bioloških društava Jugoslavije.

Od 1956. godine, kada se pojavio njegov prvi rad u Zborniku za prirodne nauke, dr Slobodan Glumac je

bio saradnik Matice srpske, član Odbora odeljenja, Upravnog odbora Matice srpske, Izvršnog odbora, a skoro 11 godina je bio sekretar Odeljenja za prirodne nauke. Bio je potpredsednik Matice srpske od 1991. godine, dugogodišnji član Redakcije, a zatim urednik Zbornika za prirodne nauke. Veliki deo svojih sposobnosti, svog znanja, energije i ljubavi vezao je za Maticu srpsku, zalažući se za afirmaciju prirodnih nauka u njenom okrilju. Njegovim zalaganjem je Zbornik za prirodne nauke doživeo značajnu transformaciju, kroz koju su radovi objavljeni u njemu sada dostupni svetskoj naučnoj javnosti.

Objavio je veliki broj naučnih radova iz oblasti taksonomije, ekofiziologije insekata i drugih oblasti. Autor i koautor je nekoliko srednjoškolskih i visokoškolskih udžbenika i monografija, 102 naučna rada, učestvovao je na brojnim naučnim skupovima u zemlji i inostranstvu. Najveće priznanje za svoj naučni rad dr Slobodan Glumac je dobio kada je na XV svetskom entomološkom kongresu u Vašingtonu 1976. godine izabran za člana Stalnog komiteta svetskih entomoloških kongresa (Permanent Committee of International Congresses of Entomology).

Nauka je bila velika ljubav profesora Glumca. Njoj je posvetio najviše stvaralačke snage. Istraživao je obligatornu dijapauzu kod insekata, prag razvića kod Diptera, ekofiziološke problema kod beskičmenjaka,

od hidri do insekata. Međutim, nesumnjivo najveći deo svog rada je posvetio istraživanjima jedne familije dvokrilaca, osolikim muvama. Tu je njegov doprinos u svetskoj nauci nezaobilazan. Stazama koje je on utabao i pravcima koje je nagovestio danas idu njegovi najbliži saradnici, ali i mnogi istraživači iz različitih delova sveta. Kada je to bilo potrebno, video je više i dalje od ostalih. Zato je i mogao da oformi tim ljudi koji nastavljaju putem na koji je on zakoračio pre više od 40 godina.

U penziju je otišao 1995. godine, nastavio da radi, lomeći se između želje za novim izazovima i jakog osećaja dužnosti da se mora otići "na vreme". Možda je u tom rascepu klica bolesti koja ga je pobedila. Treba podsetiti da je pre više od dvadeset godina, samo beskrajnou snagom volje, porazio sličnu podmuklu bolest. Drugi put nije uspeo.

I na kraju, nema kraja. Ostao je u ljudima koji su ga voleli, ostao je u delima koja će se čitati. U nama koji smo rasli uz njega, ostala je tuga, ali možda više od toga radost. Radost što smo imali sreće da ga poznamo i posebnu privilegiju da nas obogati znanjem, mudrošću i lepotom u duši.

Hvala mu na tome

A. Vujić.

Prof. dr Slobodan Glumac

Bibliografija

1. Glumac, S. (1953): Jedna nova fiziološka metoda za kontrolu determinacije hidri, njen značaj i mogućnosti njene šire primene. Glasn.Prir.muz.srpske zemlje, B (5-6): 493-502.
2. Glumac, S. (1953): Prilog poznavanju funkcionisanja zarnih kapsula hidre - I deo. Glasn.Prir.muz.srpske zemlje, B (5-6): 503-511.
3. Glumac, S. (1955): Prilog poznavanju funkcionisanja zarnih kapsula hidre - II deo. Glasn.Prir.muz.srpske zemlje, B, 7 (4): 175-179.
4. Glumac, S. (1955): Prilog poznavanju funkcionisanja zarnih kapsula hidre - III deo. Glasn.Prir.muz.srpske zemlje, B, 7 (4): 181-183.
5. Glumac, S. (1955): Simbioza kao faktor u formiranju vrsta hidri. Glasn.Prir.muz.srpske zemlje, B, 7 (4): 185-211.
6. Glumac, S. (1955): Osolike muve Srbije (Syrphidae, Diptera) iz zbirke Prirodnjačkog muzeja srpske zemlje u Beogradu. Zaštita bilja, 27: 3-43.
7. Glumac, S. (1955): Zbirka sirfida (Syrphidae, Diptera) Biološkog instituta u Sarajevu. God.biol.inst. u Sarajevu, 7 (1-2): 115-124.
8. Glumac, S. (1956): Syrphidae (Diptera) Slobodne teritorije Trsta (Zone "B") - Kopra i Umaga, sakupljene 1955. godine. Glasn. Prir.muz.srpske zemlje, B, 8 (3): 173-204.
9. Glumac, S. (1956): Zakonitosti rasprostranjenja i brojnosti vrsta familije Syrphidae (Diptera) u Jugoslaviji. Glasn.Prir. muz.srpske zemlje, B, 8 (3): 205-224.
10. Glumac, S. (1956): Syrphidae (Diptera) Jznog Primorja Jugoslavije - rezultati prikupljanja u 1956. godini. Glasn. Prir.muz.srpske zemlje, B, 8 (3): 225-247.
11. Glumac, S. (1956): O nekim vrstama sirfida koje su prvi put nađene na teritoriji Jugoslavije. Zbornik za prir.nauke Matice srpske, 10: 3-5.
12. Glumac, S. (1957): O uticaju zajedničkog i izolovanog gajenja organizama na razviće njihove populacije - ogledi sa *Pelmatohydra oligactis* Pall. Letop.nauč.rad.Polj.fak. 1: 1-12.
13. Glumac, S. (1958): Problem vrsta dvojnika i vrste roda *Sphaerophoria* (Syrphidae, Diptera). Letop.nauč.rad.Polj.fak. 2: 1-4.
14. Carić, V., Glumac, S. (1958): Proučavanje biologije *Tineola biselliella* Hum. i promena sredine u kojoj se razvija. Letop. nauč.rad.Polj.fak. 2: 1-5.
15. Glumac, S. (1958): Karakteristike javljanja i brojnosti sirfida (Syrphidae) Fruške gore. Zaštita prirode, 14: 20-27.
16. Glumac, S. (1958): Građe hipopigijuma (genitalia externa) sirfida (Syrphidae, Diptera) nađenih u Jugoslaviji i njihov značaj u filogenetskoj sistematici. Glasn.Prir.muz.srpske zemlje, B, 12: 99-167.
17. Jovanić, M., Glumac, S. (1959): *Hylemyia cilicrura* Rond. (Anthomyiinae, Muscidae, Diptera) - nova štetočina pšenice (*Triticum vulgare*) u Jugoslaviji. Arhiv za polj.nauke, XII (35): 1-4.
18. Glumac, S. (1959): Syrphidae (Diptera) Fruške gore. Zborn.za prir.nauke Matice srpske, 17: 37-78.
19. Glumac, S. (1959): Proučavanje građe hipopigijuma nekih vrsta sirfida (Syrphidae, Diptera) iz zbirke Britanskog prirodnjačkog muzeja. Let.nauč.rad.Polj.fak. 3: 1-14.
20. Carić, V., Glumac, S. (1959): Proučavanje biologije *Tineola biselliella* Hum. i fizičko-hemijskih promena sredine u kojoj se on razvija - II. Let.nauč.rad.Polj.fak. 3: 1-7.
21. Glumac, S., Carić, S. (1960): Mogućnost suzbijanja kukuruznog plamenca (*Pyrausta nubilalis* Hbn) delovanjem povišene temperature. Savremena poljoprivreda, 9: 715-721.
22. Glumac, S. (1960): Prirodan sistem sirfida (Syrphidae, Diptera) zasnovan na građi genitalnog aparata i načinu razvitka larava sa karakteristikama familija i tribusa. Glasn.Prir.muz., B, 16: 69-103.
23. Vukasović, P., Glumac, S., Martinović, A. (1961): Prilog proučavanju polifagije pasuljevog zizka (*Acanthoscelides obtectus* Say) u našoj zemlji. Letop.nauč.rad.Polj.fak., 5: 1-35.
24. Borojević, K., Glumac, S. (1961): Oštećenje pšenice izazvano nematodama na oglednom polju Rimski Šančevi. Savremena poljoprivreda, 3: 233-239.
25. Vukasović, P., Glumac, S. (1962): Faktori koji utiču na dijapauzu i broj generacija kod kukuruznog moljca (*Pyrausta nubilalis* Hubn.). Savremena poljoprivreda, X (6): 435-442.
26. Glumac, S. (1962): Problem mimikrije i sirfide (Syrphidae, Diptera). Arhiv bioloških nauka, XIV (1-2): 61-67.
27. Vukasović, P., Glumac, S. (1962): O uticaju količine hrane na razvitak populacije pasuljevog zizka. Letop.nauč.rad.Polj.fak. 6: 1-16.
28. Glumac, S. (1963): Analiza faune sirfida (Syrphoidea) Makedonije. Zbornik radova Cenološkog kolokvija, Zagreb: 24-29.
29. Vukasović, P., Glumac, S. (1965): Uticaj duzine osvetljenja i temperature na dijapauzu kod kukuruznog moljca (*Pyrausta nubilalis* Hubn.). Savremena poljoprivreda, 6: 551-554.
30. Glumac, S. (1965): Mimetizam i biološko objašnjenje ove pojave. Zbornik naučnih radova Simpozijuma Marksizam i biologija, Beograd: 215-220.
31. Glumac, S., Horvatić, A. (1966): Prvi rezultati primene metode polenove analize u ekološkim istraživanjima insekata. Arhiv bioloških nauka, XVIII (2): 13P-14P.
32. Vukasović, P., Glumac, S. (1967): Uticaj hrane na plodnost i duzinu života pasuljevog zizka (*Acanthoscelides obtectus* Say.). Zaštita bilja, 93-95: 11-20.
33. Glumac, S. (1968): Sirfide (Syrphoidea, Diptera) u Makedoniji. God.Fil.fak., XI (2): 845-880.

34. Glumac, S., Ivanović, J. (1969): O razvoju kukuruznog moljca (*Pyrausta nubilalis* Hubn.) na krompiru. *God.Fil.fak.*, XII (2): 889-893.
35. Glumac, S. (1970): O uticaju ligatura na metamorfozu gusenica kukuruznog moljca (*Pyrausta nubilalis* Hubn.). *Zbornik radova PMF-a*, 1: 169-173.
36. Horvatić, A., Glumac, S. (1972): O mogućnosti korišćenja metode respiratornog metabolizma u proučavanju insekata. *Zbornik radova PMF-a*, 2: 153-158.
37. Glumac, S., Horvatić, A. (1972): O nastajanju afidofagije u sirfida. *Zbornik radova PMF-a*, 2: 159-162.
38. Glumac, S., Koledin, , Horvatić, A. (1972): O uzrocima propadanja insekata na povišenoj temperaturi (delimična korekcija Bachmetjew-e krive, 1907). *Zbornik za prir. nauke Matice srpske*, 42: 144-151.
39. Glumac, S., Šimić, S. (1973): O mogućnostima za neprekidno uzgajanje kukuruznog moljca (*Pyrausta nubilalis* Hubn.) u laboratorijskim uslovima. *Zbornik radova PMF-a*, 3: 105-108.
40. Stevanović, D., Glumac, S., Šimić, S. (1974): O uticaju osvetljavanjasvetlošću različitih talasnih dužina na metamorfozu *Ostrinia nubilalis* (Hubn.). *Ekologija*, 9 (1): 55-61.
41. Stevanović, D., Glumac, S., Šimić, S. (1974): Prilog proučavanju značaja svetlosti u pojedinim periodima dijapauze kod kukuruznog moljca (*Ostrinia nubilalis* Hubn.). *Zaštita bilja*, XXV (128-129): 221-227.
42. Šimić, S., Glumac, S., Stevanović, D. (1975): O uticaju različitih svetlosnih intervala na izlazenje iz dijapauze *Ostrinia nubilalis* Hubn. *Zbornik radova PMF-a*, 7: 235-240.
43. Glumac, S. (1976): *Eristalodes taeniops* Wied. element etiopsko-mediteranske faune u Jugoslaviji? *Zborn. za prir. nauke Matice srpske*, 51: 115-116.
44. Stevanović, D., Glumac, S. (1977): O različitom uticaju temperature pri konstantnoj osvetljenosti u pojedinim periodima dijapauze kod *Ostrinia nubilalis* (Hubn.). *Zbornik radova PMF-a*, 7: 235-240.
45. Glumac, S. (1977): Einige zoogeographische Gesetzmäßigkeiten der Dipterenverbreitung in Jugoslawien. VII Intern. Symp. über Entomofaunistik in Mitteleuropa, Verhandlungen: 300-305.
46. Glumac, S., Ruškuc, D. (1977): Uporedno proučavanje varijabilnosti čistih linija *Acanthoscelides obtectus* Say. - uticaj hrane na plodnost i dužinu života. *Zbornik radova PMF-a*, 7: 241-246.
47. Glumac, S., Janković-Hladni, M., Ivanović, J., Stanić, V., Nenadović, V. (1979): The effect of thermal stress on *Ostrinia nubilalis* Hbn (Lepidoptera, Pyralidae) - I. The role of the neurosecretory cells in the survival of diapausing larvae. *Journal of Thermal Biology*, 4: 277-282.
48. Glumac, S., Ruškuc, D. (1979): Proučavanje bivoltizma *Ostrinia nubilalis* Hubn. primenom feromona. *Zbornik za prir. nauke Matice srpske*, 57: 19-23.
49. Glumac, S. (1980): Effects of larval biology on the process of speciation in the group Syrphoidea (Diptera). *Zbornik radova PMF-a*, 10: 417-422.
50. Božičić, B., Ruškuc, D., Glumac, S. (1986): Uloga predatora u regulisanju brojnosti komaraca (Culicidae, Diptera). *Zbor. rad. Prir. mat. fak. Univ. Novi Sad. ser. biol.* br.16,91-98.
51. Krnić, M., Glumac, S. (1983): Obrazovanje kadrova i istraživanje faune SR Srbije. *Zbornik Drugog simpozijuma o fauni SR Srbije*: 9-13.
52. Glumac, S., Božičić, B., Ruškuc, D. (1984): Researching of the way of feeding of some species of Mosquitoes (Diptera, Culicidae). *Acta Entomologica Jugoslavica*, 20 (1-2): 129-137.
53. Božičić, B., Šimić, S., Glumac, S. (1986): Taksonomski problemi u nekim grupama Diptera. *Biosistematika*, 12, (2): 129-137.
54. Ruškuc, D., Glumac, S. (1987): Istraživanja morfoloških razlika populacija različitog geografskog porekla iz prve i druge generacije *Ostrinia nubilalis* Hubner (Lepidoptera, Insecta) u Jugoslaviji. *Zbor.Mat.Srp., ser.prir.nauka*, 73: 25-32.
55. Šimić, S., Glumac, S. (1987): The Syrphid Fauna of Montenegro (Insecta: Diptera): A Zoogeographical Analysis within the Balkan Peninsula. *Biol. Gallo-hellenica*, 13: 99-102.
56. Glumac, S. (1988): The origin of mimicry in the family Syrphidae. *Zbor. rad. Prir. mat. fak. Univ. Novi Sad. ser. biol.*, 18: 71-74.
57. Glumac, S., Ruškuc, D. (1990): Temperatura praga razvića insekata kao biološka adaptacija - istraživanja na *Calliphora erythrocephala* Meig. (Diptera). *Zbor. Mat. srp. za prir. nauke*, 79: 21-26.
58. Grubor-Lajšić, G., Block, W., Palanački, V., Glumac, S. (1991): Cold hardiness parameters of overwintering diapause larvae of *Ostrinia nubilalis* in Vojvodina, Yugoslavia. *Cryo-Letters* 12: 177-182.
59. Radnović, D., Glumac, S. (1992): The Zoogeographical Composition of Syrphid Fauna (Diptera: Syrphidae) in Relation to Season. *Proceeding of the 4th ECE/XIII. SIEEC, Godollo*. 1991: 414-418.
60. Šimić, S., Popović, E., Glumac, S., Vujić, A. (1992): Učešće insekata u ishrani vrste *Rana kl. esculenta* L. (Amphibia: Anura) Koviljskog rita. *Zb. rad. Prir. mat. fak. Univ. Novi Sad, Ser.Biol.*, 22: 85-89.
61. Vujić, A., Glumac, S. (1993): Some views on Syrphidae (Diptera) phylogeny. *Zborn. Mat. Srp. za Prir. nauke*, 84: 13-17.
62. Banovački, Z., Tepavčević, A., Glumac, S. (1996): An Application of the Mathematical model in the insects threshold studies. *Zborn. Mat. Srp. za Prir. nauke*, 90: 89-93.

MONOGRAFIJE

1. Glumac, S. (1972): *Catalogus Faunae Jugoslaviae, Syrphoidea*, III/6. Slovenska akademija znanosti i umetnosti, Ljubljana.
2. Vujić, A., Glumac, S. (1994): *Fauna osolikih muva (Diptera: Syrphidae) Fruške gore*. Monografije Fruške gore. Matica srpska. Novi Sad.

DOKTORSKA DISERTACIJA

1. Glumac, S.: *Syrphidae (Diptera) naše zemlje, njihova sistematika i filogenija zasnovane na tipovima građe phalusa*. Doktorska disertacija. Univerzitet u Beogradu, PMF. 1957.

SAOPŠTENJA NA NAUČNIM SKUPOVIMA

1. Glumac, S.: Phylogenetical system of the Syrphid-flies based upon male genitalia structure and the type of the larvae. XI Internationaler Kongress uber Entomologie. Wien. 1960.
2. Vukasović, P., Glumac, S., Martinović, A.: Sur la polyphagie de a bruche du haricot (*Acanthoscelides obtectus*). XI Internationaler Kongress uber Entomologie. Wien. 1960.
3. Glumac, S.: Problem mimikrije i sirfide (Syrphoidea, Diptera). II kongres biologa Jugoslavije. Beograd. 1962.
4. Vukasović, P., Glumac, S.: Faktori koji utiču na dija-pauzu kod kukuruznog moljca (*Pyrausta nubilalis* Hubn.). II kongres biologa Jugoslavije. Beograd. 1962.
5. Glumac, S.: Analiza faune sirfida (Syrphoidea) Make-donije. Cenološki kolokvijum Instituta za zašt. bilja Polj. fak. Zagreb. 1963.
6. Glumac, S., Vukasović, P.: Factors affectings the diapuse and number of generations of European corn borer (*Pyrausta nubilalis* Hubn.) - influence of food and light. XII International Congress of Entomology. London. 1964.
7. Glumac, S.: Syrphid larvae as aphid predators in Yugoslavia. Symposium Ecology of Aphidophagous Insects. Prag. 1966.
8. Glumac, S.: Comparison of the System of Syrphidae (Diptera) based on the type og larvae and male genitalia structure. XIII International Congress of Entomology. Moskva. 1968.
9. Ivanović, J., Glumac, S.: The changes in the midgut amylase activity in some development stages of *Pyrausta nubilalis* larvae. XIII International Congress og Entomology. Moskva. 1968.
10. Glumac, S., Ivanović, J.: Promene digestivnog trakta gusenica *Pyrausta nubilalis* tokom dija-pauze. Sim-pozijum iz ekologije. Beograd. 1969.
11. Glumac, S., Horvatović, A.: O nastajanju afidofagije u sirfida (Syrphidae, Diptera). III kongres biologa Ju-goslavije. Ljubljana. 1969.
12. Glumac, S., Ivanović, J.: O razvoju kukuruznog moljca (*Pyrausta nubilalis* Hubn.) na krompiru. III kongres biologa Jugoslavije. Ljubljana. 1969.
13. Glumac, S., Ivanović, J.: European corn borer (*Pyrausta nubilalis* Hubn.) new pest on potato in Yugoslavia. VII International Congress of Plant Pro-tection. Paris. 1970.
14. Glumac, S. and Colleagues: Influence of low tem-perature on the European corn borer (*Ostrinia nubi-lalis* Hubn.) caterpillars. Symposium Physiological Ecology of Plants and Animals in Extreme Environ-ments. Cavtat. 1972.
15. Glumac, S.: Zoogeographic regularities in insect dis-tribution on the Balcan peninsula. XIV International Congress of Entomology. Canberra. 1972.
16. Stevanović, D., Glumac, S., Šimić, S.: O uticaju os-vetljavanja svetlošću različitih talasnih dužina na metamorfozu *Pyrausta nubilalis* (Hbn). I kongres ek-ologa Jugoslavije. Beograd. 1973.
17. Glumac, S., Koledin, : O uzrocima propadanja in-sekata na povišenim temperaturama. I kongres ek-ologa Jugoslavije. Beograd. 1973.
18. Stevanović, D., Glumac, S., Šimić, S.: O različitom delovanju faktora u toku dija-pauze kod *Ostrinia nu-bilalis* (Hubn.). IV kongres biologa Jugoslavije. Sara-jevo. 1974.
19. Šimić, S., Glumac, S., Stevanović, D.: O uticaju različitih svetlosnih intervala na izlazenje iz dija-pauze *Ostrinia nubilalis* (Hubn.). IV kongres biologa Ju-goslavije. Sarajevo. 1974.
20. Glumac, S., Koledin, : O ponašanju insekata na višim temperaturama. IV entomološki kolokvijum. Oteševu. 1974.
21. Glumac, S., Ruškuc, D.: Uticaj hrane na plodnost i duzinu zivota čiste linije pasuljevog žiška (*Acanthoscelides obtectus* Say). VI entomološki kolokvijum. Korčula. 1976.
22. Glumac, S.: O mehanizmima metamorfoze u Lepi-doptera. VI entomološki kolokvijum. Korčula. 1976.
23. Glumac, S.: Changes in the effects of neurohumoral regulation on metamorphosis of caterpillars, *O. nubi-lalis*, by influence through ligatures. XV International Congress of Entomology. Washington. 1976.
24. Glumac, S.: O izboru pogodnih karaktera pri predla-ganju filogenetskih sistema kod insekata. II simpo-zi-jum biosistematičara Jugoslavije. Novi Sad. 1977.
25. Glumac, S.: Einige zoogeographische Gesetzm-es-sigkeiten der Dipterenverbreitung in Jugoslawien. VII Internationales Symposium uber Entomofaunistik in Mitteleuropa. Lenjingrad. 1977.
26. Glumac, S., Ivanović, J., Hladni, M., Stanić, V.: De-lovanje ekstremne temperature na larve *Ostrinia nu-bilalis* u dija-pauzi. X kongres Saveza društava fiziologa Jugoslavije. Novi Sad. 1977.

27. Glumac, S., Hladni, M., Ivanović, J., Stanić, V., Nenadović, V.: Uloga neuroendokrinog sistema u aklimaciji larava *Ostrinia nubilalis* Hubn. VIII skup entomologa Jugoslavije. Tara. 1978.
28. Glumac, S.: O ulozi kapilarnosti u ishrani insekata. IX skup entomologa Jugoslavije. Subotica. 1979.
29. Ruškuc, D., Glumac, S.: Prvi rezultati proučavanja bivoltizma *Ostrinia nubilalis* Hubn. primenom feromona. IX skup entomologa Jugoslavije. Subotica. 1979.
30. Grubor, G., Miljanović, T., Palanački, V., Glumac, S.: Slobodne aminokiseline u hemolimfi gusenica *Ostrinia nubilalis* (Hbn). IX skup entomologa Jugoslavije. Subotica. 1979.
31. Glumac, S.: On the role of the capillary attraction in feeding of the sucking insects. XVI International Congress of Entomology. Kyoto. 1980.
32. Glumac, S.: Specijacija sirfida i neki faktori koji je određuju. X skup entomologa Jugoslavije. Ohrid. 1980.
33. Ruškuc, D., Glumac, S.: Morfometrijska istraživanja prve i druge generacije *Ostrinia nubilalis* Hubn. (Lepidoptera). IV simpozijum biosistematičara Jugoslavije. Djerdap. 1980.
34. Palanački V., Kosović, S., Grubor-Lajšić, G., Glumac, S.: Pojava glicerola u hemolimfi gusenica *Ostrinia nubilalis* Hubn. (Lepidoptera). IV simpozijum biosistematičara Jugoslavije. Djerdap. 1980.
35. Grubor-Lajšić, G., Palanački, V., Glumac, S.: Fosfatna aktivnost gusenica *Ostrinia nubilalis* Hubn (Lepidoptera). IX Internationales Symposium uber Entomofaunistik in Mitteleuropa. Portoroz. 1981.
36. Glumac, S., Božićić, B., Ruškuc, D.: Researching of the way of feeding of some species of Mosquitos. II European Congress of Entomologie. Kiel. 1982.
37. Grubor-Lajšić, G., Palanački, V., Glumac, S.: Promene u elektroforetskoj slici proteina hemolimfe *Ostrinia nubilalis* Hubn. tokom dijapauze. VI kongres biologa Jugoslavije. Novi Sad. 1982.
38. Ruškuc, D., Glumac, S.: Variranje morfometrijskih karaktera leptira *Ostrinia nubilalis* Hubn. (Lepidoptera) sa raznih lokaliteta. XIII godišnji skup entomologa Jugoslavije. Zadar. 1983.
39. Krnić, M., Glumac, S.: Obrazovanje kadrova i istraživanje faune SR Srbije. Plenarni referat. II Simpozijum o fauni SR Srbije. Beograd. 1983.
40. Glumac, S., Ruškuc, D.: Univoltine and bivoltine generations of *Ostrinia nubilalis* Hubn. on corn (*Zea mays*) in Yugoslavia. XVII International Congress of Entomology. Hamburg. 1984.
41. Grubor-Lajšić, G., Palanački, V., Glumac, S.: Investigation of the haemolymph of larvae *Ostrinia nubilalis* during the diapause. XVII International Congress of Entomology. Hamburg. 1984.
42. Glumac, S., Ruškuc, D.: Dijapauza kukuruznog plamenca (*Ostrinia nubilalis* Hubn.) kao skokovit proces. III kongres ekologe Jugoslavije. Sarajevo. 1984.
43. Šimić, S., Božićić, B., Glumac, S.: Taksonomski problemi u nekim grupama Diptera. I kongres biosistematičara Jugoslavije. Popova Šapka. 1985.
44. Glumac, S.: The Origin of Mimicry in the Syrphidae Family. The First International Congress of Dipterology. Budapest. 1986.
45. Vujić, A., Glumac, S.: Neke karakteristike faune sirfida (Diptera: Syrphidae) Vojvodine. VII Kongres biologa Jugoslavije. Budva. 1986.
46. Glumac, S.: Mogućnost prezentacije filogenetskih odnosa u insekata. XVI Skup entomologa Jugoslavije. Vršac. 1986.
47. Šimić, S., Glumac, S.: Zoogeographical Consideration of Syrphid Fauna (Insecta: Diptera) on the Balkan Peninsula. IV Congr. Zoogeog. and Ecol., Abstr. Vol. pp39. Kammens Vourla, Grčka. 1987.
48. Glumac, S.: Evolutionary origins of Mimicry in Insects. Proc. XVIII International congress of Entomology. Vancouver, Canada. 1988.
49. Šimić, S., Glumac, S.: Problemi zoogeografske analize nekih grupa insekata. XVIII Skup entomologa. Rez.ref.3, Gozd Martuljek. 1988.
50. Vujić, A., Glumac, S.: Taksonomski problemi u rodu *Myolepta* (Diptera: Syrphidae). II Kongres biosistematičara Jugoslavije. Kranjska gora. 1989. Abstract: p. 76.
51. Glumac, S., Ruškuc, D.: Temperatura praga razvika insekata kao biološka adaptacija-istraživanja na *Calliphora erythrocephala* Meig. XIX Skup entomologa Jugoslavije. Ulcinj. 1989.
52. Glumac, S., Vujić, A.: Some view on the Syrphidae phylogeny. Second International Congress of Dipterology. Bratislava. 1990. Abstract: p. 69.
53. Radnović, D., Glumac, S.: The Zoogeographical Composition of Syrphid Fauna (Diptera: Syrphidae) in Relation to Season. Fourth European Congress of Entomology. XIII International Symposium fur die Entomofaunistik Mitteleuropas. Godollo. 1991. Abstract: p. 183.
54. Glumac, S., Šimić, S., Vujić, A.: Usporedne vrednosti taksonomskih karaktera pri uspostavljanju filogenetskih sistema. Uvodno predavanje. XXII Skup entomologa Jugoslavije. Palić. 1995. Abstract: 5.
55. Glumac, S., Banovački, Z., Ruškuc, D.: Prag razvika - uslovna kategorija. XXII Skup entomologa Jugoslavije. Zbornik rezimeja. Palić. 1995. Abstract: 13.
56. Milankov, V., Vapa, Lj., Glumac, S., Petrić, D.: Morfološki i genetičko-biohemijski karakteri vrsta *Aedes caspius* (Pallas, 1771) i *Aedes dorsalis* (Meigen, 1830) (Diptera, Culicidae). 5. Kongres Ekologe Jugoslavije. Beograd. 1996. Abstract: 89.

THE CONTENTS OF HEAVY METALS IN THE RIVER LIM

BOŽANOVIĆ Nenad

Faculty of Sciences & Mathematics, University of Pristina, Yugoslavia

ABSTRACT

The part of water current of the river Lim near town Bijelo Pole (Montenegro) was the subject of investigation and especially the contents of heavy metals. Determining the contents of heavy metals included copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb), iron (Fe) and manganese (Mn). Samples are taken from six chosen locations once in a month in period of three months. The concentrations are obtained by atomic absorption spectrophotometer (AAS) whereas the samples are previously prepared by classic chemical methods. Statistically significant differences in average concentrations (on level of significance $\alpha = 0.05$) are found in cases of zinc, iron and chromium but they are still small so they could not be the consequence of anthropogenic influence but rather of chemistry of water. Average concentrations of nickel and manganese are approximately three times higher than maximum admissible concentration (MAC²) for drinking water. It is not completely clear are the concentrations of nickel and man-

ganese the consequence of anthropogenic impact or the consequence of specific chemodynamics of this part of river basin. In order to obtain some precise and relevant conclusions, more investigations of this part of water current and especially its sediments are needed. The average concentration of iron is slightly higher than MAC while in case of other metals the average concentrations are much smaller than MAC. It is not found some regularity in increasing or decreasing of concentrations along the river current. Nevertheless it could be noted, as a global impression, that the self-purification process contributed a lot to stabilisation of whole water system and according to the level of the concentrations of metals, which are within the limits for non-polluted rivers, the changes in distribution are mainly the consequence of the natural processes rather than anthropogenic influence.

Key words: heavy metals, water pollution, River Lim.

INTRODUCTION

River Lim with drainage area of 6016 km² takes very important place in hydrogeographic system in this part of Balkan's peninsula. Lim arises from the Plav's lake (Montenegro), flows mainly on NNW through Republic Montenegro and Republic Serbia and pours in river Drina.

In this paper are presented the results of investigation of the river Lim near town Bijelo Pole (Montenegro). Development of industry in fifties and sixties brought the problems of pollution to this area. Part of river basin, especially downstream from town Berane, became organically and inorganically polluted. That process of river pollution especially increased after building the factory for producing sulphate cellulose and paper in Berane. Many reports of Institute for Hydrometeorology of Republic Montenegro confirmed that in sixties and Seventies River Lim was biologically polluted. In mentioned period of time in some parts of river complete pestilences of fish have

happened. For many years Lim was one of the most polluted water currents in Republic Montenegro.

After closing the factory for producing cellulose in Berane and, partly, because of decreasing of industrial producing at all, the state of water current downstream from Berane became much better, mainly because of process of self-purification.

As the part of permanent monitoring process of the river Lim (especially downstream from Berane) we chose to investigate the contents of heavy metals in water because of the fact that heavy metals are not only one of the best indicators of industrial producing but also one of the most dangerous factors of anthropogenic pollution as they are, practically, undestroyable in natural conditions. The distinction between anthropogenic and naturally occurring heavy metals in such system as the Lim drainage area, should be regarded as a task of the highest fundamental, as well as ecological significance.

MATERIALS AND METHODS

Sampling

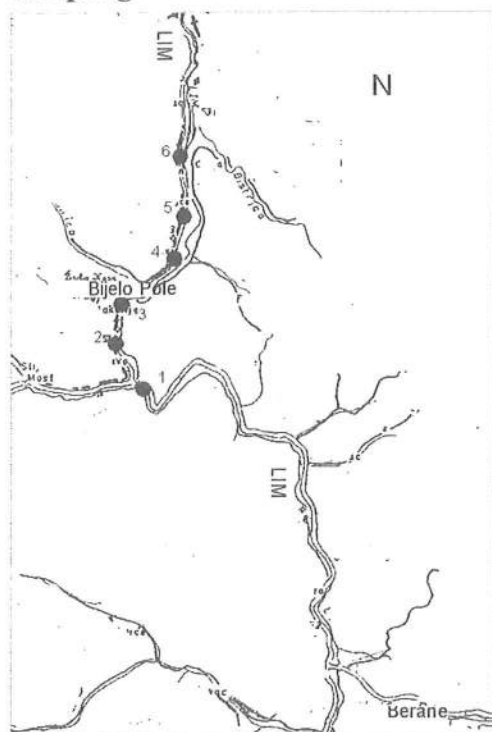


Figure 1. Part of the river Lim with sampling locations

The samples of water are taken from chosen locations near Bijelo Pole (see Fig.1.) on length of approximately 35km and sampling locations are presented on Fig.1. in downstream order: 1.Ri, 2.Ro, 3.Z, 4.R, 5.S and 6.Iz. Sampling was carried out in plastic bottles (1000 cm³) once in a month in period of three months (April, May and June 1996.). Immediately after sampling the samples are transported to the laboratory for preparation and analysis.

Preparation of the samples for analysis

In laboratory, the samples are passed through filter Whatman 42, which is previously washed, by 3% nitric acid and distillate water. After that the samples are put in normal pots (1000 cm³). From each sample is taken 500 cm³ and evaporated in sand bath till the volume of 50cm³. After evaporating the samples are quantitatively carried in glasses (100 cm³) and continued with evaporating to dry matter. To dry matter is added 5-10 cm³ 2M nitric acid and than the solution is carried into three normal pots (50 cm³) and filled with distillate water. That process prepares the samples for determining the concentrations

of heavy metals by atomic absorption spectrophotometer (AAS). At the same time, together with samples, the control probe was prepared from 500-cm³ distillate water.

Concentration values of metals were determined by method of atomic absorption spectrophotometry ("PERKIN ELMER 1100B") at Chemistry Department of Faculty of Natural Sciences & Mathematics, University of Pristina.

RESULTS

Determining of heavy metals concentrations included: copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb), iron (Fe) and manganese (Mn). Obtained results are presented in Table 1. as well as the mean for every metal (counted for whole period of three months) with level of confidence and maximal and minimal values (also taken for whole period, (Table 2.).

In mark for the sample number means month.

• δ is standard deviation, $n = 18$

• t factor is counted on level of significance $\alpha = 0.05$

• MAC (maximum admissible concentration) standards for every metal are taken from "Guideline for Drinking-Water Quality", Recommendations I-III, WHO Geneva, 1984. and Directives of European Council 80/778/EEC, 1986².

Table 1. The contents of heavy metals at the sampling points

Sample ($\mu\text{g}/\text{dm}^3$)	Cu	Zn	Fe	Mn	Pb	Cr	Ni
1. Ri4	4.5	18.6	69.1	59.8	7.5	14.9	31.5
2. Ro4	5.5	21.4	75.1	68.9	6.2	14.5	29.1
3. Z4	4.9	19.8	71.2	66.8	5.5	15.1	30.1
4. R4	4.8	21.4	87.2	66.1	6.8	16.1	28.1
5. S4	3.7	17.3	82.6	49.8	5.2	17.2	27.9
6. Iz4	5.4	13.4	68.2	51.2	7.1	18.2	32.5
7. Ri5	4.7	25.6	60.2	59.8	6.1	13.9	28.7
8. Ro5	4.1	22.3	58.2	49.7	7.2	14.8	32.8
9. Z5	5.0	27.3	55.1	65.8	7.3	15.7	27.4
10. R5	4.7	26.1	65.3	59.1	7.9	12.8	30.1
11. S5	3.8	19.9	51.4	57.2	6.8	15.1	29.9
12. Iz5	3.3	21.5	61.2	69.1	8.1	13.5	32.9
13. Ri6	3.9	32.4	58.2	62.8	5.7	11.2	32.8
14. Ro6	4.9	31.0	47.2	58.1	5.5	9.7	29.3
15. Z6	4.8	29.0	49.1	65.2	6.2	11.8	29.7
16. R6	5.2	31.2	49.1	49.9	7.2	13.7	29.8
17. S6	5.1	29.8	55.1	69.7	5.8	9.1	31.2
18. Iz6	4.2	27.1	51.8	65.2	6.2	12.8	27.8

Table 2. Statistically presented values

Metal ($\mu\text{g}/\text{dm}^3$)	X_{\max}	X_{\min}	$\bar{X} \pm t \frac{s}{\sqrt{n}}$
Cu	5.5	3.3	4.6 ± 0.31
Zn	32.4	13.4	24.2 ± 2.70
Cr	18.2	9.1	13.9 ± 1.19
Ni	32.9	27.4	30.1 ± 0.91
Pb	8.1	5.2	6.6 ± 3.27
Fe	87.2	47.2	61.9 ± 30.83
Mn	69.7	49.7	60.8 ± 30.25

DISCUSSION

Variations in contents of heavy metals among some locations could be the consequences of many factors⁴ including:

- differences in contents of heavy metals in source
- differences in chemistry of water
- differences in adsorptive properties of river sediment
- anthropogenic influence
- natural external factors (erosion, wind)
- biological accumulation

Some of these, for example, external natural factors and biological accumulations, are very difficult to define because of their changability¹ in space and time, so they are included in this work only as possibilities. Among the factors mentioned above the most important are the chemistry of water³ and anthropogenic influence.

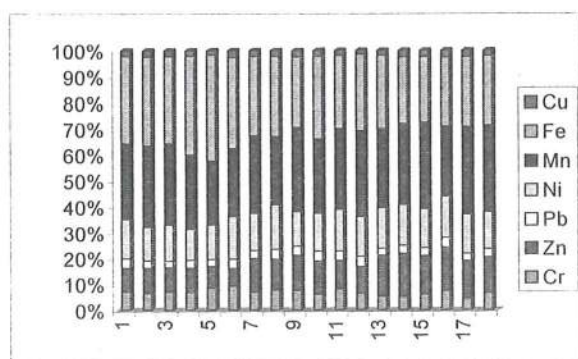


Figure 2. Proportional participation of metals

Proportional participations of every metal at sampling points are presented in Fig.2 and we can see that participation follows the order: $\text{Cu} < \text{Pb} < \text{Cr} < \text{Zn} < \text{Ni} < \text{Mn} < \text{Fe}$ what is understandable in case of manganese and iron because they represent the basic macroelements and constituents of river sediments¹.

Standard deviation does not exceed 20% of mean for every metal except zinc (22,47%).

On next figures y-axis represents concentration of the metal and x-axis number of the samples taken for whole period of three months.

Copper

On Fig.3. it could be seen that there are no extreme points in distribution of copper. The average value of concentration is far below MAC for drinking water. Standard deviation is 13.54% of mean.

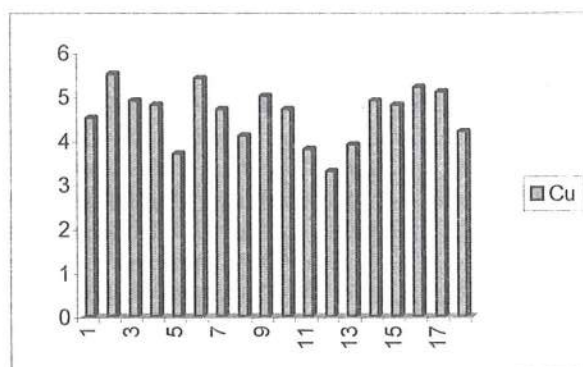


Figure 3. Distribution of cooper

Zinc

On Fig.4. it could be seen the average increasing of concentration in June comparing with those in April and May taken together. The means (June's and together for April and May) are significantly different on level of significance $\alpha = 0.05$. This average increasing of concentration is the consequence of, so far, unknown factor and the average concentrations in June ($30.08 \mu\text{g}/\text{dm}^3$) is still 4 times smaller than MAC so we can not speak about some radical anthropogenic influence.

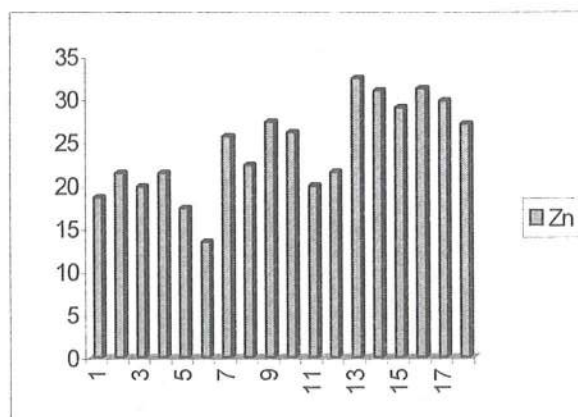


Figure 4. Distribution of zinc

Chromium

On Fig.5. we can see the average decreasing of contents of chromium in May and June, comparing with April, which is statistically significant. Standard deviation is 17.21% of mean, which is counted for whole period of three months and is much lower than MAC.

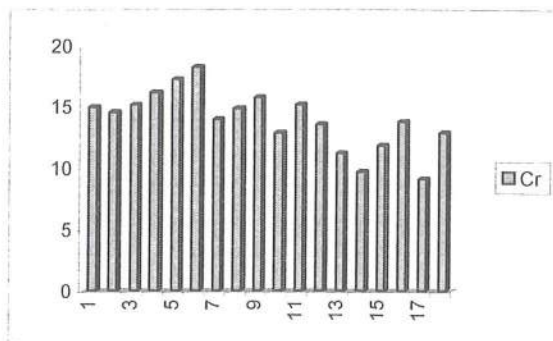


Figure 5. Distribution of chromium

Nickel

Distribution of concentrations (Fig.6.) does not show some big variations. Standard deviation is 6.08% of mean and which is counted for period of three months. It should be stressed that average concentration of nickel is approximately 3 times higher than MAC.

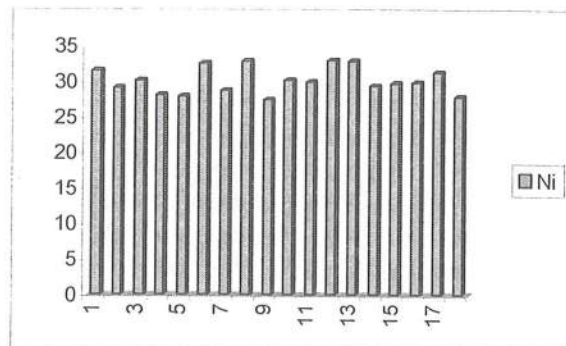


Figure 6. Distribution of nickel

Lead

In case of lead (Fig.7.) we do not have statistically significant changes of concentration. Standard deviation is 13.24% of mean which is counted for period of three months and also much smaller than MAC.

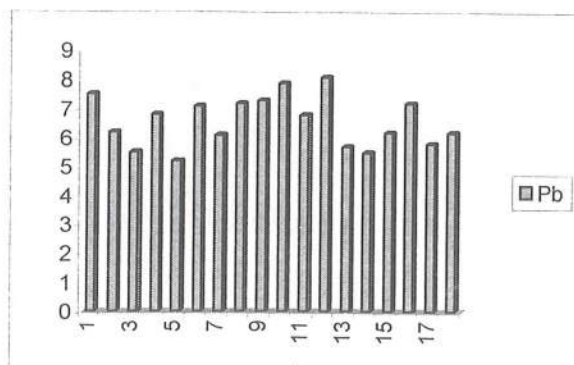


Figure 7. Distribution of lead

Iron

As it was in chromium's case the same happens here where we see (Fig.8.) statistically significant decreasing of average concentration in May and June taken together comparing with April ($\alpha = 0.05$). Average concentration, taken for whole three months, is slightly higher than MAC.

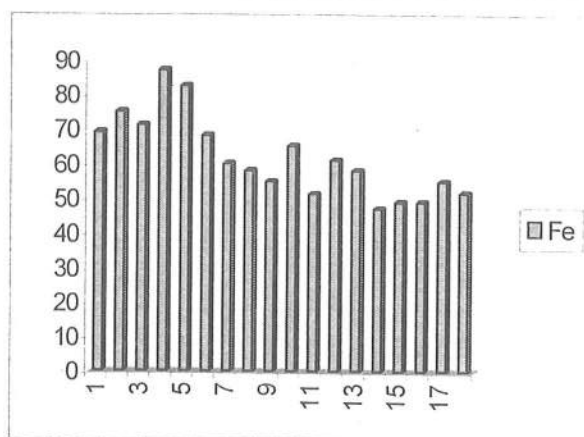


Figure 8. Distribution of iron

Manganese

Manganese does not show the significantly changes in distribution. Standard deviation is 13.24% of mean and this mean is approximately 3 times higher than MAC for drinking water.

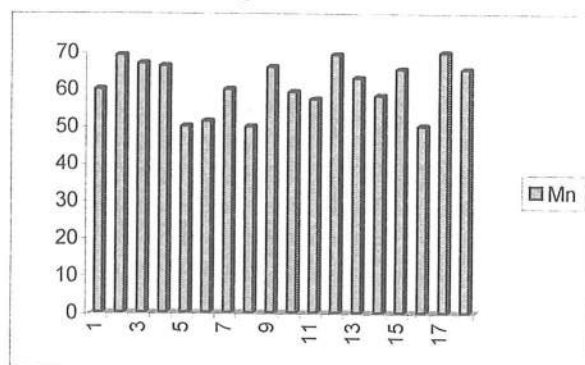


Figure 9. Distribution of manganese

CONCLUSIONS

After all mentioned here we can say that statistically significant changes of concentrations occur in cases of zinc, chromium and iron but that changes are still small so they can not be the consequence of anthropogenic factor but, more likely, of chemistry of water system. Average concentrations of nickel and manganese are approximately 3 times higher than MAC for drinking water, while the concentration of iron is slightly higher than MAC. It is not completely clear are the concentrations of nickel and manganese the consequence of anthropogenic impact or the consequence of specific chemodynamics of this part of river basin. In order to obtain some precise and relevant conclusions, more investigations of this part of water current and especially its sediments are needed. The other metals occurred in trace amounts equally at all sites, either at the site situated upstream or downstream of Bijelo Pole. None of the metals shows the

regularity in increasing or decreasing of concentrations along the river current. It could be noted, as a global impression, that the self-purification process contributed a lot to stabilization of whole water system and according to the level of the concentrations of metals, which are within the limits for non-polluted rivers, the changes in distribution are mainly the consequence of the natural processes rather than anthropogenic influence.

REFERENCES

1. Veselinović S.D., Gržetić A.I., Đarmati A.Š., Marković A.D., 1995. Stanja i procesi u životnoj sredini. Fakultet za fizičku hemiju univerziteta u Beogradu, 326-354, Beograd.
2. Guideline for Drinking-Water Quality, Recommendations I-III, WHO, 1984, Geneva.
3. Fergusson E. J., 1990. The heavy elements chemistry, environmental impact and health effects. Pergamon Press, 243-313, University of Canterbury, New Zealand
4. Purić, M., 1996. Interakcija sediment voda kao faktor hemodinamike metala u rijeci Tari. Crnogorska akademija nauka i umjetnosti, 19-24, Podgorica.

REZIME

SADRŽAJ TEŠKIH METALA U RECI LIM

Nenad BOŽANOVIĆ

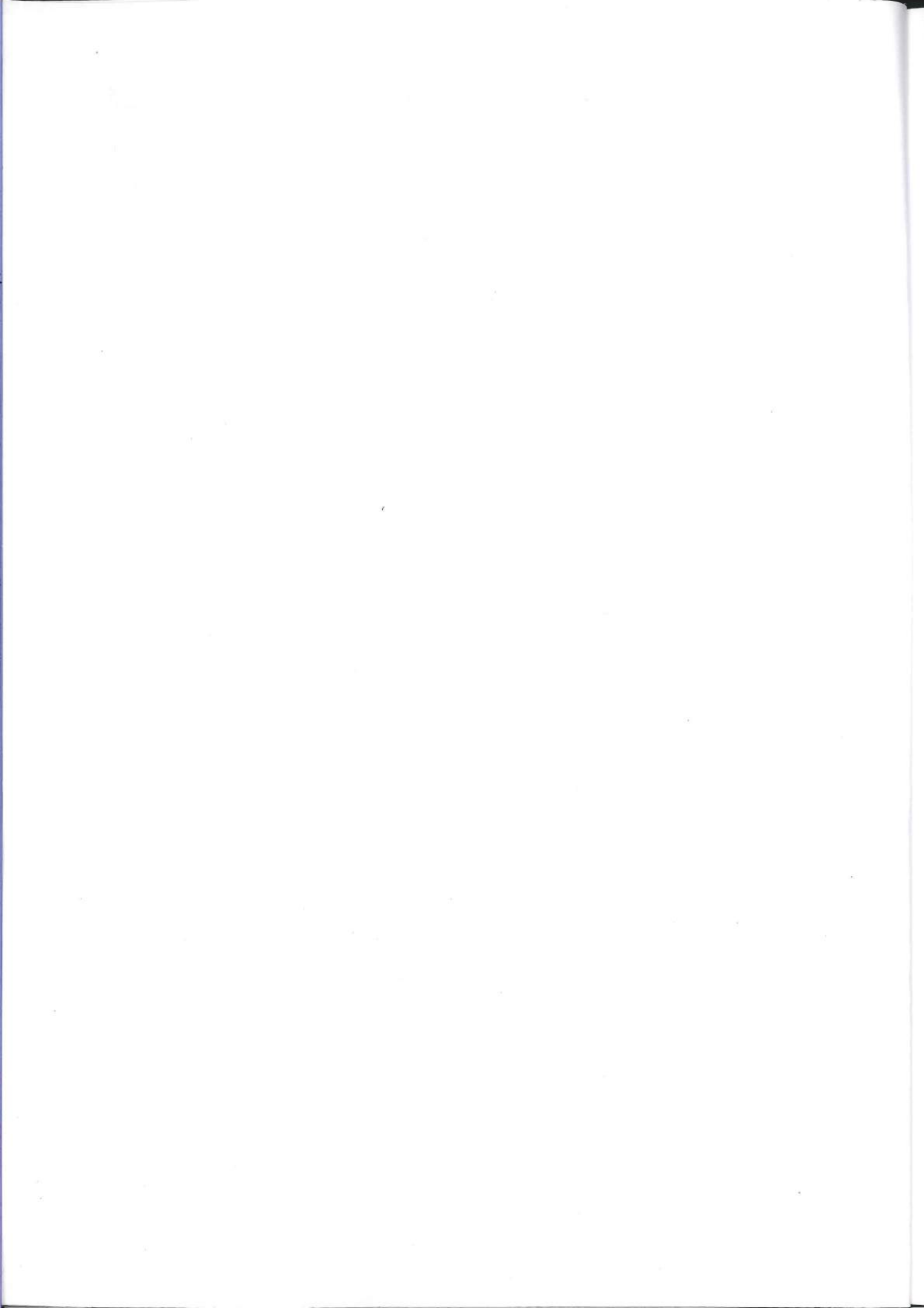
Prirodno-matematički Fakultet, Univerzitet u Prištini, Yugoslavia

U ovom radu prikazani su rezultati fizičko-hemijskih ispitivanja vodotoka reke Lim blizu Bijelog Polja

(Crna Gora). Određivan je sadržaj teških metala u vodi i to bakra, cinka, hroma, nikla, olova, gvožđa i mangana. Uzorci su uzimani na šest izabranih lokacija, jednom mesečno u toku tri meseca. Koncentracije teških metala određivane su na atomskom apsorpcionom spektrofotometru (AAS) a pre toga su uzorci pripremljeni klasičnim hemijskim metodama. Nađene su statistički značajne razlike prosečnih mesečnih koncentracija u slučaju cinka, hroma i gvožđa na nivou značajnosti $\alpha = 0.05$. Navedene razlike koncentracija po mesečnim ciklusima, iako statistički značajne ipak nisu dovoljno velike da bi se mogle pripisati antropogenom uticaju već su najverovatnije posledica razlika u uticaju hemodinamike vode u različitim delovima vodotoka. Jedino kod mangana i nikla prosečne koncentracije su veće oko tri puta od maksimalno dozvoljena koncentracija² (MDK) za pijaću vodu. Za sada je nejasno da li su povećane koncentracije nikla i mangana posledica antropogenog uticaja ili su posledica specifičnosti hemodinamike ovog dela sliva. U cilju donošenja preciznih i sigurnih zaključaka biće potrebno dalje istraživanje kako vode tako i sedimenta reke Lim. Kod gvožđa je prosečna koncentracija malo veća od MDK dok su kod ostalih metala prosečne koncentracije ispod MDK. Nije nađena nikakva pravilnost u smanjenju ili povećanju sadržaja metala duž vodotoka. Nakon izvršenih ispitivanja nameće se opšti utisak da, s obzirom da su koncentracije metala u granicama proseka za nezagađene reke, promene u distribuciji kao i hemodinamici metala predstavljaju odraz prirodnih procesa u većoj meri nego antropogenih faktora.

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A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART III. The Linear Sweep Voltammetry Behaviour of (100) oriented Copper Single Crystal Electrode

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper(100) electrodes from acetate, nitrate and perchlorate solutions have been investigated using Linear Sweep Voltammetry (L.S.V.).

It appeared that the different anions used did not change the voltammetric characteristics significantly.

The voltammetric behaviour of the copper (100) single crystal electrode showed underpotential deposition and dissolution of lead exhibited by two cathodic peaks and two anodic counterparts, each pair of peaks asymmetrically placed on the potential axis (appreciable peak potential separation).

The L.S.V. results obtained strongly suggest that UPD of lead on Cu(100) starts as an adsorption and proceeds as higher order 2D transformation into close-packed epitaxial crystalline monolayer. The structure of the closest-packed lead epitaxial monolayer on Cu(100) is proposed.

The above conclusion is supported by the "adsorption isotherm" evaluated from the L.S.V. underpotential deposition data showing two parts connected by a "shoulder"; the first and second pair of voltammetric deposition and dissolution peaks exhibiting an anodic potential shift with increasing lead concentration; the deposition/dissolution peak potential separations exhibiting well defined dependence on the lead concentration.

Key words: Underpotential deposition; Linear sweep voltammetry, Cu, Pb, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition (UPD) there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was lead on copper polycrystals and single crystals. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The substrate possesses high hydrogen evolution overvoltage and therefore deposition of lead is not complicated by hydrogen co-adsorption processes.

The technique employed was linear sweep voltammetry.

MATERIALS AND METHODS

The experimental work described in this paper was done predominantly using linear sweep voltammetry (L.S.V.) technique.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H. Tinsley and Co." potentiometer (type 3387B). The waveform generator provided either a ramp type voltage output for L.S.V.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed.

The cell used for the L.S.V. experiments is presented in Fig. 1. The cell was made entirely of glass. The working electrode, C, and Luggin capillary, L, were

positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc $\approx 1.5 \text{ cm}^2$ in area, positioned parallel to the working electrode.

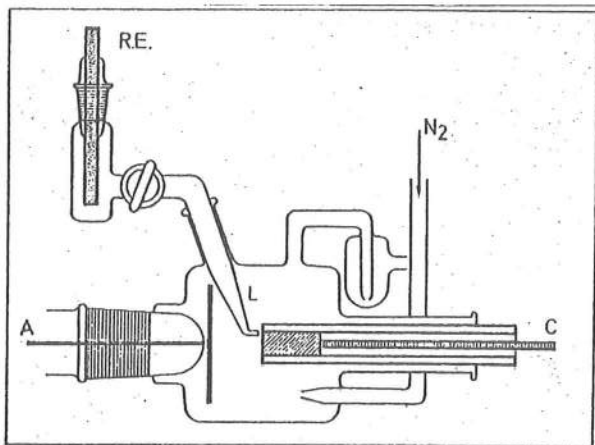


Figure 1. The cell used for most of the L.S.V. and potential step experiments

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8 \text{ cm}$ in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25 \text{ g}$, of amalgamated zinc¹.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4} \text{ cm}$ and $3 \cdot 10^{-4} \text{ cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5} \text{ cm}$ and $3 \cdot 10^{-5} \text{ cm}$ grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere².

The three copper single crystals (111), (110) and (100) had to be chemically polished under somewhat different conditions if the result was to be up to the standard. The polishing mixture containing 33vol.% each of concentrated Analar grade HNO_3 , glacial acetic acid and orthophosphoric acid, was common to all copper electrodes used. The difference in treatment between polycrystalline and each of the copper single crystals began when the temperature of the polishing agents and the time of immersion was to be decided.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C , and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation³⁻⁵.

This polishing process required a considerable amount of practice before consistent results could be obtained.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25 cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry. In this case it constituted the whole experiment.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the chemical polishing had been successful in producing a well defined crystal plane (in the case of the single crystal of course). For any particular system, repeated linear sweep experiments were performed before any additional measurement were made in order to establish an arbiter to which all future voltammetry could be referred. The procedure described here for L.S.V. is that which enabled a given solution/electrode combination to be used for a whole day's experiments without any deterioration in the result over this period.

Firstly the cell complete with working electrode (not yet freshly chemically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and chemically (or only mechanically) polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the chemical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Voltammetric experiments were carried out in the normal way; the potential being cycled continuously and sweeps recorded when necessary at a variety of sweep speeds.

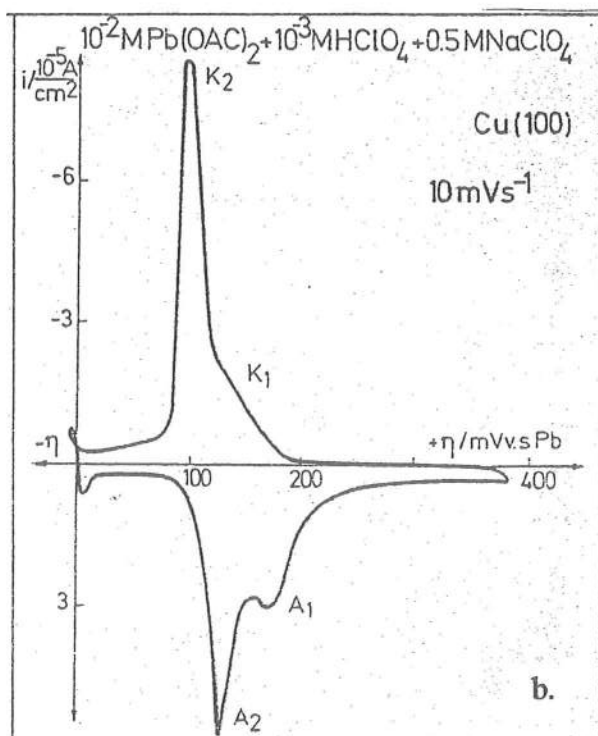
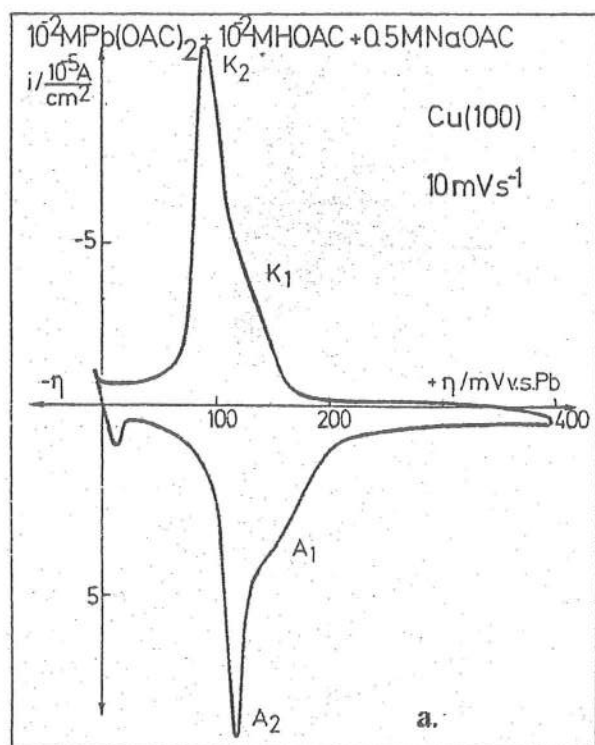
RESULTS

Copper single crystal with (100) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:

$x\text{MPb(OAC)}_2 + 10^{-2}\text{M HOAC} + 0.5\text{M NaOAC}$	$10^{-4}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{MPbO} + 10^{-3}\text{MHClO}_4 + 0.5\text{M NaClO}_4$	$10^{-3}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{MPb(OAC)}_2 + 10^{-3}\text{MHClO}_4 + 0.5\text{M NaClO}_4$	$10^{-4}\text{M} \leq x \leq 10^{-1}\text{M}$
$x\text{MPb(OAC)}_2 + 10^{-3}\text{MHClO}_4 + 0.5\text{M NaNO}_3$	$10^{-3}\text{M} \leq x \leq 10^{-1}\text{M}$

The linear sweep voltammograms for the underpotential deposition, UPD, of lead from those solutions onto the Cu(100) oriented surface are presented in Fig. 2. a., b. and c.. A pre peak, K_1 , followed by a sharp main peak, K_2 , and their anodic counterparts, A_1 and A_2 , were observed.

If repetitive cycling was performed, such that the anodic end of the sweep potential range entered copper dissolution by 1-2mV, the voltammograms would change its shape somewhat. The A_2 and K_2 peaks



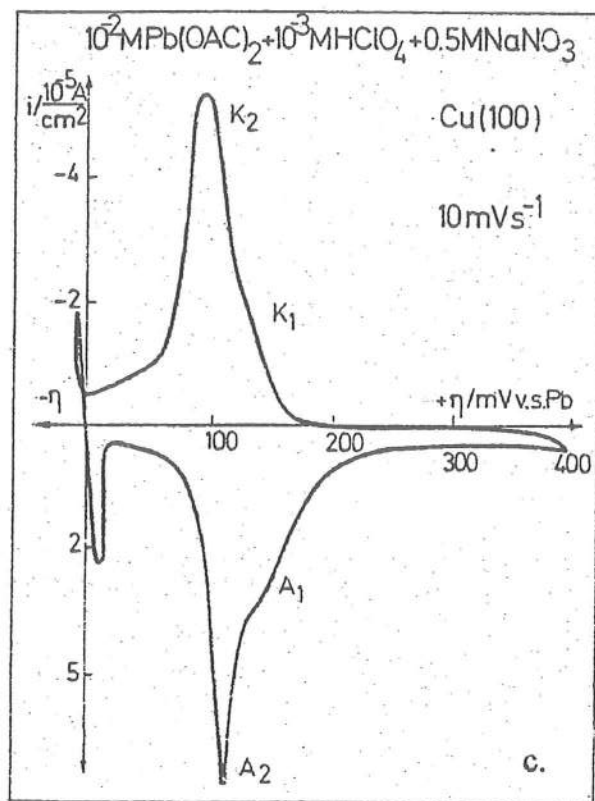


Figure 2. Linear sweep voltammetry for lead underpotential deposition onto Cu(100).

became sharper, and A1 reduced in size so that its charge became equal to the charge associated with K1. The overall charge ($A_1 + A_2$), however, did not change. It appears therefore that such cycling improve the Cu(100) oriented surface.

The potentials and charges associated with the peaks are shown in Table. 1.

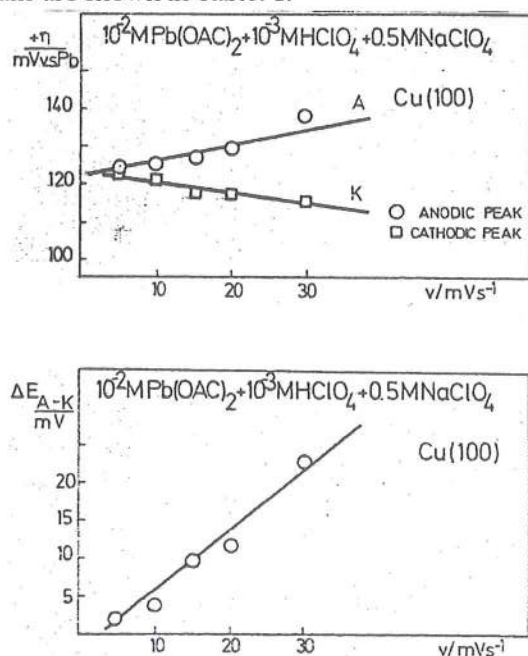


Figure 3. a. Peak potential dependence on the sweep speed.
b. Peak potential separation dependence on the sweep speed

The change of peak potentials K_2 and A_2 , and their peak potential separation, ΔE_{A-K} , due to changing sweep speeds are shown in Fig. 3. a. and b..

The influence of the lead concentration on the same quantities are presented in Fig 4.a. and b..

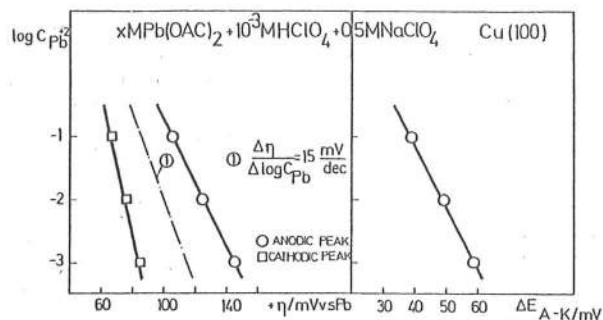


Figure 4. a. Peak potential dependence on lead concentration.
b. Peak potential separation dependence on lead concentration.

DISCUSSION

A comparison of the data presented with those obtained from the same or similar solutions on the Ag(100) electrode⁶⁻⁹, Cu(111)⁴ and Cu(110)⁵ electrode shows significant differences and similarities: although the number of peaks could be said to be the same, their shape and the charge under them differs appreciably. The two peak system in those cases was attributed to a two-step deposition process: first step - adsorption and second step - transformation into a 2D crystalline, close-packed monolayer.

The half peak width for K_2 in the case of Cu(100)/Pb is 18 ± 2 mV. The charge encompassed by K_1 is approximately $90 \cdot 10^{-6} \text{ As cm}^{-2}$, and the total charge, ($K_1 + K_2$) is $(276 \pm 3) \cdot 10^{-6} \text{ As cm}^{-2}$. In addition, the peak potential for K_2 and A_2 changes with increasing lead concentration exhibiting the trend established for peaks corresponding to crystalline layer formation for lead UPD on the two previously shown copper single crystal orientations^{4,5}.

It appears therefore that the first step in lead UPD on Cu(100), characterized by prepeak K_1 , would be a random adsorption on favorable coordination sites. The charge of $90 \cdot 10^{-6} \text{ As cm}^{-2}$, if a roughness factor of 1.1 is taken into account, suggests an arrangement of lead particles according to a superlattice model^{10-12, 13} (a structure achieved if only position marked with A of Fig. 5. are occupied).

The second step, reflected in a sharp peak, K_2 , consists of a 2D transformation into epitaxial phase layer proposed in Fig. 5. The total charge involved in the deposition or the stripping process, of $276 \cdot 10^{-6} \text{ As cm}^{-2}$, is by no means enough for the formation of a close-packed lead monolayer. It does however, agree very well with the charge needed to form the epitaxial closest-packed epitaxial monolayer ($234 \cdot 10^{-6} \text{ As cm}^{-2}$), if roughness factor of 1.1 or so, is taken into account.

Atoms in this arrangement are very close together and the resulting 2D lattice obviously resembles the one for the (100) plane of the bulk lead. Therefore, it is not difficult to imagine such a monolayer, already having strong interactions with the substrate, participating in a band structure which extends over the substrate and developing properties of a well defined crystalline phase.

The isotherm obtained from the voltammogram in Fig. 2.b., supports this proposed lead monolayer formation, Fig. 6. After the initial adsorbed layer is put down, the additional material needed for the 2D epitaxial crystalline lattice is deposited in what seem to be a higher order 2D phase transformation occurring over a potential range of 40mV.

CONCLUSIONS

Once more it was convincingly confirmed that careful and successful polishing of the substrate used in UPD studies is of the utmost importance, if reliable, quantitative and qualitative data are to be obtained.

Different anions used in lead solution preparation (namely acetate, nitrate and perchlorate) did not change significantly the voltammograms characteristics obtained.

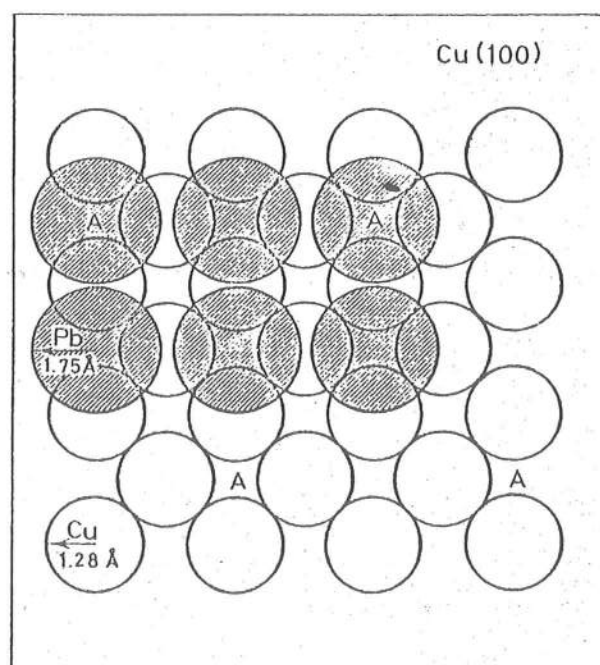


Figure 5. The structure of the closest-packed lead epitaxial monolayer on Cu(100) surface.

Table. 1. Average UPD peak values for 10-2M Pb solutions and $v = 10\text{mV}\cdot\text{s}^{-1}$

Electrode Surface Orientation	Anion	Average Peak K_2 Potential mVvs.Pb	Calculated Close-packed Lead Layer 10^{-4}Ascm^{-2}	Calculated Epitaxial Lead Layer 10^{-4}Ascm^{-2}	Measured UPD Layer charge 10^{-4}Ascm^{-2}	
					K_1	$K_1 + K_2$
(100)	OAC	74 ± 2	310	234	90	275
(100)	NO_3^-	70 ± 3	310	234	90	280
(100)	ClO_4^-	72 ± 2	310	234	90	273

Lead deposition and dissolution in the UPD region on the (110) oriented copper electrode surface, from solutions used, was reflected in two cathodic, K_1 and K_2 , and two anodic, A_1 and A_2 . Both, the first peak pair potentials, K_1/A_1 , and the second peak pair potentials, K_2/A_2 , became, on average 15mV per decade, more anodic with increasing lead concentration.

The charge encompassed by K_1/A_1 was $(90 \pm 5) \cdot 10^{-6}\text{Ascm}^{-2}$, and the charge under K_2/A_2 peaks was $(186 \pm 3) \cdot 10^{-6}\text{Ascm}^{-2}$ (the sum of the two being $(276 \pm 3) \cdot 10^{-6}\text{Ascm}^{-2}$).

Peak potential separation $\Delta E_{A_2-K_2}$, was 60mV at 10^{-3}MPb and became smaller with increasing lead concentration assuming the value of 40mV at 10^{-1}MPb .

The "adsorption isotherm" evaluated from the underpotential deposition voltammograms experimentally obtained have shown that 33% of the total

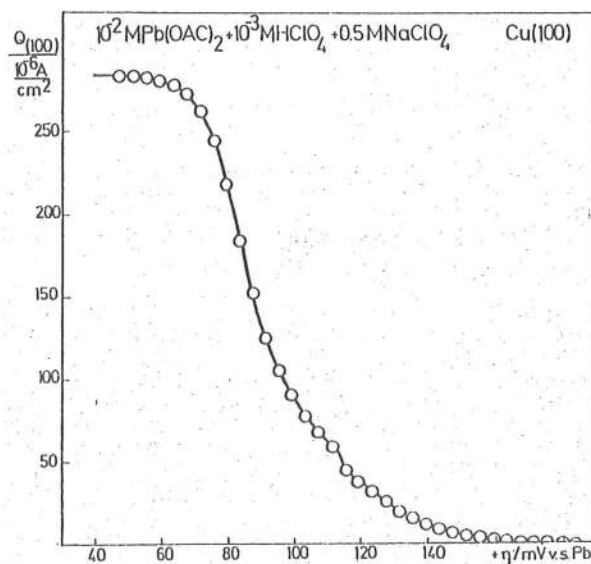


Figure 6. The isotherm obtained on the basis of the voltammogram presented in Fig.2. b.

cathodic peaks ($K_1 + K_2$) charge was deposited within 55mV potential range (a charge very close to $90 \cdot 10^{-6} \text{ As cm}^{-2}$), the additional 67% following the structural change start of the monolayer depicted by the "shoulder" (until full charge of $276 \cdot 10^{-6} \text{ As cm}^{-2}$ was reached). It appeared therefore that before the layer is fully completed it begins reorganization into a close-packed epitaxial structure.

The experimental results obtained strongly suggest that UPD of lead on Cu(100) starts as an adsorption (K_1) and proceeds as a higher order 2D transformation into close-packed crystalline monolayer ($K_1 + K_2$).

A model for the structure of the closest-packed lead epitaxial monolayer formed during lead UPD on the Cu(100) surface was also presented.

Acknowledgment

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REFERENCES

- 1.-Meites, L.: "Polarographic Techniques", 2nd edition, Interscience, New York (1965).
- 2.-Pinner, R., Electroplating, October and November (1953) 360, 401.
- 3.-Jovičević, J.N., Bewick, A., Univ. Thought, IV(2), inpress, Pristina 1997.
- 4.-Jovičević, J.N., Bewick, A., Univ. Thought, IV(2), inpress, Pristina 1997.
- 5.-Jovičević, J.N., Bewick, A., Univ. Thought, IV(2), inpress, Pristina 1997.
- 6.-Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 7.-Thomas, B., Bewick, A., J. Electroanal. Chem., 65 (1975) 911.
- 8.-Thomas, B., Bewick, A., J. Electroanal. Chem., 70 (1976) 239.
- 9.-Thomas, B., Bewick, A., J. Electroanal. Chem., 84 (1977) 127.
- 10.-Hilbert, F., Mayer, C., Lorenz, W.J., J. Electroanal. Chem., 47 (1973) 167.
- 11.-Lorenz, W.J., Chem. Ing.-Tech., 45 (1973) 175.
- 12.-Lorenz, W.J., Hermann, H.D., Wuthrich, N., Hilbert, F., J. Electrochem. Soc., 121 (1974) 1167.
- 13.-MacRae, A.U., Muller, K., Lander, J.J., Morrison, J., Surface Science, 15 (1969) 483.

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA OLOVA NA BAKRU - III DIO PONAŠANJE BAKARNE ELEKTRODE KRISTALOGRAFSKE ORIJENTACIJE (100) PRI LINEARNOJ CIKLIČKOJ PROMJENI POTENCIJALA

Jovan N. JOVIČEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000Priština, Jugoslavija.

Ovo je treći rad iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova (iz acetatnih, nitratnih i perhloratnih rastvora) na polikristalnim i monokristalnim bakarnim elektrodama.

Rad predstavlja rezultate dobijene linearnom cikličnom promjenom potencijala (L.S.V.) bakarne monokristalne elektrode sa površinom kristallografske orijentacije (100) u području potencijala pozitivnijih od reverzibilnog potencijala olova u datoj sredini.

Još jednom je uvjerljivo pokazano da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala ukoliko se žele dobiti pouzdani kvalitativni i kvantitativni podaci.

Elektrotaloženje i rastvaranje olova metodom linearne cikličke promjene potencijala u području potencijala pozitivnijih od reverzibilnog potencijala olova u datom rastvoru na monokristalnoj bakarnoj površini kristallografske orijentacije (100) odražava se u obliku dva katodna, K_1 i K_2 , i dva komplementarna anodna talasa, A_1 i A_2 . Prisustvo različitih aniona u upotrebljenim rastvorima nije značajnije uticalo na rezultate dobijene linearnom cikličkom promjenom potencijala.

Potencijal vrha talasa K_2 talasa iznosi $(+74 \pm 4) \text{ mV}$ vs. Pb u svim ispitivanim rastvorima. Vrijednosti potencijala vrhova talasa K_1 , A_1 i K_2 , A_2 postajali su anodniji (prosječno za 15mV po dekadi) sa porastom koncentracije olova u upotrebljenim elektrolitima. Ovakvo ponašanje karakteristično je za kristalne faze (monoslojeve).

Razlika u potencijalima vrhova talasa, $\Delta E_{A_2-K_2}$ drugog para talasa iznosila je 60 mV pri 10^{-3} MPb , i mijenjala se sa promjenom koncentracije olova u upotrebljenim rastvorima, da bi iznosila 40mV pri 10^{-1} MPb .

Električni naboj ograničen talasima (K_1 ili A_1) iznosio je $(90 \pm 5) \cdot 10^{-6} \text{ As cm}^{-2}$ a električni naboj pod drugim parom (K_2 ili A_2) iznosio je $(186 \pm 3) \cdot 10^{-6} \text{ As cm}^{-2}$, dok je suma ($K_1 + K_2$), odnosno ($A_1 + A_2$) iznosila $(276 \pm 3) \cdot 10^{-6} \text{ As cm}^{-2}$.

"Adsorpciona izoterma" izračunata na osnovu voltamograma za proces elektrotaloženja olova, u području potencijala pozitivnijih od reverzibilnog poten-

cijala olova, pokazala je da se 33% ukupnog električnog naboja, (K_1+K_2), razmijeni uz promjenu potencijala Cu(110) od 55mV, a da preostalih 67% slijedi nakon započinjanja strukturnih promjena u monosloju odraženih na izoterma "stepenicom" (dok se ne razmijeni puni iznos električnog naboja od $(276 \pm 3) \cdot 10^{-6} \text{ As cm}^{-2}$). Izgleda da do reorganizacije epitaksijalne strukture prvog sloja dolazi i prije nego što se cio epitaksijalno adsorbuje.

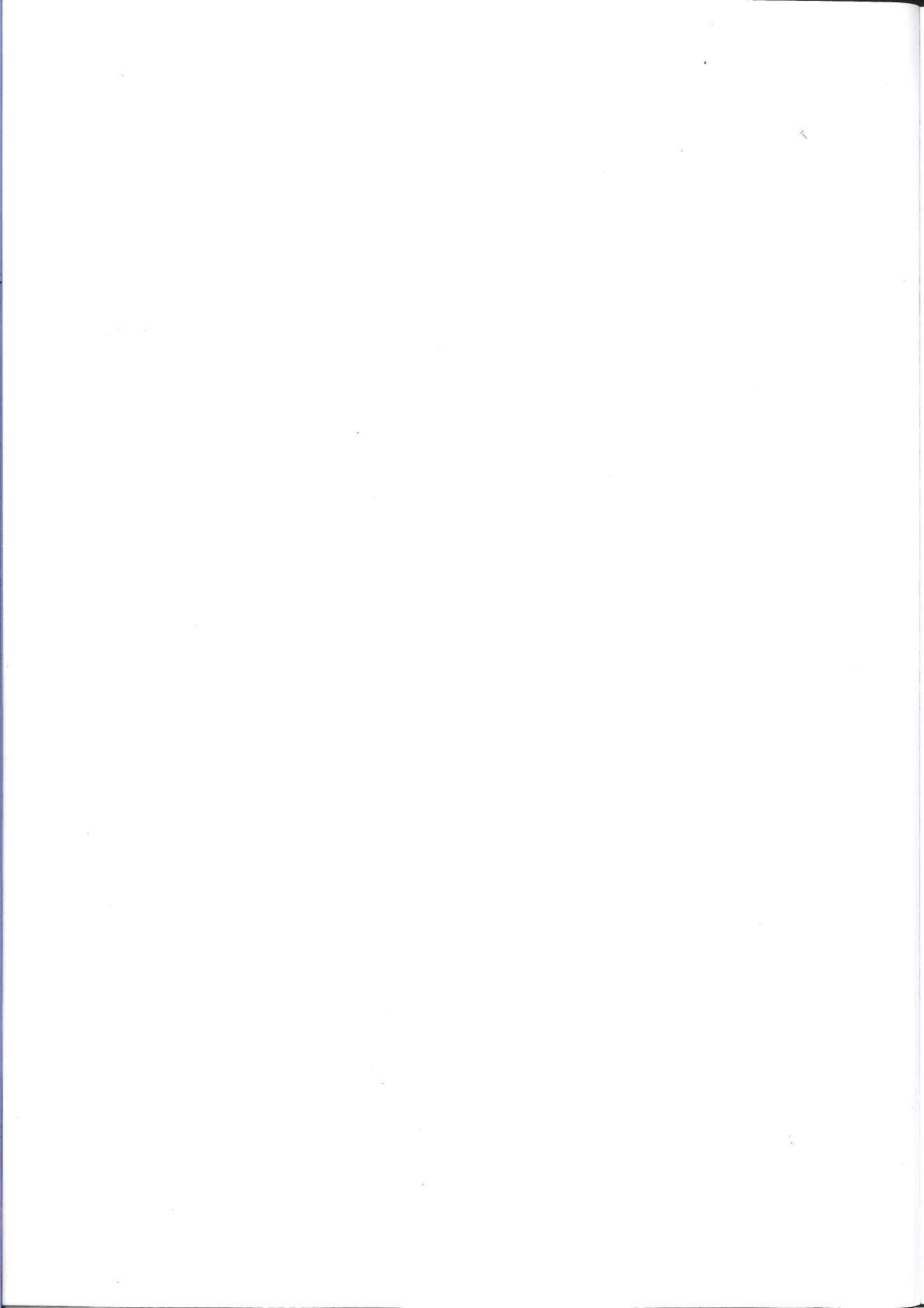
Navedeni rezultati iztraživanja snažno upućuju na to da elektrotaloženje olova na (100) površini bakarne elektrode, pri potencijalima pozitivnijim od

reverzibilnog potencijala olova u datom elektrolitu, započinje adsorpcijom, K_1 , a nastavlja se 2D faznom transformacijom višeg reda, K_2 , u gustopakovani epitaksijalni kristalnoidni monosloj.

Predložen je model strukture najgušće pakovanog epitaksijalnog olovnog monosloja na Cu(100) površini elektrode nastalog elektrotaloženjem olova pri potencijalima pozitivnijim od reverzibilnog potencijala olova.

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A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART IV.

The Potential Step Results: Underpotential Deposition on (111) oriented Copper Single Crystal Electrode

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper(111) electrodes from acetate, nitrate and perchlorate solutions have been investigated using single and double potential step techniques.

It appeared that the different anions used did not change the current-time responses characteristics significantly.

The results obtained in L.S.V.⁷⁻¹⁰ and particularly the potential step experiments presented enable the following conclusion to be made:

a.- The underpotential deposition of lead on the Cu(111) oriented electrode surface is a first order 2D phase formation process proceeding through 2D instantaneous nucleation and the subsequent growth of overlapping centres controlled by charge transfer; the slow step of the overall reaction is the incorporation of the build-

ing material into the advancing edge of the growing 2D patches.

b.- The structure of the crystalline 2D layer formed is the epitaxially closest-packed monolayer lead lattice⁷ on the underlying copper (111) substrate.

c.- The UPD lead monolayer formation was found to be, in the case of copper(111) substrates, an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

The above conclusions are supported by the "discontinuous adsorption isotherm" evaluated from the potentiostatic underpotential deposition data and analysis of the growth transients at constant potential which showed behaviour characteristic of nucleation and growth processes.

Key words: Underpotential deposition, Potentiostatic step, Cu, Pb, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition¹⁻¹⁰ there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was lead on copper (111), (110) and (100) oriented single crystal surfaces. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrates possess high hy-

drogen evolution overvoltage and therefore hydrogen co-adsorption processes do not complicate deposition of lead.

Linear sweep voltammetry¹⁻¹⁰, however carefully and successfully performed, is not sufficiently diagnostic tool to characterize underpotential monolayers and the possible phase changes taking part within them. Therefore help from potential step techniques, which are known to provide clear information on the mechanism of phase formation, was required. The analysis of the current against time transients, observed after initiating phase formation at constant potential using a potential step should yield additional data on the formation of 2D phase films during UPD.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorized can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} Acm⁻²) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a preset number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location,

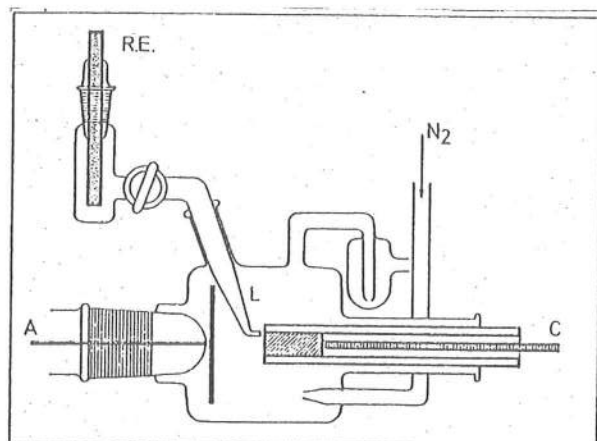


Figure 1.a) The cell used for most of the L.S.V. and potential step experiments

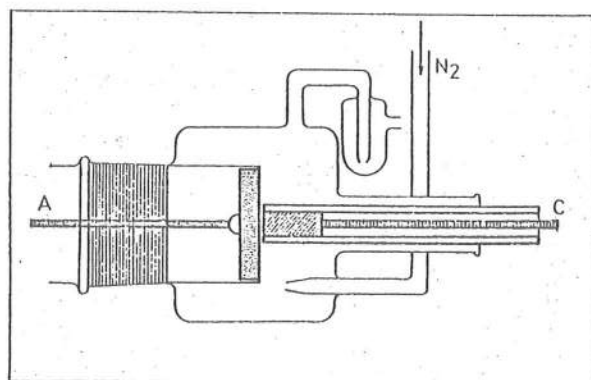


Figure 1.b) The cell used for potential step experiments on a very long time scale

so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will increase linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, $(SN)_n$, is given by $(SN)_n = n^{1/2}$. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig.1. a) and b). The cell given in Fig.1.a) was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc ≈ 1.5 cm² in area, positioned parallel to the working electrode.

The cell in Fig.1.b) was used for potential step experiments controlled by potentiometers. This cell

was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area 4.5cm^2 ; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin ($1 \cdot 10^{-4}\text{cm}$) teflon foil.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx 0.8\text{cm}$ in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25\text{g}$, of amalgamated zinc¹⁸.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}\text{cm}$ and $3 \cdot 10^{-4}\text{cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}\text{cm}$ and $3 \cdot 10^{-5}\text{cm}$ grade). Initially the largest grade was used and then

progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere^{7,11}.

The (111) oriented single crystal was immersed for 3 seconds in the acid mixture heated to over 75°C while stirring, left without stirring for another 3 seconds, then stirred and again left still for 3 seconds, finally the solution was stirred, the electrode removed and washed under a strong stream of tap water and eventually in triply distilled water. The whole procedure was repeated a second time. Then the electrode would be immersed in 30 vol.% solution of orthophosphoric acid and stirred for 10 seconds, washed in tap water and finally with plenty of triply distilled water. If gas evolution occurred on the electrode immersed in the polishing mixture earlier than 3 seconds, then the time which the electrode spent standing still was made shorter.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was re-

moved from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell scaled with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the length of the deposition one, to ensure steady state conditions.

The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two preset potentials. The cell current was monitored with a battery driven Current picoammeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

Copper single crystal with (111) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:

$xM Pb(OAc)_2 + 10^{-2}M HOAc + 0.5M NaOAc$	$10^{-4}M \leq x \leq 10^{-1}M$
$xM PbO + 10^{-3}M HClO_4 + 0.5M NaClO_4$	$10^{-3}M \leq x \leq 10^{-1}M$
$xM Pb(OAc)_2 + 10^{-3}M HClO_4 + 0.5M NaClO_4$	$10^{-4}M \leq x \leq 10^{-1}M$
$xM Pb(OAc)_2 + 10^{-3}M HClO_4 + 0.5M NaNO_3$	$10^{-3}M \leq x \leq 10^{-1}M$

This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD.

The composition and pH of the solutions used was decided on the basis of knowledge gathered on the subject^{1,18,19}. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2 - 5.5), and in such a situation:



Therefore:

$$E^{Pb/PbO} = -819 + 29.5 \log \frac{1}{[OH^-]^2}$$

which for different pH yields:

pH = 7	$E_{Pb/PbO} = -406mV \text{ vs. S.C.E.}$
pH = 5.4	$E_{Pb/PbO} = -312mV \text{ vs. S.C.E.}$
pH = 3	$E_{Pb/PbO} = -170mV \text{ vs. S.C.E.}$

The potential region in which lead UPD is observed in $10^{-3}M$ lead solution on copper spans approximately between -240 and -340mV vs. S.C.E (provided that $a_{Pb^{+2}} = [Pb^{+2}]$. Solutions were acidified to pH = 2 - 3 in order to push the potential $E_{Pb/PbO}$ sufficiently anodic to the UPD potential region of investigation, thus assuring conditions with no interference from PbO formation.

The single potential step results

After L.S.V. had been recorded the potential of the working electrode was changed in a step from the starting value, E_s , to a new value, η , in the region of UPD as indicated by the beginning of the voltammetric peak and the onset of bulk deposition (see Fig. 2.).

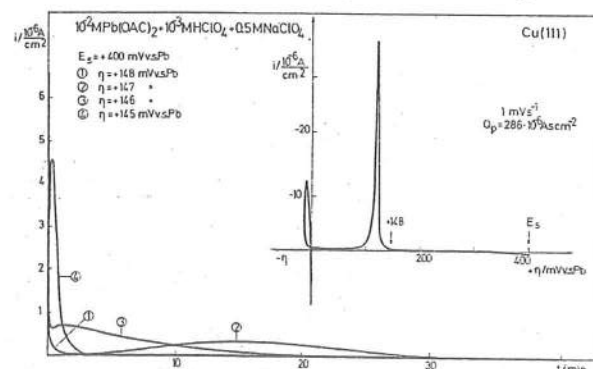


Figure. 2. Current-time transients for a single potential step from E_s to η for values just into the deposition peak. Insert: voltammogram for deposition process showing the relevant values of the potential.

Current-time transients obtained in such an way are presented in Fig. 2. and Fig. 3. The first one shows transients obtained for η values corresponding to po-

tentials at very beginning of the voltammetric deposition peak, and the second one, transients obtained for η values equal to or more negative than the peak potential.

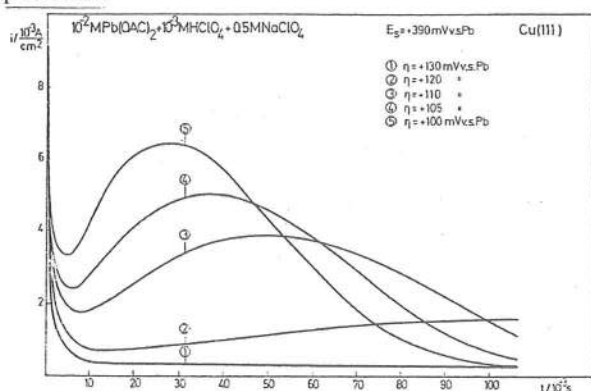


Figure 3. Current-time transients for a single potential step from E_s to η for values of η well into the L.S.V. deposition peak.

The double potential step results

The results obtained using a double potential step are consistent with the conclusion already reached⁵⁻¹⁰, namely that lead UPD on Cu(111) takes place by a process involving 2D instantaneous nucleation and the subsequent growth of 2D patches.

When the duration of the first pulse τ_1 , was increased, the amplitude of the first pulse, η_1 , and the second pulse, η_2 , remaining constant, the current-time relationships of the form given in Fig. 4. were obtained.

Nuclei formed during the first pulse grew at the

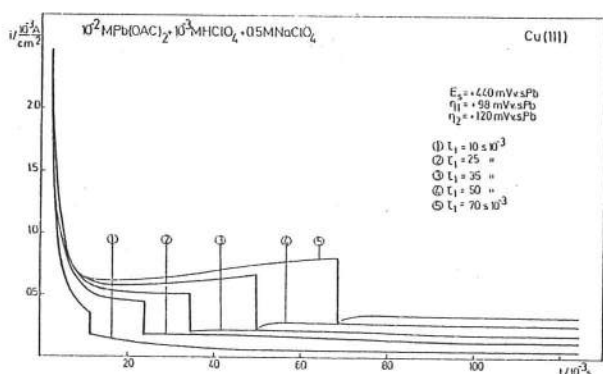


Figure 4. Current-time responses to double potential step applied in lead UPD. When time duration of the first step gradually increases.

potential of the second, thus completing a full monolayer. Naturally, the longer τ_1 , all other parameters remaining the same, the higher the current during the reign of the first pulse and consequently the shorter the time needed for the layer to be deposited in full.

When τ_1 and η_2 were maintained constant and η_1 varied from values anodic to the L.S.V. peak to those well within it, transients of a form presented in Fig. 5. were obtained.

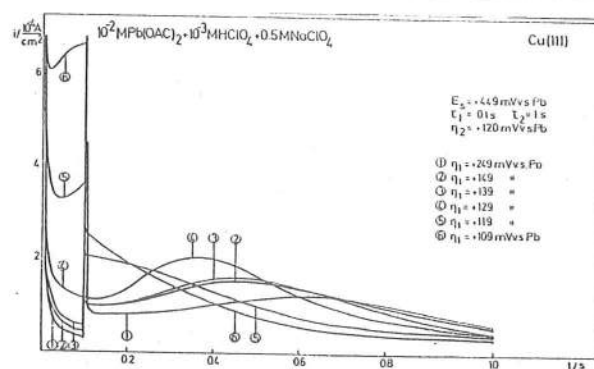


Figure 5. Current-time responses to double potential steps.

When the potential of the first pulse was smaller than that of the second, (curve 1 in Fig. 5.), the $i-t$ transients in the second pulse closely resembled those obtained for single step experiments under the same conditions. When $\eta_1 \geq \eta_2$, nuclei produced during the first pulse continued to grow under the second completing a full monolayer. The time needed for the completion decreased with increasing η_1 , as was expected.

In all cases, when the charge under the first pulse was added to the charge belonging to the second pulse and the double layer charge was subtracted, the total was close to the predicted value, $212 \cdot 10^{-6} \text{ As cm}^{-2}$ for the model shown earlier⁷.

When double pulse potential experiments were performed in 10^{-3} M lead solutions, planar diffusion control played an important part in deciding the shape of the $i-t$ transients obtained in Fig. 6.

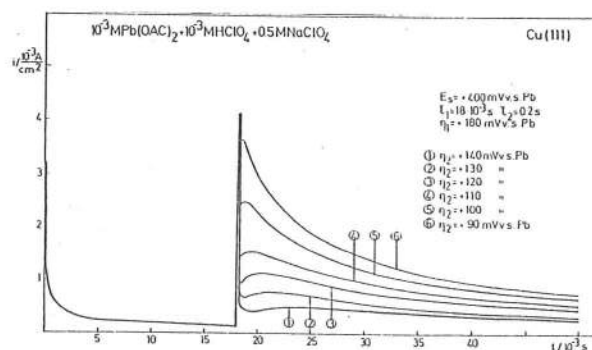


Figure 6. Current-time responses to double potential steps applied in lead UPD in diluted lead solution.

Even at low η_2 potentials, full development of the rising $i-t$ transients was either inhibited or prevented by bulk diffusion control, and at higher η_2 values the control by planar diffusion becomes obvious. These transients, at the same time, closely resemble those obtained for lead UPD potential step experiments on Ag(111)¹⁻⁴ indicating once more the probable reasons for absence of well defined rising $i-t$ transients in that case.

DISCUSSION

Detailed analysis of the transients given in Fig. 2. and 3. showed that the initial fall-off of the current succeeding the double charging current exhibits characteristics common to relationships reflecting planar diffusion controlled deposition processes.

It was suggested¹² that, in the case of the adsorption of neutral atoms on an electrode at a rate high enough to be controlled by planar diffusion, the surface concentration of adsorbed species, Γ , should be related to the volume concentration of the same species at the electrode surface, $C_x=0$, through an adsorption isotherm:

$$\Gamma = \frac{\Gamma_{\max} C}{a + C} \quad (1)$$

a , being a parameter characteristic to the isotherm. The isotherm was linearized:

$$\Gamma = K \cdot C \quad \text{where} \quad K = \frac{\Gamma_{\max}}{a} \quad (2)$$

and the Laplace transform method applied to solve the diffusion problem to give the relationship between the surface concentration C and the volume concentration C_b :

$$C = C_b \left[1 - \exp\left(-\frac{x}{K} - \frac{Dt}{k^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{K}\right) \right] \quad (3)$$

Therefore:

$$\left(\frac{dC}{dx}\right)_{x=0} = -\frac{C_b}{K} \exp\left[\left(\frac{Dt}{K^2}\right) \operatorname{erfc}\left(\frac{\sqrt{Dt}}{K}\right) + \frac{C_b}{\sqrt{\pi}Dt}\right] \cdot \left[\exp\left(\frac{Dt}{K^2}\right) \exp\left(-\frac{dt}{K^2}\right)\right] \quad (4)$$

Implementation of Fick's first law transforms Eq. (4) into:

$$i = xFD \left(\frac{dC}{dx}\right)_{x=0} = zF \left[-\frac{DC_b}{K} \exp\left(\frac{Dt}{K^2}\right) \operatorname{erfc}\left(\frac{\sqrt{Dt}}{K}\right) + \frac{C_b\sqrt{D}}{\sqrt{\pi}t} \right] \quad (5)$$

For small C_{bulk} values and short times Eq. (5) can be approximated to the form:

$$i = \frac{zFC_b\sqrt{D}}{\sqrt{\pi}t} \quad (6)$$

Astley et al.¹³ have derived an identical equation for the case of metal deposition in which the diffusion zones of each nucleus rapidly overlapped and the rate of the reaction was controlled by diffusion perpendicular to the surface. The slopes of i vs $t^{-1/2}$ for this equation are constant at short times and equal to $zFC_b\sqrt{D}/\sqrt{\pi}$, independent of η . Before the overpotential is high enough for the limiting diffusion controlled current to be achieved, the plot should show a

characteristic intercept on the $t^{-1/2}$ axis, and develop curvature at longer times.

The experimentally obtained plots of i vs. $t^{-1/2}$ for the initial falling currents of the recorded i - t transients are in reasonable agreement with this predictions, Fig. 7. The amount of lead put down in this way are approximately 5-10% of the total monolayer charge, and most probably this is all random adsorption of lead species at preferred sites.

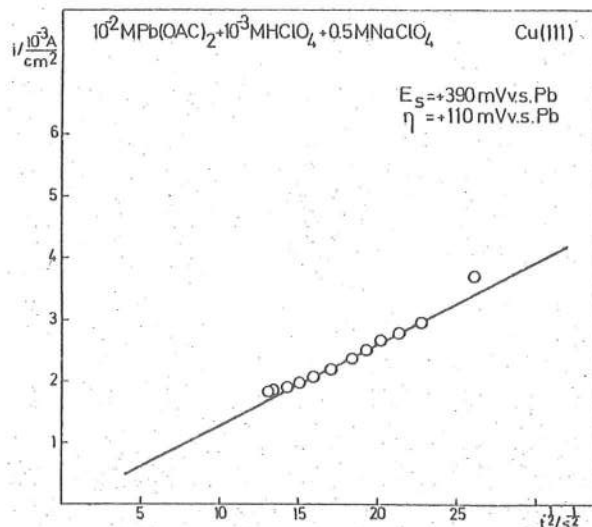


Figure 7. An i vs. $t^{-1/2}$ relationship obtained for the very initial portion of the curve number 3 in Fig. 3.

The subsequent rise of current proved to be linear with time, Fig. 8., which suggested a process of phase formation through 2D instantaneous nucleation^{14,15}.

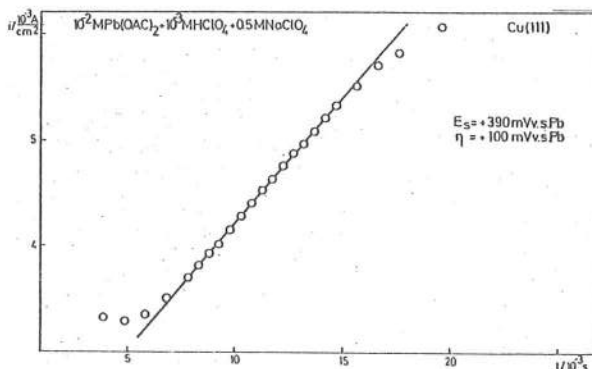


Figure 8. The rising portion of current-time transient number 5 in Fig. 3. Enlarged to show the initial part.

It has been shown^{14,15} that the current density-time relationship for the initial stages of 2D instantaneous nucleation and subsequent rate controlling lattice growth under potentiostatic conditions is of the linear form:

$$i = \frac{2zF\pi MN_0 k^2 l t}{\rho} \quad (7)$$

However, conclusive proof for such a crystal growth process is obtained only by obtaining a fit to the complete equation describing the formation of the full monolayer:

$$i = \frac{2zF\pi MN_0 k^2 t}{\rho} \exp\left(-\frac{\pi M^2 N_0 k^2 t^2}{\rho^2}\right) \quad (8)$$

This predicts a linear relationship between $\log(i/t)$ and t^2 .

In Fig. 9. a plot of $\log(i/t)$ vs. t^2 is shown for the same i - t transient plotted in Fig. 8. It shows a good fit to the predicted linear form, thus proving that the UPD of lead on Cu(111) takes place by 2D crystal growth mechanism involving the formation and subsequent growth of nuclei formed instantaneously. The transients obtained for other values of also gave good linear plots of i/t against t^2 .

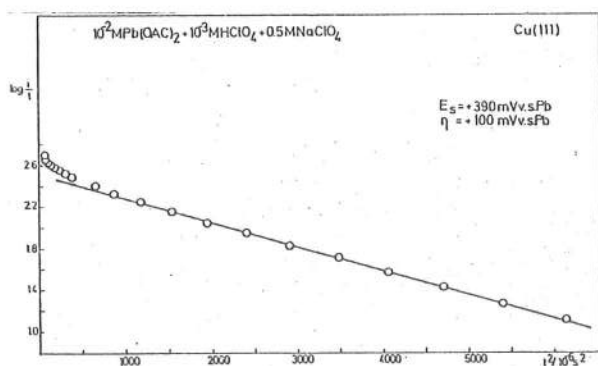


Figure 9. Test of transient number 5 of Fig. 3. According to equation (8).

Analysis of the charge encompassed by the i - t transients gave the expected results, Fig. 10. When the η values were gradually advanced (millivolt by millivolt), starting from a potential well anodic to the voltammetric peak, the i - t transients for values up to $\eta = +149$ mV vs. Pb showed only monotonous fall of current and the charge corresponded to the adsorption of only a small amount of Pb. It was only when a value of $\eta = +147$ mV vs. Pb was reached that the full lead UPD monolayer ($283 \cdot 10^{-6} \text{ As cm}^{-2}$) was deposited. At this potential the deposition peak took approximately 30 minutes to complete (curve 2 in Fig. 2.). Thus the transition from a dilute adsorbed layer to a full crystalline layer was observed to take place within a potential interval of 1 mV on time scale of these experiments. For $\eta = +146$ mV vs. Pb, the time needed for the monolayer to be deposited ($280 \cdot 10^{-6} \text{ As cm}^{-2}$) was almost halved. Every other η value more negative than +147 mV vs. Pb produces increasingly shorter i - t transients but always encompassed approximately the same monolayer charge.

Therefore these experiments, performed with two potentiometers, show a "discontinuous isotherm", Fig. 10. with a change from 5% to 100% (if double layer charge is subtracted) in the charge of the monolayer

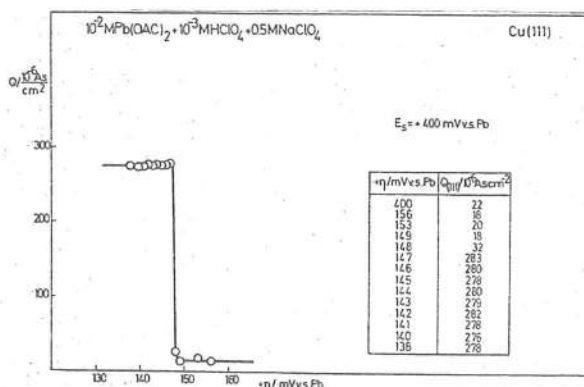


Figure 10. Discontinuous isotherm obtained by single potential step experiments in lead UPD.

proposed earlier⁷, taking place within a 1 mV potential difference.

This result shows absolutely conclusively for the first time that first order phase transformations, the formation of a 2D crystalline layer by a normal nucleative mechanism does take place in UPD systems, contrary to the doubts of Lorenz, Schmidt and coworkers¹⁶.

Experiments using a longer timescale than that used would probably give an even narrower potential difference for the "discontinuous isotherm". However, the measurement problem would become increasingly severe. To follow the formation of a monolayer in 30 minutes require the measurements of currents of about $10^{-7} \text{ A cm}^{-2}$. These results show the difficulty of trying to recognize such crystal growth processes by L.S.V. analysis. The extreme potential dependence of nucleative processes means that impossibly low sweep speeds would need to be used to obtain very narrow peaks in L.S.V. e.g. a sweep speed of about 1 mV in 30 mins ($\approx 10^{-6} \text{ Vs}^{-1}$) would be needed to give a peak width of 1 mV for the present system.

Attempts using the same technique to obtain similar clear cut results for lead UPD on Ag(111) were not successful. This can be understood, if the results obtained for a single potential step in 10^{-3} M lead solutions on Cu(111), Fig. 11.a. and b. are compared to those already published for Ag(111)¹⁻⁴. Simple calculations using Eq.(6) show that contrary to the case of the long i - t transients, Fig. 2. For which the diffusion limited current density is still much higher after 15 minutes ($3.5 \cdot 10^{-6} \text{ A cm}^{-2}$) than the recorded current (order of magnitude $10^{-7} \text{ A cm}^{-2}$), in the case of 10^{-3} M lead solutions the planar diffusion limiting current is already reached after a few milliseconds (Fig. 11.a. and b.), Fig. 12. At step potentials more anodic than $\eta = +60$ mV vs. Pb, there are signs of rising i - t transient caused by crystal growth but soon (Fig. 11.) the limiting diffusion current prevails and the kinetics of the crystal growth process are obliterated.

Therefore by comparison, it appears that the very fast deposition kinetics and thus higher current densi-

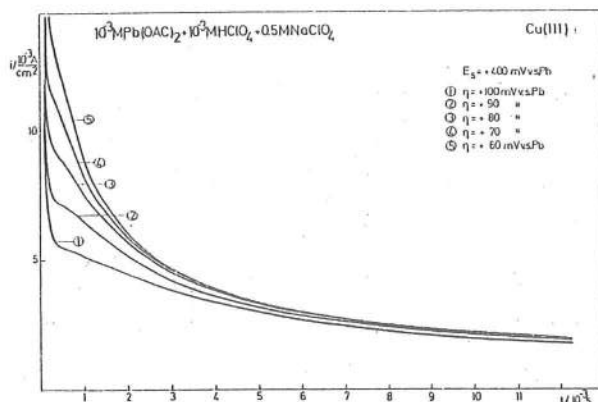


Figure 11.a. Current-time transients obtained in dilute solution for a potential steps in the UPD region.

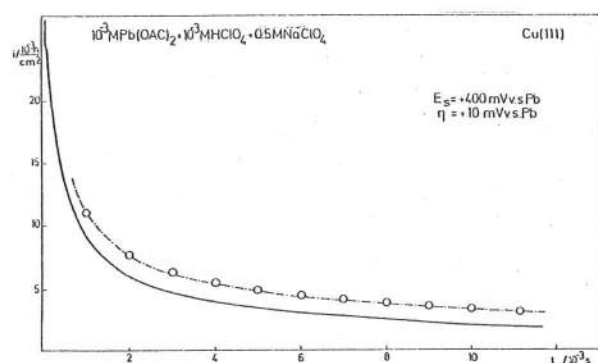


Figure 11.b. Current-time transient obtained in dilute solution for a potential step in the UPD region; (-----) calculated diffusion limited current.

ties involved in lead UPD on Ag(111), lead to mass transfer control and the loss of *i*-*t* transients suitable for kinetic and mechanistic analysis.

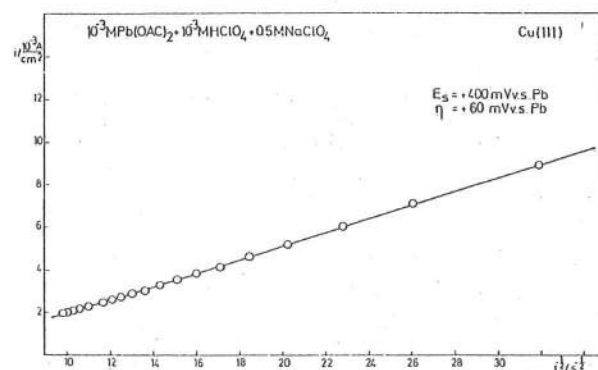


Figure 12. Plot of *i* vs. *t*-1/2 for curve 5 of Fig. 11.a.

In the case of 10^{-4} M lead solutions the influence of planar diffusion on the process is even more obvious, Fig. 13.a. and b. At a sweep speed $v = 10^{-3} \text{Vs}^{-1}$, lead UPD on Cu(111) electrode occurred in an usually broad peak (compare it with figure 7 recorded for the same sweep speed but for 10^{-2} M Pb solution).

If the sweep speed was increased twentyfold, Fig. 13.b., diffusion control became very important, and the

UPD current did not reach a zero value (the result of monolayer completion) before the onset of bulk deposition. If scanning is interrupted at certain potentials and then resumed after a certain interval at fixed potential, depending on how long the intermission had lasted and at which potential it took place, additional amounts of the monolayer were deposited. If the interruption lasted for 10 seconds (point 1 in Fig. 13.b. the additional UPD process ran into diffusion control. If the interruption lasted for the same time at two other potentials, similar behaviour was observed (2 and 3 in Fig. 13.b.) If however, the scanning was interrupted for 3 or 5 minutes (points 4 and 5 respectively in Fig. 13.b.) a picture similar to the one in Fig. 13.a. was restored.

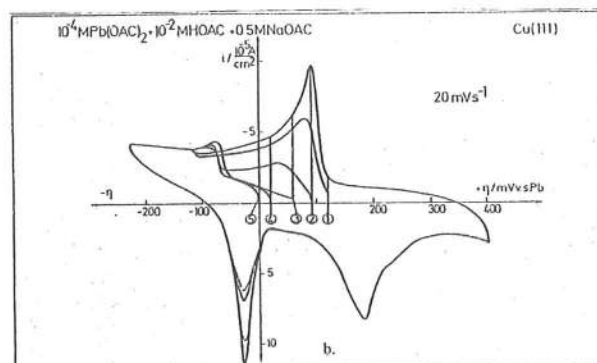
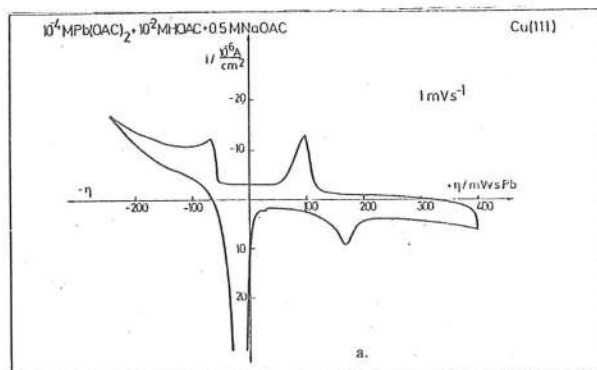


Figure 13. L.S.V. for UPD of Pb from dilute solution onto Cu(111); interruptions: 1,2,3 - 10s; 4 - 180s; 5 - 300s.

It appears that at higher sweep speeds the monolayer does not have the time to be deposited under diffusion limiting conditions before the potential of the bulk deposition is reached. At low enough sweep speeds this is not the case, the monolayer has enough time to deposit even under diffusion limited rates.

Analysis of a number of *i*-*t* transients obtained on the same electrode for different η values should produce information about nucleation kinetics.

The slope of the rising portion of an *i*-*t* transient in the case of 2D instantaneous nucleation is defined by:

$$\alpha_1 = \frac{\Delta i}{\Delta t} = \frac{2zF\pi MN_0k^2l}{\rho} \quad (9)$$

Therefore assuming all other terms as constant, N_0k^2 can be evaluated from:

$$N_0k^2 = \frac{\alpha_1 \rho}{2zF\pi ml} \quad (10)$$

After introducing the value for UPD lead monolayer charge on Cu(111) ($Q(111) = 212 \cdot 10^{-6} \text{ As cm}^{-2}$) to calculate:

$$\frac{\rho}{M} = \frac{Q(111)}{2zF} \quad (11)$$

actual values for N_0k^2 were obtained using the expression:

$$N_0k^2 = \frac{\alpha_1 Q(111)}{2z^2 F^2 \pi l^2} \quad (12)$$

It is impossible, unfortunately, to separate the growth rate constant, k , from the number of nuclei formed instantaneously.

However, the plot of $\log N_0k^2 = f(\eta)$, given in Fig. 14., confirms that the UPD of lead on Cu(111) is a nucleation process controlled by the charge transfer reaction:

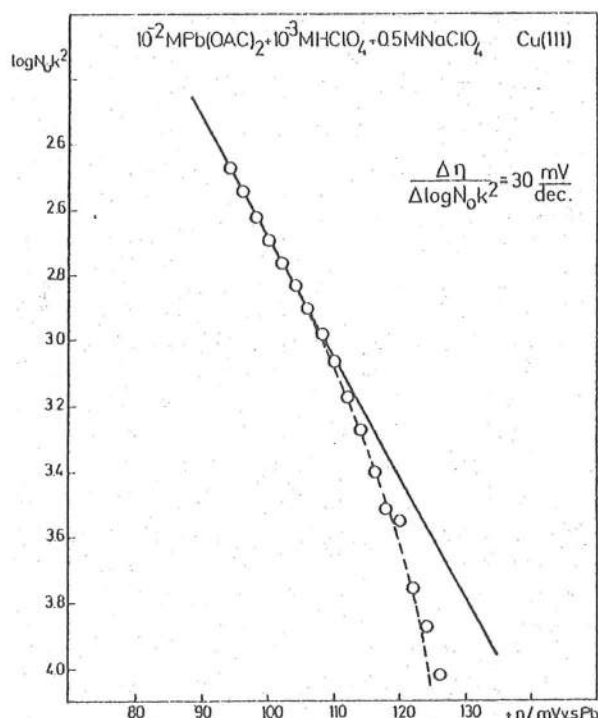
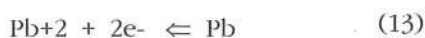


Figure 14. Potential dependence of N_0k^2 ; (-----) the same dependence calculated according to Eq.(14).



The limiting slope $\Delta\eta / \Delta\log N_0k^2 = 30\text{mV/decade}$ is the value predicted by the growth rate equation:

$$k^2 = k_o^2 \exp\left(\frac{2\alpha_c zF\eta}{RT}\right) \quad (14)$$

if $\alpha_c = 0.5$ is assumed, and the data gives a very good fit to the theoretical line shown dashed which takes account of the full form for the potential dependence of the rate constant,

$$k = k_o \left(\exp - \frac{\alpha zF\eta}{RT} - \exp \frac{(1-\alpha) zF\eta}{RT} \right) \quad (14)$$

Having established the mechanism of the lead UPD process on Cu(111) and the structure of the final layer it is now possible to analyze the L.S.V. peaks and in particular, to show in detail why these peaks do not become as sharp as those predicted by the limiting Frumkin isotherm with $g = 4$ in:

$$a_r = \frac{k\theta}{(1-\theta)} \exp(-g\theta) \quad (15)$$

This has become possible due to the analysis by Rangarajan¹⁷ of the L.S.V. response of crystal growth processes. In the case of 2D instantaneous nucleation and subsequent growth following the relationships given by Eq.(7) and Eq.(8), the explicitly expressed charge for the dependence on time of the phase formation can be presented as:

$$q = q_m [1 - \exp[-BF(t)]] \quad (16)$$

and therefore the current versus time relationship constructing L.S.V. for the same process by:

$$i = q_m B \left(\frac{dF}{dt} \right) \exp[-BF(t)] \quad (17)$$

where: q_m is the charge of a completed monolayer, B is a dimensionless parameter proportional to $1/V^2$ (V being a dimensionless sweep speed $V = zFv/4RT$, where v is the sweep speed), and $F(t)$ a dimensionless parameter defined as:

$$F(t) = \left\{ \left[\frac{\alpha_a}{\alpha_c + \alpha_a} \exp(4\alpha_c Vt) \right] + \left[\frac{\alpha_c}{\alpha_c + \alpha_a} \exp(-4\alpha_a Vt) \right] - 1 \right\} \quad (18)$$

If transfer coefficients are assumed $\alpha_a = \alpha_c = 0.5$ and $z = 2$, Eq.(18) transforms into:

$$F(t) = [\cosh 2Vt - 1]^2 \quad (19)$$

$$\frac{dF}{dt} = 4 Vt \sinh 2Vt [\cosh 2Vt - 1] \quad (20)$$

Using the dimensionless L.S.V. peak potential definition¹⁷:

$$E_p = \frac{zF\eta}{4RT} \quad (21)$$

and that for L.S.V. peak maximum current¹⁷:

$$i_p = \frac{4iRT}{q_m z F v} \quad (21)$$

where: $\eta = vt$ and $q_m = 212 \cdot 10^{-6} \text{ As cm}^{-2} = Q_{(111)}$ the theoretical plot of those values against $\log B$ was obtained. Fig. 15.

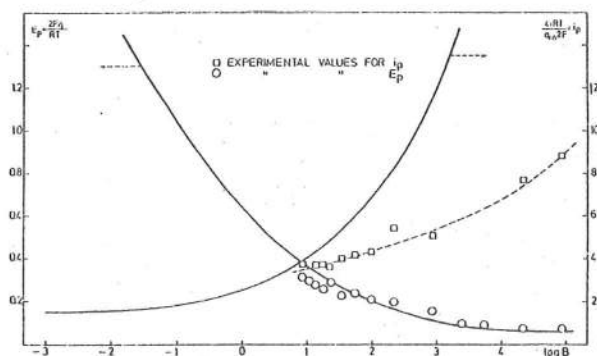


Figure 15. Theoretical (full line) and experimental (dashed line) plots of the dimensionless peak potential, E_p , and peak current, i_p , against the dimensionless parameter B .

It appears that at very high sweep speeds (small B) the L.S.V. peak potential changes exponentially, while at low speeds $v \leq 10^{-3} \text{ Vs}^{-1}$ (high B) it remains almost constant. At the same time, the peak current changes oppositely, at high sweep speeds it barely changes, and at low sweep speeds it changes exponentially.

When the experimentally obtained peak potentials and peak currents were plotted according to the same principle, curves formed by circles and squares in Fig. 15. Were obtained.

The dimensionless peak potential versus $\log B$ curve is in good agreement with theoretically predicted values. The dimensionless peak current dependence on $\log B$, however, although showing the predicted tendency, deviates quantitatively from the theoretically predicted values in the region of high B values (low sweep speeds). This is probably due to the fact that the analytical treatment¹⁷ does not take into account the slow kinetics of nucleation (induction period).

Expressing B in terms of the quantities already defined earlier gives:

$$B = \frac{16\pi N_0 M^2 k^2 R^2 T^2}{F^2 \rho^2 v^2} \quad (22)$$

From the potential step i - t transients obtained at a number of Cu(111) oriented electrodes, the value of $N_0 k^2 M^2 / \rho^2$ was found to be in the region between $1.4 - 8.5 \text{ s}^{-2}$ extrapolated to $\eta = 0$ (the reversible UPD monolayer potential). These values were used to calculate a linear sweep voltammogram for lead UPD on Cu(111) according to Eq.(17). Assuming $\alpha_a = \alpha_c = 0.5$:

$$i = \frac{16\pi N_0 k^2 M^2}{\rho^2} \cdot \frac{q_m t}{V} \sinh 2 Vt [\cosh 2 Vt - 1] \cdot \exp \left(- \frac{4\pi N_0 k^2 M^2}{\rho^2 V^2} [\cosh 2 Vt - 1]^2 \right) \quad (23)$$

Fig. 16.a. is the resultant L.S.V. calculated for a sweep speed $v = 10 \text{ mVs}^{-1}$ and for the lower value of $N_0 k^2 M^2 / \rho^2$.

Fig. 16.b. is the result for the higher value of $N_0 k^2 M^2 / \rho^2$. The half peak widths were respectively 3.6 and 2.5 mV, which is in reasonably good agreement with the experimentally obtained values for the same system which average about 5 mV.

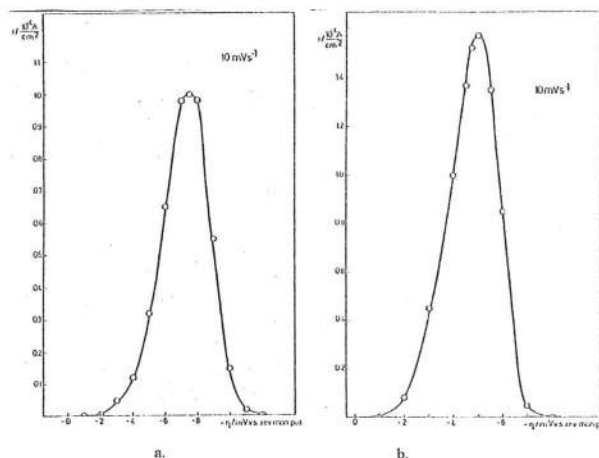


Figure 16.a. Voltammogram calculated according to Eq.(23) for experimentally obtained value $N_0 k^2 M^2 / \rho^2 = 1.4 \text{ s}^{-2}$, sweep speed $v = 10 \text{ mVs}^{-1}$.

b. Voltammogram calculated according to Eq.(23) for experimentally obtained value $N_0 k^2 M^2 / \rho^2 = 1.4 \text{ s}^{-2}$, sweep speed $v = 10 \text{ mVs}^{-1}$.

These results confirm the view expressed earlier that in the case of a first order phase transformation the L.S.V. peaks cannot be infinitely sharp and therefore it is not possible in practice to obtain the perfect discontinuous isotherm demanded by some authors¹⁶ as a criterion for true phase formation.

CONSLUSIONS

The results obtained in L.S.V.⁷⁻¹⁰ and potential step experiments presented above enable the following conclusion to be made:

1.- The underpotential deposition of lead on the Cu(111) oriented electrode surface is a first order 2D phase formation process proceeding through 2D instantaneous nucleation and the subsequent growth of overlapping centres controlled by charge transfer; the slow step of the overall reaction is the incorporation of the building material into the advancing edge of the growing 2d patches.

2.- The structure of the crystalline 2D layer formed is the epitaxially closest-packed monolayer lead lattice⁷ on the underlying copper (111) substrate.

3.- The UPD monolayer formation was found to be, in the case of copper(111) substrates, an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

Acknowledgment

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REFERENCES

- 1.-Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 2.-Thomas, B., Bewick, A., J.Electroanal. Chem., 65 (1975) 911.
- 3.- Thomas, B., Bewick, A., J.Electroanal. Chem., 70 (1976) 239.
- 4.-Thomas, B., Bewick, A., J.Electroanal. Chem., 84 (1977) 127.
- 5.- Jovićević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 6.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 7.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 8.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 9.-Jovićević, J.N., Bewick, A., Univ. Thought, this issue, Pristina 1997.
- 10.- Bewick, A., Jovićević, J.N., Thomas, B., Trans. Faraday Disc., 12 (1977) 24
- 11.-Pinner, R., Electroplating, October and November (1953) 360, 401.
- 12.-Delahay, P., Trachtenberg, I., J. Am. Chem. Soc., 79 (1957) 2355
- 13.-Astley, D.J., Harrison, J.A., Thirsk, H.R., J. Electroanal. Chem., 19(1968)325
- 14.- Harrison, J.A., Thirsk, H.R.: Vol.5, p.p.67, "Electroanalytical Chemistry", ed. Bard, A.J., Marcela Decker Inc., New York (1971).
- 15.-Fleischmann, M., Thirsk, H.R.: Vol. 3, "Advances in electrochemistry and electrochemical engineering", ed. Delahay, P. and Tobias, C.W., Interscience, London (1963).
- 16.-Lorenz, W.J., Schmidt, E., Staikov, G., Bart, H., Trans. Faraday Symp. No.12, Southampton, December 1977.
- 17.-Rangarajan, S.K., Trans. Faraday Symp. No.12, Southampton, (1977).
- 18.- "Handbook of Chemistry and Physics", ed. R.Weast, 55th edition, Chemical Rubber co., Cleveland, (1974/75).
- 19.- Sillen, G., "Stability Constants of metal ion Complexes", Chem. Soc., Special publication No.25, (1971).

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTRO-TALOŽENJA OLOVA NA BAKRU - IV DIO
REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTOTALOŽENJE PRI POTENCIJALIMA POZITIVNIJIM OD REVERZIBILNOG NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (111)

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000 Priština, Jugoslavija

Ovo je četvrti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova (iz acetatnih, nitratnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene potenciostat-skom metodom jednostrukog, dvostrukog i trostrukog pulsa na monokristalnoj elektrodi površinske kristalografke orijentacije (111) u području potencijala pozitivnijih od reverzibilnog potencijala olova u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/ rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Različiti upotrebljeni anjoni ne utiču značajnije na karakteristike eksperimentalno dobijenih podataka.

Rezultati dobijeni cikličkom voltametrijom ranije⁷⁻¹⁰, a posebno rezultati prikazani u ovome radu dobijeni potenciostat-skom pulsnom metodom omogućuju slijedeće zaključke:

- elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog u ispitivanim rastvorima na monokristalnim površinama bakra kristalografske orijentacije (111) je aktivaciono kontrolisan proces formiranja dvodimanzione faze putem 2D trenutne nukleacije i daljeg rasta stvorenih u rastu preklapajućih centara; spori stupanj ukupne reakcije je ugradnja građevnog materijala u ivice rasta dvodimenzionih kristalnih ostrva;

- struktura kristalnog dvodimenzionog sloja je epitaksijalna najgušće pakovana monoslojna rešetka formirana na bakarnoj podlozi kristalografske orijentacije (111);

- u slučaju bakarne podloge kristalografske orijentacije (111) elektrotaloženje olova pri potencijalima

pozitivnijim od reverzibilnog predstavlja neizostavnu predhodnicu debljim talozima olova i ima značajan uticaj na započinjanje elektrotaloženja pri katodnim prenapetostima.

Navedeni zaključke potvrđuje "diskontinualna adsorpciona izoterma" dobijena iz potencijostatskih podataka elektrotaloženja olova pri potencijalima pozitivnijim od reverzibilnog i rastući strujni odgovori na iste potencijostatske pulseve koji su po svom obliku i analiziranim vrijednostima karakteristični za procese nukleacije i rasta dvodimenzionih slojeva.

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A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART V. The Potential Step Results: Underpotential Deposition on (110) oriented Copper Single Crystal Electrode

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper(110) electrodes from acetate, nitrate and perchlorate solutions have been investigated using single and double potential step techniques.

It appeared that the different anions used did not change the current-time responses characteristics significantly.

Results obtained by potential step experiments in the case of lead UPD on Cu(110) show that the kinetics of higher order transformations in 2D systems can be followed and investigated by electrochemical means.

The combined results obtained by L.S.V⁸ and by potential step experiments presented here lead to conclusion that:

a.- The UPD of lead on the Cu(110) oriented electrode surface most probably involves a higher-order, 2D transformation process from

the epitaxial closest-packed layer⁸ into close-packed crystalline lead monolayer.

b.- The structure of the final UPD deposit is a close-packed lead monolayer probably distorted to a certain extent by the structure of the underlying copper surface.

c.- The UPD lead monolayer formation, in the case of copper(111) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

The above conclusions are supported by the "adsorption isotherm" evaluated from the potentiostatic underpotential deposition data and analysis of the growth transients at constant potential which showed behaviour characteristic of higher order 2D phase transformation processes.

Key words: Underpotential deposition, Potentiostatic step, Cu, Pb, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition^{1-10,17} there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was lead on copper (111), (110) and (100) oriented single crystal surfaces. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrates possess high hydrogen evolution overvoltage and therefore hydrogen co-adsorption processes do not complicate deposition of lead.

Linear sweep voltammetry¹⁻¹⁰, however carefully and successfully performed, is not sufficiently diagnostic tool to characterize underpotential monolayers and the possible phase changes taking part within them. Therefore help from potential step techniques, which are known to provide clear information on the mechanism of phase formation, was required. The analysis of the current against time transients, observed after initiating phase formation at constant potential using a potential step should yield additional data on the formation of 2D phase films during UPD.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorized can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} Acm $^{-2}$) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a preset number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location, so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will in-

crease linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, $(SN)_n$, is given by $(SN)_n = n^{1/2}$. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig.1. a) and b). The cell given in Fig.1.a) was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc ≈ 1.5 cm 2 in area, positioned parallel to the working electrode.

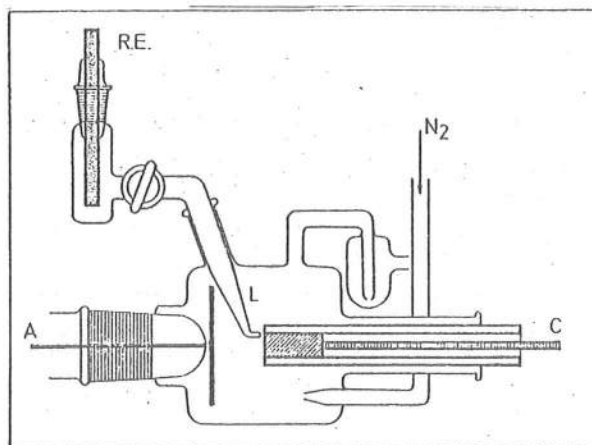


Figure 1.a) The cell used for most of the L.S.V. and potential step experiments

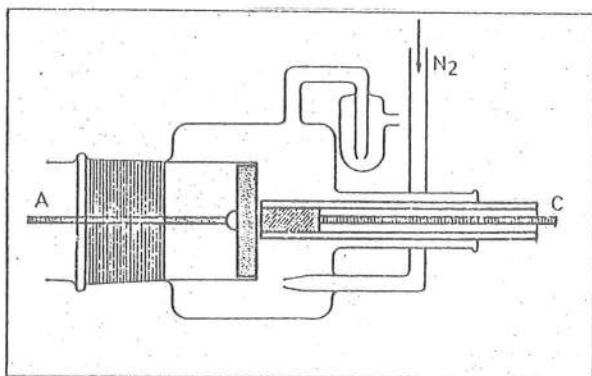


Figure 1.b) The cell used for potential step experiments on a very long time scale

The cell in Fig.1.b) was used for potential step experiments controlled by potentiometers. This cell was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area 4.5cm 2 ; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin ($1 \cdot 10^{-4}$ cm) teflon foil.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) ≈ 0.8 cm in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of ≈ 25 g, of amalgamated zinc¹¹.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}$ cm and $5 \cdot 10^{-4}$ cm grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}$ cm and $3 \cdot 10^{-5}$ cm grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere^{8,12}.

The (110) oriented single crystal was immersed in the acid mixture heated to 65°C , alternately standing still and stirred every 4 seconds for 4 times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) orientation⁷.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the length of the deposition one, to ensure steady state conditions.

The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

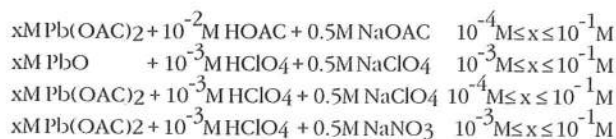
If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two preset potentials. The cell current was monitored with a battery driven Current picoammeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

Copper single crystal with (111) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:

Copper single crystal with (111) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:



This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD.

The composition and pH of the solutions used was decided on the basis of knowledge gathered on the subject^{1,13,14}. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2 - 5.5), and in such a situation:



Therefore:

$$E_{\text{Pb/PbO}} = -819 + 29.5 \log \frac{1}{[\text{OH}^-]^2}$$

pH = 7	$E_{\text{Pb/PbO}} = -406 \text{mV vs. S.C.E.}$
pH = 5.4	$E_{\text{Pb/PbO}} = -312 \text{mV vs. S.C.E.}$
pH = 3	$E_{\text{Pb/PbO}} = -170 \text{mV vs. S.C.E.}$

The potential region in which lead UPD is observed in 10^{-3}M lead solution on copper spans approximately between -240 and -340mV vs. S.C.E. provided that $a_{\text{Pb}^{+2}} = [\text{Pb}^{+2}]$. Solutions were acidified to pH = 2-3 in order to push the potential $E_{\text{Pb/PbO}}$ sufficiently anodic to the UPD potential region of investigation, thus assuring conditions with no interference from PbO formation.

The single potential step results

After L.S.V. had been recorded the potential of the working electrode was changed in a step from the starting value, E_s , to a new value, η , in the region of UPD as indicated by the beginning of the voltammetric peak and the onset of bulk deposition (see Fig. 2.).

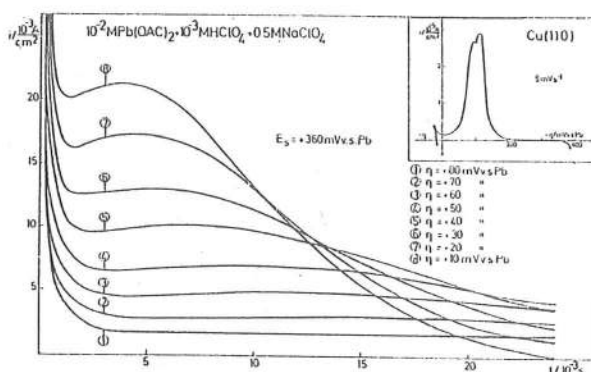


Figure 2. Current-time responses to single potential steps from E_s to EMBED Equation.3 for values just into the deposition peak. Insert: voltammogram for deposition process showing the relevant values of the potential.

Single potential steps inducing lead UPD on Cu(110) oriented electrode surface produced current-time relationships typical representatives of which are given in Fig. 2.

Steps, η , applied into the potential region of the first voltammetric peak K_1 (see Fig. 2. insert) yield monotonously falling transients encompassing charge values increasing with increasing η . Steps applied into the potential region of the second voltammetric peak, K_2 , produced rising i-t transients.

The double potential step results

Results obtained in double potential step experiments are presented in Fig. 3.a.,b.,c.,d. and e. These were obtained when the first pulse, η_1 , corresponded to the potential at the rising portion of the first voltamogram peak, and the second pulse, η_2 , was varied starting with the potential at the beginning of the second peak and continuing into it. The double pulse technique gave i-t transients with a more pronounced rising portion than obtained for the same potential in single potential step experiments.

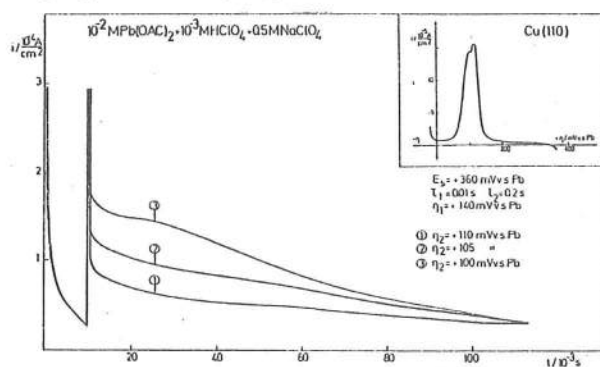


Figure 3. Current-time transients obtained from double potential step experiments.

The rising portion of an i-t transient becomes more obvious when η_1 enters further into the first voltammetric peak potential region, Fig. 3.e. In this way, the higher-order crystalline formation process

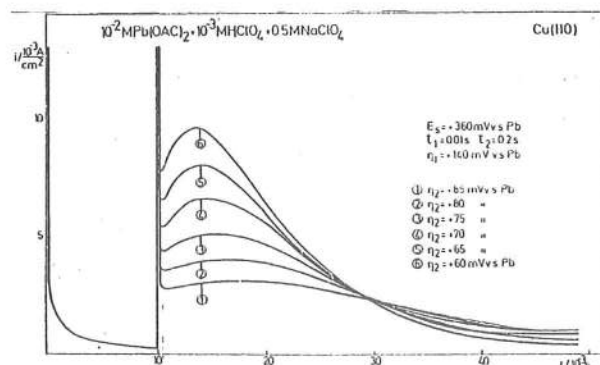
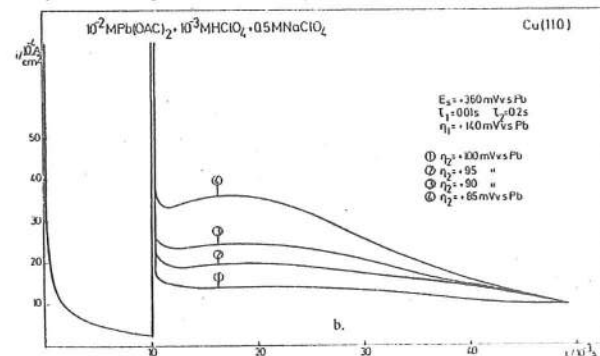


Figure 3. Current-time transients obtained from double potential step experiments.

proceeding mainly at η_2 can be separated from the epitaxial layer deposition process, taking part partially at η_1 .

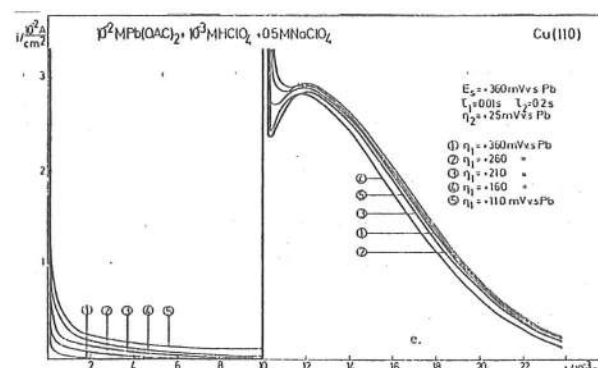
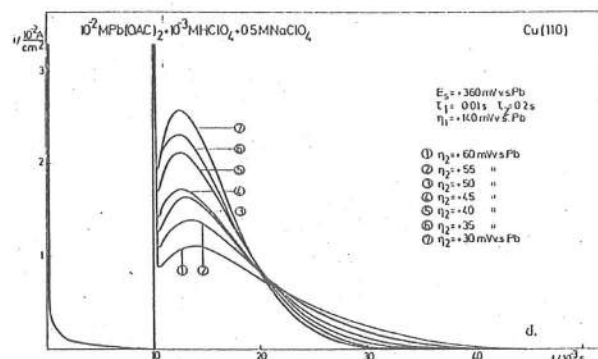


Figure 3. Current-time transients obtained from double potential step experiments.

DISCUSSION

Detailed analysis of the transients showed that the monotonously decreasing transients observed in the case when η was in the region of the first L.S.V. peak were consistent with adsorption onto preferred sites^{7,15,16}, Fig. 4.:

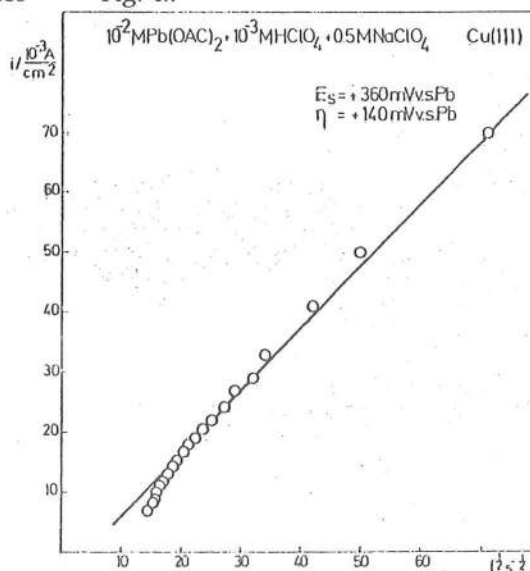


Figure 4. i vs. $t^{-1/2}$ plots of the transients obtained for a single pulse, η , into the beginning of the first voltammetric UPD peak, K_1 .

$$i = \frac{zFC_b \sqrt{D}}{\sqrt{\pi t}} \quad (1)$$

This also proved to be valid for the initial fall-off of the i - t transients when the potential was pulsed into the second voltammetric peak. Therefore the compound i - t transients were deconvoluted, by subtracting the i - t component due to diffusion controlled adsorption. This process resulted in well defined rising i - t transients as in Fig. 5. The suspected linearity of the initial rising portion of the i - t transients, Fig. 6, was confirmed by the deconvolution procedure, Fig. 5.

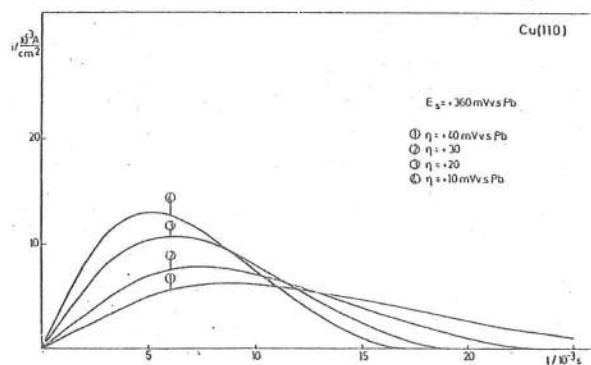


Figure 5. Deconvoluted i vs. t transients from Fig. 2.

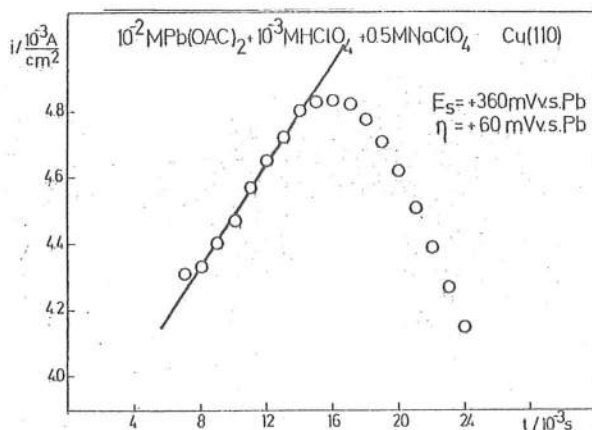


Fig. 6. An enlarged drawing of the i vs. t transient number 3 of Fig. 2.

When deconvolution was applied to the transients obtained for η values belonging to the first voltammetric peak, rising i - t transients were found for which the total increased with increasing η . This result contrasts sharply with that found for the (111) surface⁷.

The linearity of the $\log i/t$ vs. $(t^2)^{17-19}$ plots:

$$i = \frac{2zF\pi MN_0 k^2 l t}{\rho} \exp\left(-\frac{\pi M^2 N_0 k^2 t^2}{\rho^2}\right) \quad (2)$$

obtained by analysis of the original i - t transients, Fig. 7.a., was confirmed by the same analysis performed on the deconvoluted i - t transients, Fig. 7.b.

If the slope α_1 , in the^X:

$$\alpha_1 = \frac{\Delta i}{\Delta t} = \frac{2zF\pi MN_0 k^2 l}{\rho} \quad (3)$$

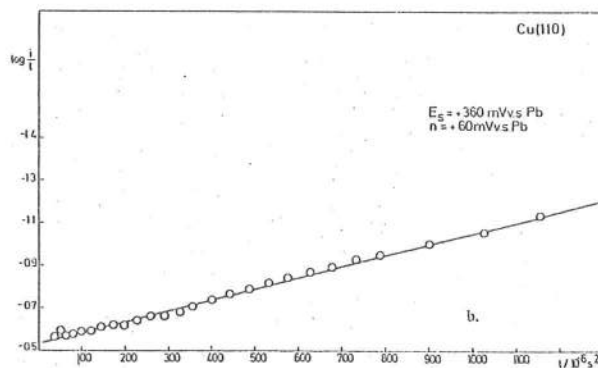
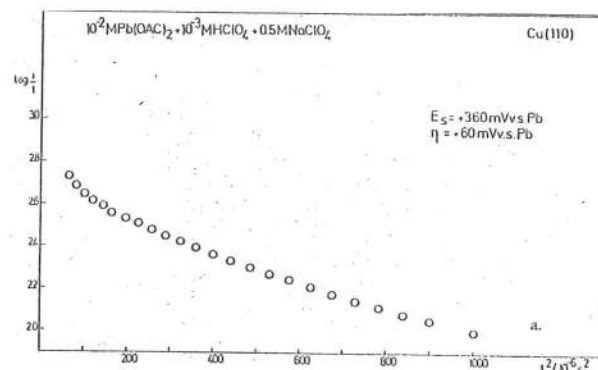


Figure 7. a. Plot of the $\log(i/t)$ vs. t^2 for transient number 3 in Fig. 2.

b. Plot of the deconvoluted $\log(i/t)$ vs. t^2 for transient number 3 in Fig. 2.

is divided by the slope obtained from the $\log i/t$ vs. t^2 analysis, Eq.(2) given as:

$$\alpha_2 = \frac{\Delta i}{\Delta t} = \frac{\pi M^2 N_0 k^2}{2.303 \rho^2} \quad (4)$$

the result is:

$$\frac{\alpha_1}{\alpha_2} = \frac{4.606 zF\rho l}{M} \quad (5)$$

When this ratios between the slopes α_1 , obtained from the rising linear portions of the i - t transients (Fig. 2) and the slopes α_2 obtained from plots of the complete transient (Fig. 7.a.) were plotted against potential the curve given in Fig. 8.a. was obtained (see Eq.(6)).

This represents the change in the density of deposit as the deposition potential is varied. At the same time, it gives the upper part of the complete "isotherm"⁸ for the UPD deposition of lead.

Virtually the same conclusions can be drawn from the analysis of the i - t transients about the maximum. Using Taylor series expansion²⁰ around t_m (the time at the maximum current) for small displacements u , the following expression can be derived²¹:

$$i_{-u} + i_{+u} \approx 2i_m - \frac{5.6 M^2 i_m^3 u^2}{z^2 F^2 \rho^2} \quad (7)$$

and

$$\frac{i_{-u} + i_{+u} - 2i_m}{i_m^3 u^2} = \frac{5.6 M^2}{z^2 F^2 \rho^2} \quad (8)$$

When this was applied to the deconvoluted i - t transients the curves shown in Fig. 9. and Fig. 8.b., were obtained.

The complete isotherm⁸ and the charges measured under the peaks obtained in L.S.V. experiments indicated that the lead UPD on Cu(110) proceeds basically in two stages: the first stage, identified by the first voltammetric peak, K₁, being adsorption onto preferred sites to give the structure proposed⁸; the second stage which actually starts before the first has been completed and being identified by the second voltammetric peak, K₂, being a phase transformation process of the adsorbed layer into a crystalline structure of close-packed lead.

The current-time transients obtained by the single potential pulse technique are consistent with this basic suggestion. The charge under them increases as the potential is made more negative and after the potential of the maximum of the second voltammetric peak is exceeded the charge approaches and reaches that needed for a full close-packed lead monolayer ($\approx 346 \cdot 10^{-6} \text{ As cm}^{-2}$ when the double layer charge is subtracted compared to the ideal value of $310 \cdot 10^{-6} \text{ As cm}^{-2}$). It remains constant at this value for all potentials more negative than that at the end of the second voltammetric peak.

The deconvoluted i - t transients have confirmed that the initiation of the crystalline phase starts already at potentials within the first voltammetric peak, Fig. 8.a. and b. and Fig. 9. The density of this phase increases with increasing negative potential, Fig. 9., until a point very close to the maximum potential of the second L.S.V. peak, K₂, then it remains constant.

This can also be seen from the data given in the Fig. 8.a. and b. The limiting values at more negative potentials are approximately $125 \cdot 10^{-6} \text{ As cm}^{-2}$, which is in good agreement with the value calculated for the charge needed ($122 \cdot 10^{-6} \text{ As cm}^{-2}$) for the additional deposition of material necessary to convert the existing epitaxial closest-packed layer⁸ into the close-packed crystalline layer.

Superposition of the "isotherm" given in Fig. 8.b. onto the upper part of the complete isotherm⁸ gives a good fit.

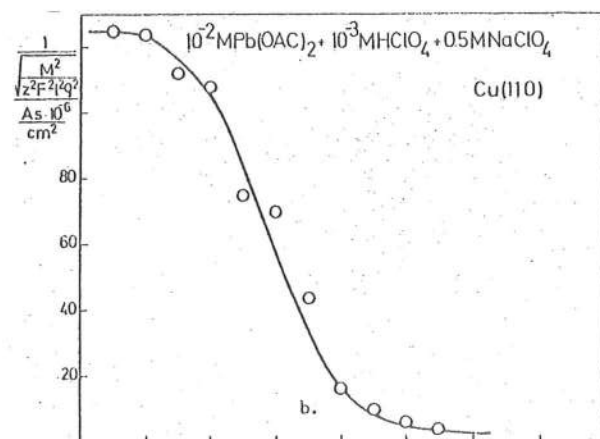
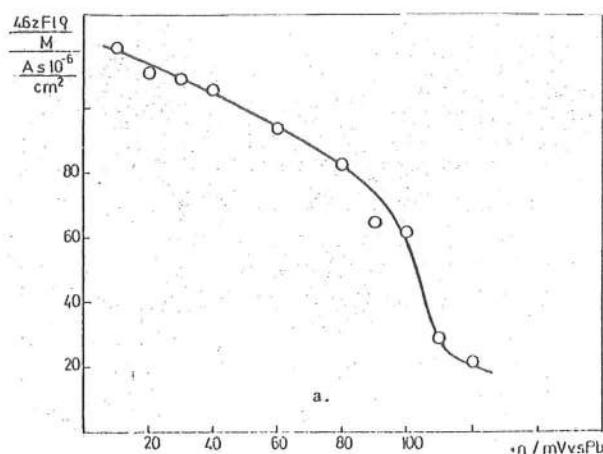


Figure 8. Variation of the monolayer charge with the applied potential obtained from responses to single potential steps.

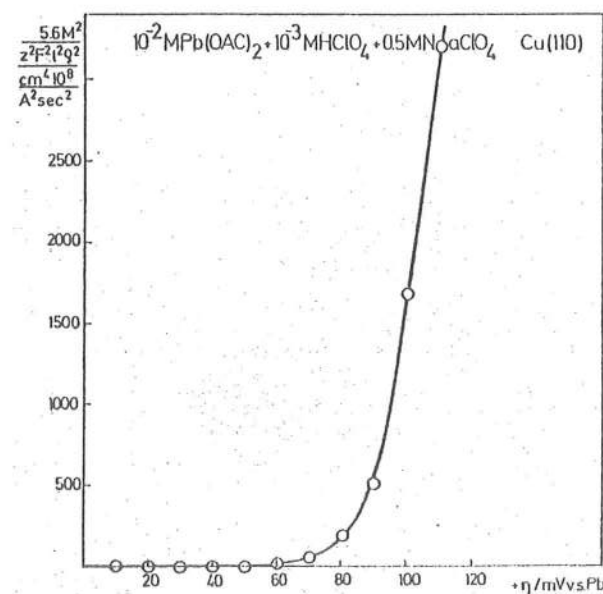


Figure 9. Variation of the quantity $5.6M^2/z^2F^2\rho^2$ with potential from analysis of the i - t transient at the maximum.

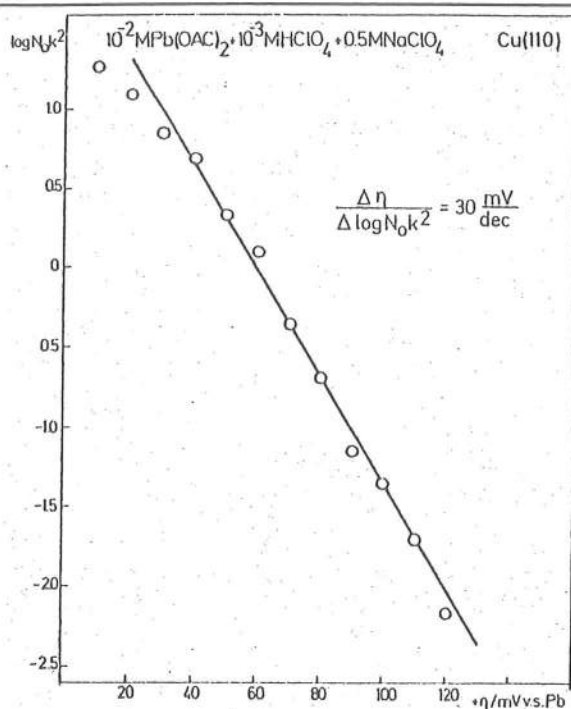


Figure 10. Plot of $\log N_0 k^2$ vs. potential, using data from deconvoluted transient.

Values of $(\log N_0 k^2)$ obtained from the slopes of the deconvoluted i-t transients (see Eq.(9) - Eq.(12))¹⁷ were plotted against potential. This produced a linear relationship, Fig. 10., with a slope of $(\Delta \eta / \Delta \log N_0 k^2) = 30 \text{ mV/decade}$, confirming charge transfer control over the deposition process (Eq.(11) and Eq.(12))¹⁸.

This, of course, was not the case in 10^{-4} M and 10^{-3} M lead solutions, where deposition control was taken over by planar diffusion, Fig. 11.

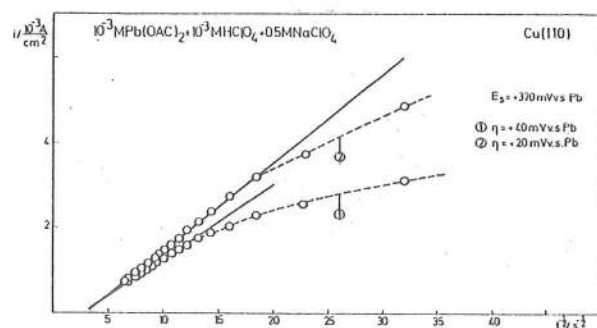


Figure 11. i vs. $t^{-1/2}$ plots for transients obtained from double potential step experiments using dilute solutions.

These results from potential step experiments might at first sight seem contradictory to the conclusions reached from the L.S.V. measurements⁸ i.e. that the UPD of lead on Cu(110) most probably involves a higher order phase transformation. Indeed, all data obtained by the analysis of the single pulse transients point to mechanism involving 2D instantaneous nucleation and growth controlled by charge transfer with the slow step at the edge of the growing centres.

However, it is possible for a higher order 2D phase transformation to be reflected in i-t transients with the characteristics just mentioned. A second order phase transformation, for example, is assumed to proceed through local density changes and their spreading throughout the entire system²².

If the front of such a local higher density region is approximated to an advancing boundary belonging to an irregularly-shaped 2D form, although by definition it is not sharp as in the case of a first order transformation, then the incorporation of the less dense neighbouring material into it will be linearly proportional to the supply of the material needed. Since material can be available only by charge transfer deposition, the process of spreading of the high-density patch will be reflected in a linear increase in the current with time due to the material being deposited onto the electrode surface.

The phenomenon of instantaneous nucleation in such a system can be explained as follows. Because of inhomogeneities in the substrate there will also be inhomogeneities and density variations in the epitaxial layer in addition to those produced by transient fluctuations. Therefore it is not difficult to imagine higher density areas within the UPD monolayer developing primarily at active sites, most probably dislocations, on the surface.

Such a process would give density and charge changes with potential as observed in Fig. 8.a.,b. and Fig. 9.

On this view, the result obtained from the single potential step experiments would be consistent with conclusions reached on the basis of the L.S.V. experiments⁸.

Going even further, both the L.S.V. and the potential step results put together would lead to the following explanation:

Lead UPD on the Cu(110) oriented electrode surface proceeds as a higher order transformation from the epitaxial structure proposed⁸, through density fluctuations initiated at active surface sites (most probably at dislocations of certain activity) and spreading over the entire surface finally yielding a higher-density, close-packed crystalline structure.

CONCLUSIONS

Results obtained by potential step experiments in the case of lead UPD on Cu(110) show that the kinetics of higher order transformations in 2D systems can be followed and investigated by electrochemical means.

The combined results obtained by L.S.V.⁸ and by potential step experiments lead to conclusion that:

a.- The UPD of lead on the Cu(110) oriented electrode surface most probably involves a higher-order, 2D-transformation process from the epitaxial close-packed layer⁸ into close-packed crystalline lead monolayer.

b.- The structure of the final UPD deposit is a close-packed lead monolayer probably distorted to a certain extent by the structure of the underlying copper surface.

c.- The UPD lead monolayer formation, in the case of copper(110) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

Acknowledgment

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REFERENCES

- 1.-Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 2.-Thomas, B., Bewick, A., J.Electroanal. Chem., 65 (1975) 911.
- 3.-Thomas, B., Bewick, A., J.Electroanal. Chem., 70 (1976) 239.
- 4.-Thomas, B., Bewick, A., J.Electroanal. Chem., 84 (1977) 127.
- 5.-Jovićević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 6.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 7.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 8.-Jovićević, J.N., Bewick, A., Univ. Thought, IV (2), in press, Pristina 1997.
- 9.-Jovićević, J.N., Bewick, A., Univ. of Prishtina (Serbia), Nat.Sci., this issue
- 10.-Bewick, A., Jovićević, J.N., Thomas, B., Trans. Faraday Disc., 12 (1977) 24
- 11.-Meits, L., "Polarographic Techniques", 2nd edition, Interscience, New York (1965).
- 12.-Pinner, R., Electroplating, October and November (1953) 360, 401.
- 13.-"Handbook of Chemistry and Physics", ed. R.Weast, 55th edition, Chemical Rubber co., Cleveland, (1974/75).
- 14.-Sillen, G., "Stability Constants of metal ion Complexes", Chem. Soc., Special publication No.25, (1971).
- 15.-Astley, D.J., Harrison, J.A., Thirsk, H.R., J. Electroanal. Chem., 19(1968)325
- 16.-Delahay, P., Trachtenberg, I., J. Am. Chem. Soc., 79 (1957) 2355
- 17.-Jovićević, J.N., Bewick, A., Univ. Thought, this issue, Pristina 1997.
- 18.-Harrison, J.A., Thirsk, H.R.: Vol.5, p.p.67, "Electroanalytical Chemistry", ed. Bard, A.J., Marcela Decker Inc., New York (1971).
- 19.-Fleischmann, M., Thirsk, H.R.: Vol. 3, "Advances in electrochemistry and electrochemical engineering", ed. Delahay, P. and Tobias, C.W., Interscience, London (1963).
- 20.-Fleischmann, M., Thirsk, H.R., Electorchim. Acta, 2 (1960) 22, 9 (1964) 757.
- 21.-Pattison, J., Ph.D. Thesis, University of Durham (1963).
- 22.-Hannay, H.B., ed. "Treatise on Solid State Chemistry", Vol.5, "Changes of State", Plenum Press, New York (1975).

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTOTALOŽENJA OLOVA NA BAKRU - V DIO.
REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTOTALOŽENJE PRI POTENCIJALIMA POZITIVNIJIM OD REVERZIBILNOG NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (110)

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000 Priština, Jugoslavija

Ovo je peti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova (iz acetatnih, nitratnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene potenciostatskom metodom jednostrukog, dvostrukog i trostrukog pulsa na monokristalnoj elektrodi površinske kristalografke orijentacije (110) u području potencijala pozitivnijih od reverzibilnog potencijala olova u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Različiti upotrebljeni anjoni ne utiču značajnije na karakteristike eksperimentalno dobijenih podataka.

Rezultati dobijeni cikličkom voltametrijom ranije^{7-10,12}, a posebno rezultati prikazani u ovome radu dobijeni potenciostatskom pulsnom metodom omogućuju slijedeće zaključke:

- elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog u ispitivanim rastvorima na monokristalnim površinama bakra kristalografke orijentacije (110) je aktivaciono kontrolisan proces koji najvjerovatnije uključuje i proces dvodimenzione transformacije višeg reda iz epitaksijalnog najgušće pakovanog u gustopakovani kristalni monosloj olova;
- stuktura tog finalnog taloga je gustopakovani olovni monosloj vjerovatno djelomično izobličen

strukturom bakarne podloge kristalografske orijentacije (110);

- u slučaju bakarne podloge kristalografske orijentacije (110) elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog predstavlja neizostavnu predhodnicu debljim talozima olova i ima značajan uticaj na započinjanje elektrotaloženja pri katodnim prenapetostima.

Navedene zaključke potvrđuje "adsorpciona izoterma" dobijena iz potencijostatskih podataka elektrotaloženja olova pri potencijalima pozitivnijim od reverzibilnog i analiza rastućih strujnih odgovora na potencijostatske pulseva karakterističnih za procese transformacije višeg reda u dvodimenzionim fazama.

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A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART VI. The Potential Step Results: Underpotential Deposition on (100) oriented Copper Single Crystal Electrode

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The underpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper (100) electrodes from acetate, nitrate and perchlorate solutions have been investigated using single and double potential step techniques.

It appeared that the different anions used did not change the current-time responses characteristics significantly.

Results obtained by potential step experiments in the case of lead UPD on Cu(100) show that the kinetics of higher order transformations in 2D systems can be followed and investigated by electrochemical means.

The combined results obtained by L.S.V.⁹ and by potential step experiments lead to conclusion that:

a.- The UPD of lead on the Cu(100) oriented electrode surface appears to be a higher-order

2D-transformation proceeding from a less dense superlattice structure into a crystalline monolayer of much higher density.

b.- The final structure of the lead monolayer appears to be the closest-packed epitaxial lattice of the form proposed earlier⁹.

c.- The UPD lead monolayer formation, in the case of copper(100) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

The above conclusions are supported by the "adsorption isotherm" evaluated from the potentiostatic underpotential deposition data and analysis of the growth transients at constant potential which showed behaviour characteristic of higher order 2D phase transformation processes.

Key words: Underpotential deposition, Potentiostatic step, Cu, Pb, Phase formation, Single crystal

INTRODUCTION

Despite extensive studies of metal underpotential deposition¹⁻¹², there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was lead on copper (111), (110) and (100) oriented single crystal surfaces. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrates possess high hydrogen evolution overvoltage and therefore hydrogen co-adsorption processes do not complicate deposition of lead.

Linear sweep voltammetry^{1-9,12}, however carefully and successfully performed, is not sufficiently diagnostic tool to characterize underpotential monolayers and the possible phase changes taking part within them. Therefore help from potential step techniques, which are known to provide clear information on the mechanism of phase formation, was required. The analysis of the current against time transients, observed after initiating phase formation at constant potential using a potential step should yield additional data on the formation of 2D phase films during UPD.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorized can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} Acm $^{-2}$) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a preset number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location, so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will in-

crease linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, $(SN)_n$, is given by $(SN)_n = n^{1/2}$. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig.1. a) and b). The cell given in Fig.1.a) was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc ≈ 1.5 cm 2 in area, positioned parallel to the working electrode.

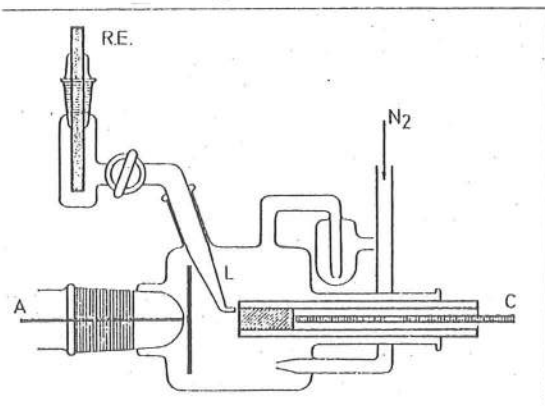


Figure. 1.a. The cell used for most of the L.S.V. and potential step experiments.

The cell in Fig.1.b) was used for potential step experiments controlled by potentiometers. This cell was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area 4.5cm 2 ; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin (cm) teflon foil.

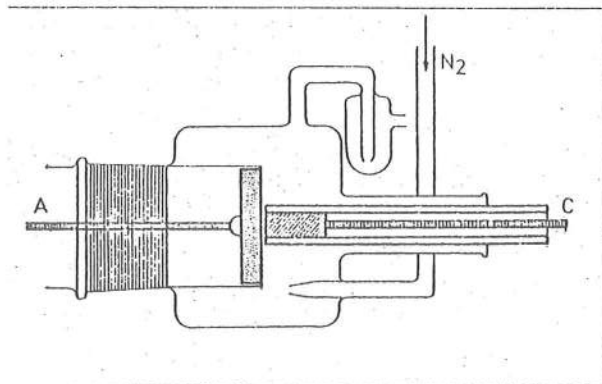


Figure. 1.b. The cell used for potential step experiments on very long timescale.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%)

≈ 0.8 cm in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25\text{g}$, of amalgamated zinc¹³.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}\text{cm}$ and $3 \cdot 10^{-4}\text{cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}\text{cm}$ and $3 \cdot 10^{-5}\text{cm}$ grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere^{9,14}.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C , and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation⁷⁻¹².

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell scaled with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by

tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the length of the deposition one, to ensure steady state conditions.

The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two preset potentials. The cell current was monitored with a battery driven Current picoammeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

Copper single crystal with (100) oriented surface, was examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:

$xM Pb(OAc)_2 + 10^{-2}M HOAc + 0.5M NaOAc$ $10^{-4}M \leq x \leq 10^{-1}M$
 $xM PbO + 10^{-3}M HClO_4 + 0.5M NaClO_4$ $10^{-3}M \leq x \leq 10^{-1}M$
 $xM Pb(OAc)_2 + 10^{-3}M HClO_4 + 0.5M NaClO_4$ $10^{-4}M \leq x \leq 10^{-1}M$
 $xM Pb(OAc)_2 + 10^{-3}M HClO_4 + 0.5M NaNO_3$ $10^{-3}M \leq x \leq 10^{-1}M$

This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD.

The composition and pH of the solutions used was decided on the basis of knowledge gathered on the subject^{15,16}. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2 - 5.5), and in such a situation:



Therefore:

$$E_{Pb/PbO} = -819 + 29.5 \log \frac{1}{[OH^-]^2}$$

which for different pH yields:

pH = 7	$E_{Pb/PbO} = -406mV \text{ vs. S.C.E.}$
pH = 5.4	$E_{Pb/PbO} = -312mV \text{ vs. S.C.E.}$
pH = 3	$E_{Pb/PbO} = -170mV \text{ vs. S.C.E.}$

The potential region in which lead UPD is observed in $10^{-3}M$ lead solution on copper spans approximately between -240 and -340mV vs. S.C.E. provided that $a_{Pb^{+2}} = [Pb^{+2}]$. Solutions were acidified to pH = 2 - 3 in order to push the potential $E_{Pb/PbO}$ sufficiently anodic to the UPD potential region of investigation, thus assuring conditions with no interference from PbO formation.

The single potential step results

After L.S.V. had been recorded the potential of the working electrode was changed in a step from the starting value, E_s , to a new value, η , in the region of UPD as indicated by the beginning of the voltammetric peak and the onset of bulk deposition (see Fig. 2.). Single potential steps applied in the region of lead UPD on the Cu(100) surface produced i-t transients typically of the form given in Fig. 2.

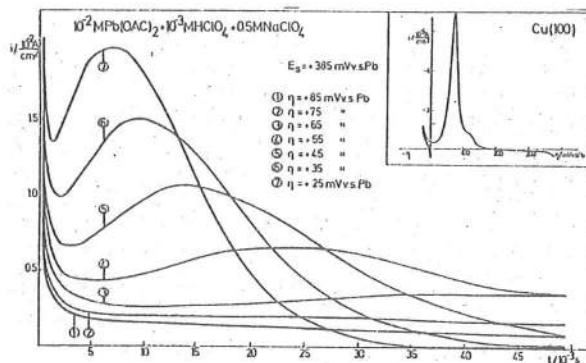


Figure 2. Current-time responses to single potential steps applied in lead UPD.

The double potential step results

Double potential step experiments using values of η_1 at the beginning of the first voltammetric peak and of a short duration, helped little to obtain better defined rising transients in the second pulse, η_2 , Fig. 3., a. and b. However, when η_1 and τ_1 were increased, the i-t transients in the second pulse showed clear characteristics of phase formation, Fig. 4. As in the case of similar experiments performed on Cu(110)¹¹, this seems to be a good way to separate, to a certain extent, the two processes taking part in lead UPD on Cu(100), adsorption leading to a superlattice structure (mainly during the first pulse) and phase formation leading to a full crystalline monolayer (mainly in the second pulse).

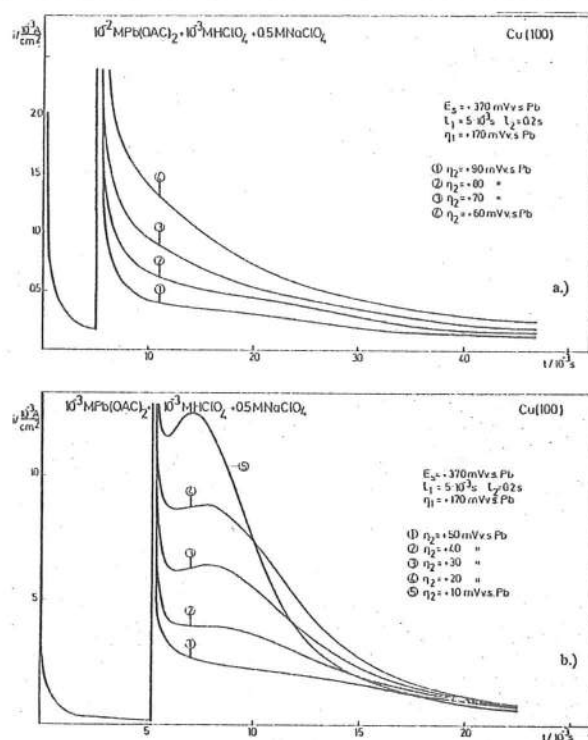


Figure 3. Current-time transients for double potential steps.

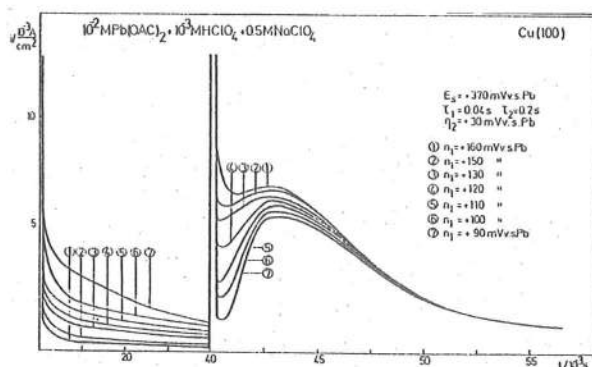
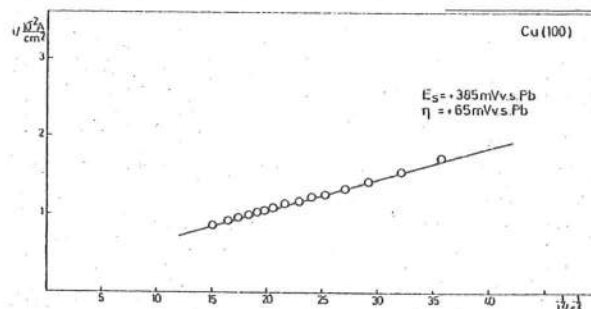


Figure 4. Current-time transients for double potential steps.

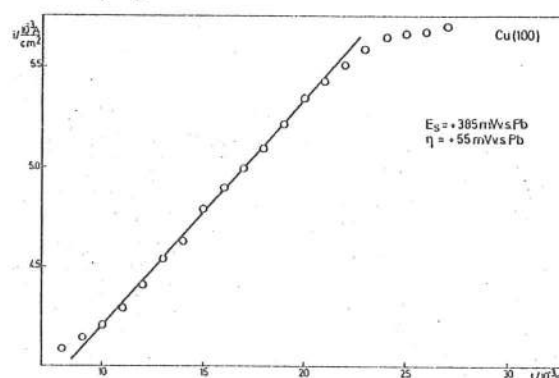
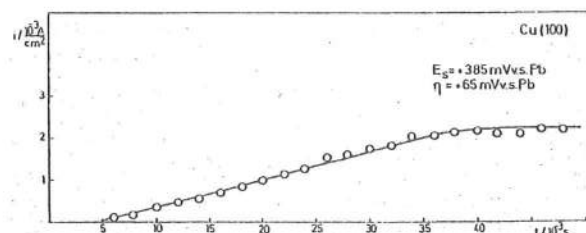
DISCUSSION

If the potential of the pulse, E_s , was in the region of the L.S.V. peak more anodic than the peak potential K_2 , then monotonously falling i - t transients were obtained. The charge passed increased as the potential was made more cathodic. The charge reached a limiting value, approximately $282 \cdot 10^{-6} \text{ As cm}^{-2}$ and close to that needed for the deposition of the full monolayer recorded in the L.S.V. experiments ($276 \cdot 10^{-6} \text{ As cm}^{-2}$) only when η was equal to or more cathodic than K_2 . Rising portions of the transients indicate a nucleative, two-dimensional phase formation process.

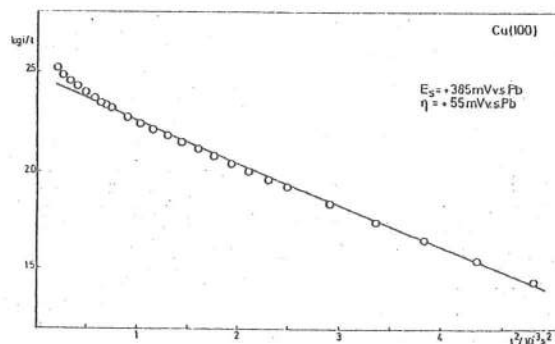
Analysis of the monotonously falling current versus time transients showed a linear relationship between i and $t^{-1/2}$ (Eq. (6))^{10,18}. This is most simply accounted for by diffusion controlled random adsorption of lead species onto favorable sites¹⁷, Fig. 5.

Figure 5. Plot of i versus $t^{-1/2}$ for i - t transient number 3 in Fig. 2.

An indication that the rising portions of the original i - t transients might be linear, Fig. 6.a., was confirmed by the analysis performed on the deconvoluted transients, Fig. 6. b.

Figure 6.a. Enlarged rising portion of i - t transient number 3 in Fig. 2.Figure 6.b. Enlarged rising portion of the deconvoluted i - t transient number 3 in Fig. 2.

The original transients were also plotted as $\log(i/t)$ vs. t^2 as in Fig. 7. These were approximately linear but the linearity was even better for the deconvoluted transients.

Figure 7. Plot of $\log(i/t)$ vs. t^2 for i - t transient number 3 in Fig. 2.

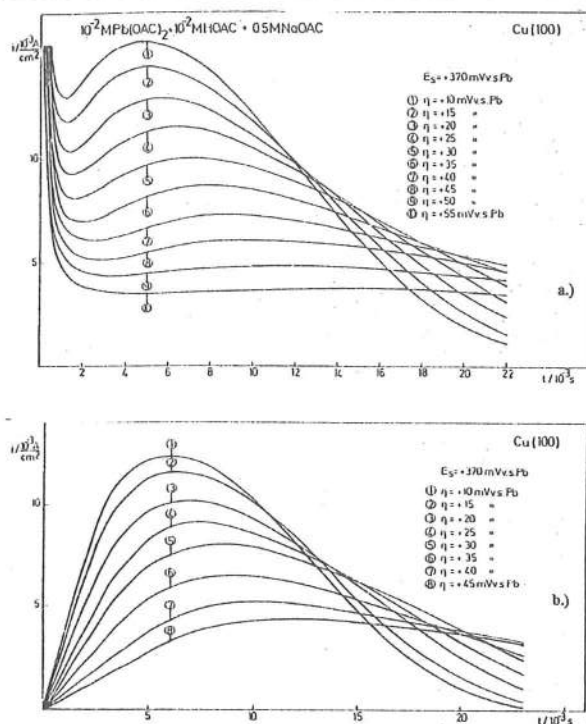


Figure 8. The originally recorded a.) and the deconvoluted b.) *i*-*t* transients for single potential steps.

The set of deconvoluted transients (Fig. 8.a., b.) was analyzed about the maxima (Eq. (7) and (8)^{11,19}). These plots give values for density of the layer which vary greatly with potential, Fig. 9.

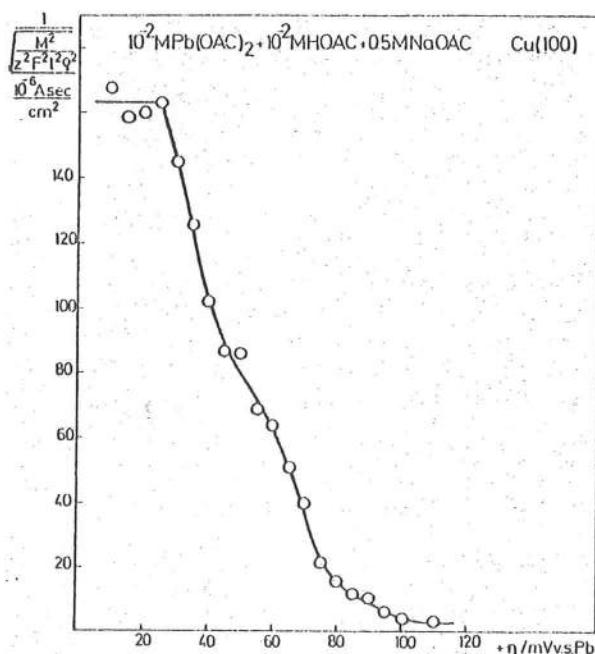


Figure 9. Monolayer charge and density change with potential obtained from analysis around the maxima of the *i*-*t* transients.

The slopes of the rising portion of the deconvoluted transients were used to evaluate $N_0 k_2$. The plot of $\log(N_0 k_2)$ vs. η (see Eq. (3) - (8), using $Q_{(100)} = 234 \cdot 10^{-6} \text{ As cm}^{-2}$, gave a linear relationship with a slope of 30 mV/decade, Fig. 10.

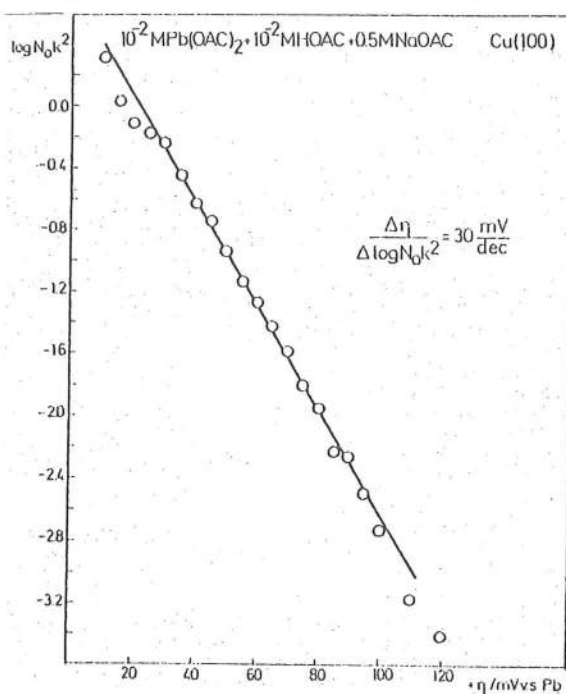


Figure 10. Plots of $\log N_0 k_2^2$ vs. potential obtained from deconvoluted transients.

Comparison with the results obtained in the same system from L.S.V. experiments⁹, Fig. 5 and Fig. 6., shows that the charge at the constant portion of Fig. 9., ($164 \cdot 10^{-6} \text{ As cm}^{-2}$), is in good agreement with the charge of the second voltammetric peak, K_2 , ($180 \cdot 10^{-6} \text{ As cm}^{-2}$). The data of Fig. 9. Shows a continuous increase in the monolayer density with potential, starting from the potentials region of the first L.S.V. peak, K_1 , until potentials near the end of the second voltammetric peak, K_2 , when it becomes constant. The shape of this function suggests a continuous phase transformation from a structure of relatively small density into a structure of higher constant density.

By comparison with the results and analysis already given for deposition on the (111)^{7,10} and (110)^{8,11} substrates, it can be concluded that the data given above is due to a higher order 2D phase transformation. The superlattice adsorbed structure, proposed⁹ in Fig. 5. (position A occupied by lead particles) transforms, through locally initiated higher density fluctuations²⁰ (most probably induces at active surface sites produced by dislocations) after the supply of material needed is secured by charge transfer controlled reaction, into 2D epitaxially closest-packed lead monolayer proposed⁹. The increase in the density and the amounts of additional material needed to produce the crystalline epitaxial structure can be followed by the relationship given in Fig. 9.

Single potential step experiments performed in 10^{-3} M Lead solutions yielded monotonously falling *i*-*t* functions, Fig. 11., which gave linear plots of *i* versus $t^{-1/2}$ showing once more that the kinetics of lead UPD on Cu(100) is fast enough to run into planar diffusion control¹⁸ relatively soon in diluted lead solutions.

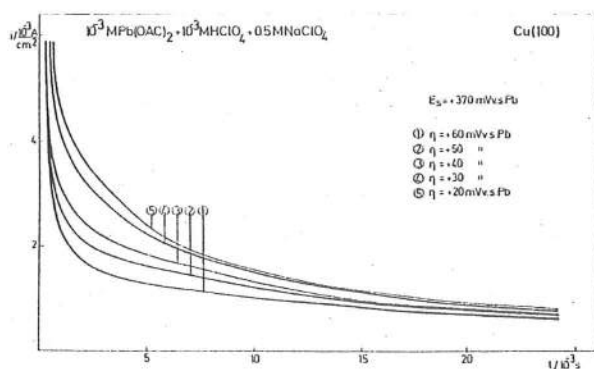


Figure. 11. Current-time transients for single potential steps in diluted lead solutions.

CONCLUSIONS

Results obtained by potential step experiments in the case of lead UPD on Cu(100) show that the kinetics of higher order transformations in 2D systems can be followed and investigated by electrochemical means.

The combined results obtained by L.S.V.⁹ and by potential step experiments lead to conclusion that:

a.- The UPD of lead on the Cu(100) oriented electrode surface appears to be a higher-order 2D-transformation proceeding from a less dense superlattice structure into a crystalline monolayer of much higher density.

b.- The final structure of the lead monolayer appears to be the closest-packed epitaxial lattice of the form proposed earlier⁹.

c.- The UPD lead monolayer formation, in the case of copper(100) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

Acknowledgment

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REFERENCES

- 1.-Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 2.-Thomas, B., Bewick, A., J. Electroanal. Chem., 65 (1975) 911.
- 3.- Thomas, B., Bewick, A., J. Electroanal. Chem., 70 (1976) 239.
- 4.-Thomas, B., Bewick, A., J. Electroanal. Chem., 84 (1977) 127.
- 5.- Jovićević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 6.-Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.

7.-Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.

8.-Jovićević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.

9.-Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.

10.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.

11.- Jovićević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.

12.- Bewick, A., Jovićević, J.N., Thomas, B., Trans. Faraday Disc., 12 (1977) 24

13.-Meits, L., "Polarographic Techniques", 2nd edition, Interscience, New York (1965).

14.-Pinner, R., Electroplating, October and November (1953) 360, 401.

15.- "Handbook of Chemistry and Physics", ed. R.Weast, 55th edition, Chemical Rubber co., Cleveland, (1974/75).

16.- Sillen, G., "Stability Constants of metal ion Complexes", Chem. Soc., Special publication No.25, (1971).

17.-Delahay, P., Trachtenberg, I., J. Am. Chem. Soc., 79 (1957) 2355

18.-Astley, D.J., Harrison, J.A., Thirsk, H.R., J. Electroanal. Chem., 19(1968)325

19.- Pattison, J., Ph.D. Thesis, University of Durham (1963).

20.-Hannay, H.B., ed. "Treatise on Solid State Chemistry", Vol.5, "Changes of State", Plenum Press, New York (1975).

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTOTALOŽENJA OLOVA NA BAKRU - VI DIO.

REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTOTALOŽNJE PRI POTENCIJALIMA POZITIVNIJIM OD REVERZIBILNOG NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (100)

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000 Priština, Jugoslavija

Ovo je šesti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova (iz acetatnih, nitratnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene potenciostat-skom metodom jednostrukog, dvostrukog i trostrukog pulsa na monokristalnoj elektrodi površinske kristalografke orijentacije (100) u području potencijala pozitivnijih od reverzibilnog potencijala olova u datoj sredini.

Još jednom se uvjerljivo pokazalo da je pažljivo i uspješno poliranje površine radne elektrode od najvećeg značaja pri ispitivanjima područja potencijala pozitivnijih od reverzibilnog potencijala taloženja/rastvaranja ispitivanog metala, ukoliko se žele dobiti pouzdani kvantitativni i kvalitativni podaci.

Različiti upotrebljeni anjoni ne utiču značajnije na karakteristike eksperimentalno dobijenih podataka.

Rezultati dobijeni cikličkom voltametrijom ranije^{1-9,12}, a posebno rezultati prikazani u ovome radu dobijeni potenciostatskom pulsnom metodom omogućuju slijedeće zaključke:

- elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog u ispitivanim rastvorima na monokristalnim površinama bakra kristalografske orijentacije (100) je aktivaciono kontrolisan proces koji najvjerojatnije uključuje i proces dvodimenzionalne transformacije višeg reda iz epitaksijalnog manje gustog sloja ranije predložene superstrukture⁹ u gustopak-

ovani epitaksijalni mnogo gušći kristalni monosloj olova;

- struktura tog finalnog taloga je gustopakovani epitaksijalni olovni monosloj vjerovatno djelomično izobličen strukturom bakarne podloge kristalografske orijentacije (100);

- u slučaju bakarne podloge kristalografske orijentacije (100) elektrotaloženje olova pri potencijalima pozitivnijim od reverzibilnog predstavlja neizostavnu predhodnicu debljim talozima olova i ima značajan uticaj na započinjanje elektrotaloženja pri katodnim prenapetostima.

Navedene zaključke potvrđuje "adsorpciona izoterma" dobijena iz potenciostatskih podataka elektrotaloženja olova pri potencijalima pozitivnijim od reverzibilnog i analiza rastućih strujnih odgovora na potenciostatske pulseve karakterističnih za procese transformacije višeg reda u dvodimenzionalnim fazama.

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A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART VII. The Potential Step Results: Overpotential Deposition on (111), (110) and (100) oriented Copper Single Crystal Electrode

Jovan N. JOVIĆEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Present address: Chemistry Department, Faculty of Natural Sciences & Mathematics, University of Prishtina, 38000 Prishtina, Yugoslavia

ABSTRACT

The overpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper (111), (110) and (100) electrode from acetate, nitrate and perchlorate solutions have been investigated using single, double and triple potential step techniques.

It appeared that the different anions used did not change the current-time responses characteristics significantly.

The UPD lead monolayer formation, in the case of copper (111), (110) and (100) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

The charge corresponding to the UPD monolayer of lead ($\approx 280 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(111), $\approx 340 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(110) and $\approx 300 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(100) oriented substrate) was observed under the very initial fall-off seen on the current-time transients obtained at very short times, pre-

ceding the current-time relationships for the overpotential deposition.

Indication of a rising *i-t* transient reflecting bulk lead deposition on Cu(111) were usually observed at $\eta = -6 \text{ mV vs. Pb}$ (some carefully prepared experiments revealed that overpotentials of $\eta = -4 \text{ mV vs. Pb}$ and $\eta = -5 \text{ mV vs. Pb}$ could produce the same results), in the case of the Cu(100) electrode, it was $\eta_2 = -6 \text{ mV vs. Pb}$, while an overpotential of $\eta_2 = -6 \text{ mV vs. Pb}$ was needed for similar effects on Cu(110).

The observed *i* vs. t^2 linearity corresponds to 3D instantaneous nucleation of lead on top of the previously formed UPD monolayers and the further growth of the 3D centres. The results show no appreciable 3D nucleation occurring until the monolayer is completed. The very small 3D nucleation overpotentials recorded, varying in the order $\eta(111) \leq \eta(100) \leq \eta(110)$ must be due to the influence of these layers.

Key words: Overpotential deposition, Potentiostatic step, Cu, Pb, Phase formation, Single crystal

INTRODUCTION

The history of electrochemical metal deposition is no younger than the history of electrochemistry. It was a subject of theoretical as well as experimental research as early as 1834¹. Nevertheless, explanations for many of the phenomena involved are still not available. This is still particularly true for the deposition of metals on foreign substrates, where only relatively recently the phenomenon of a deposition occurring at more positive potentials than that of the bulk of the deposited metal/metal ion electrode - underpotential deposition has been closely investigated.

The knowledge gathered about metal deposition so far strongly suggests that the deposition of a metal on a similar substrate and on a dissimilar substrate, although having many features in common, does ex-

hibit important differences. Nevertheless, an electrodeposition process could be divided basically into two parts^{2,12}:

- adatom formation,
- phase formation and electrocrystallization.

An adatom formation process includes:

a) transport of a solvated cation from the bulk of the electrolyte to the electrode/electrolyte interfacial boundary^{2,9,12},

b) charge exchange between the electrode and the cation (reduction), accompanied by partial desolvation of the ion^{2,3,7,13}. This provides an almost neutral and partly desolvated particle adsorbed at the electrode surface (adatom or adion) and able to move laterally over the surface.

Phase formation and electrocrystallization include incorporation of adatoms (adions) into already existing crystal lattice, or their gathering together to form nuclei of a new crystal lattice^{3,7,8,11-17}.

In reality, these two main groups of processes are so interdependent and mixed in time that it is very difficult to separate, evaluate and follow their individual contributions to the overall process.

Despite extensive studies of metal underpotential deposition there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was lead on vitreous carbon. The underpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrate possesses high hydrogen evolution overvoltage and therefore hydrogen co-adsorption processes do not complicate deposition of lead.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator (type R.B.1), or two "H. Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorized can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} Acm⁻²) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a preset number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location, so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will increase linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, (SN)_n, is given by (SN)_n=n^{1/2}. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig. 1. a) and b). The cell given in Fig. 1. a) was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mesh disc ≈1.5 cm² in area, positioned parallel to the working electrode.

The cell in Fig. 1. b) was used for potential step experiments controlled by potentiometers. This cell was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area 4.5cm²; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin (1·10⁻⁴ cm) teflon foil.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) ≈0.8cm in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure

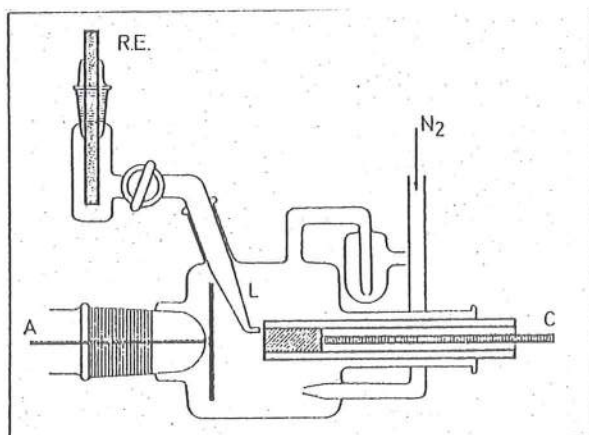


Figure 1.a. The cell used for most of the L.S.V. and potential step experiments.

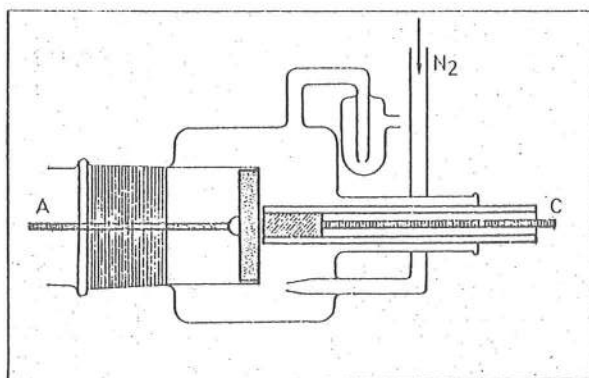


Figure 1.b. The cell used for potential step experiments on a very long timescale.

that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) sealed into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulfuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of KMnO_4 and then from solution containing a trace amount of ortho- H_3PO_4 .

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 min-

utes. Nitrogen was purified by purging it through a solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx 25\text{g}$, of amalgamated zinc¹⁸.

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvy cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}\text{ cm}$ and $3 \cdot 10^{-4}\text{ cm}$ grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}\text{ cm}$ and $3 \cdot 10^{-5}\text{ cm}$ grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewhere¹⁹.

The (111) oriented single crystal was immersed for 3 seconds in the acid mixture heated to over 75°C while stirring, left without stirring for another 3 seconds, then stirred and again left still for 3 seconds, finally the solution was stirred, the electrode removed and washed under a strong stream of tap water and eventually in triply distilled water. The whole procedure was repeated a second time. Then the electrode would be immersed in 30 vol.% solution of orthophosphoric acid and stirred for 10 seconds, washed in tap water and finally with plenty of triply distilled water. If gas evolution occurred on the electrode immersed in the polishing mixture earlier than 3 seconds, then the time which the electrode spent standing still was made shorter.

The (110) oriented single crystal was immersed in the acid mixture heated to 65°C , alternately standing still and stirred every 4 seconds for 4 times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) orientation.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C , and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectrosc-

copy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarized at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell sealed with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarizing the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the

length of the deposition one, to ensure steady state conditions.

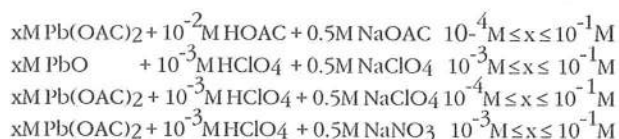
The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two preset potentials. The cell current was monitored with a battery driven Current picoammeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

Copper single crystals with (111), (110) and (100) oriented surfaces, were examined in solutions containing three different anions (perchlorate, acetate and nitrate), and four different lead concentrations:



This relatively wide variation in solution composition and concentration was necessary to understand all the variables affecting the UPD and OPD interdependence.

The composition and pH of the solutions used was decided on the basis of knowledge gathered on the subject^{1,18,19,42}. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2 - 5.5), and in such a situation:



Therefore:

$$E_{\text{Pb/PbO}} = -819 + 29.5 \log \frac{1}{[\text{OH}^-]^2}$$

which for different pH yields:

pH = 7	$E_{\text{Pb/PbO}} = -406\text{mV vs. S.C.E.}$
pH = 5.4	$E_{\text{Pb/PbO}} = -312\text{mV vs. S.C.E.}$
pH = 3	$E_{\text{Pb/PbO}} = -170\text{mV vs. S.C.E.}$

The potential region in which lead UPD is observed in 10^{-3} M lead solution on copper spans approximately between -240 and -340 mV vs. S.C.E (provided that $a_{Pb^{+2}} = [Pb^{+2}]$). Solutions were acidified to pH = 2 - 3 in order to push the potential $E_{Pb/PbO}$ sufficiently anodic to the UPD potential region of investigation, thus assuring conditions with no interference from PbO formation.

Single, double and triple potential steps were used on copper single crystal electrodes in an attempt to examine the possible interdependence between the underpotential deposition (UPD) and the overpotential deposition (OPD) of lead.

In the single potential step experiments the working electrode potential was changed from a starting value, E_s , well anodic to the UPD monolayer formation potential, to an overpotential value, η_1 , sufficiently cathodic to induce and sustain overpotential lead deposition.

Double potential steps involved a potential change from E_s anodic to the lead UPD region to the reversible bulk potential, η_1 , (or a little anodic to it) followed by step from η_1 to η_2 entering the overpotential region of lead bulk deposition.

The triple potential step usually consisted of three pulses:

1.- A potential step from E_s to a value η_1 as in the double step method.

2.- A nucleation overpotential step, η_2 , of duration, τ_1 .

3.- A growth pulse, η_3 , less cathodic than η_2 but high enough to preserve the growth of nuclei formed during the previous nucleation pulse.

Virtually the same shaped current-time transients were obtained when single or double potential steps

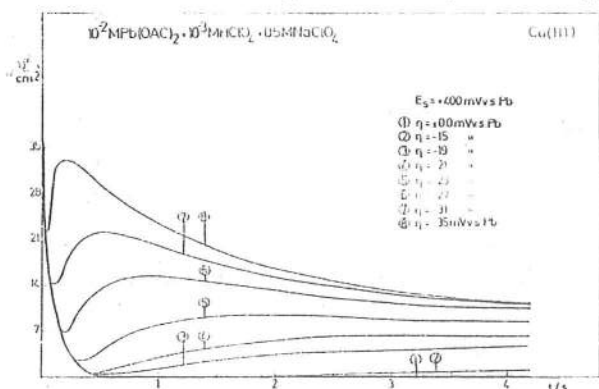


Figure 2.a. Current-time transients for single potential steps.

were applied, Fig. 2.a. and b. respectively.

In the first case, the monolayer charge of about $280 \cdot 10^{-6} \text{ As cm}^{-2}$ (for the Cu(111) oriented substrate²¹) was provided by the very initial fall-off seen on the current-time transients obtained at very short times.

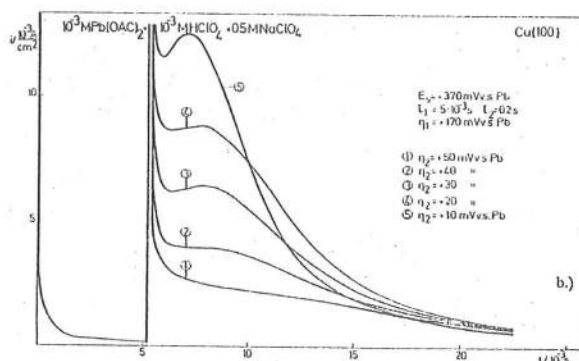


Figure 2.b. Current-time responses to double potential steps.

In the second case, approximately the same charge (corresponding to the UPD of lead) could be observed under the i - t transient, preceding the current-time relationships for the overpotential deposition.

The same was true for the other two substrate orientations, except that the initial charge would match that required for the UPD monolayer formation on the corresponding surface ($\approx 340 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(110)²² and $\approx 300 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(100)²³).

The characteristics of these i - t transients did not change significantly when different lead concentrations or different anions were used, Fig. 3.a. and b. Of course, the planar diffusion controlled plateau current was reached earlier in the case of the less concentrated solutions.

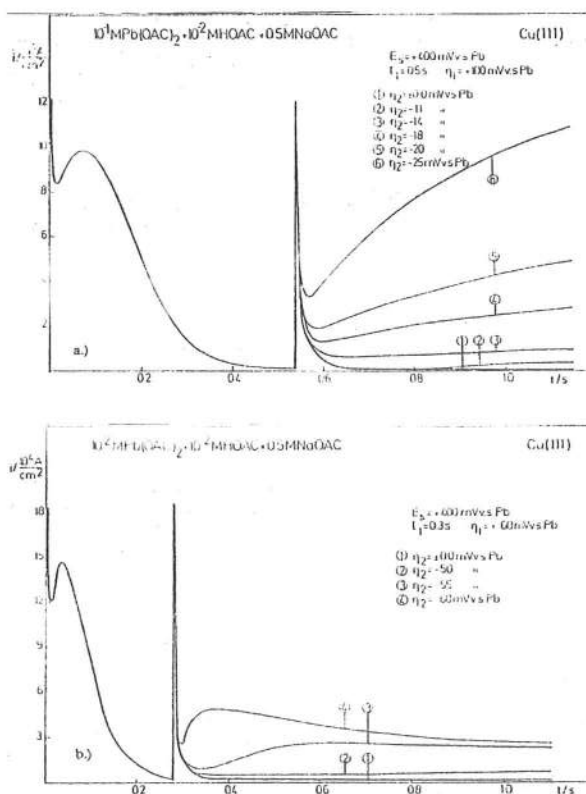


Figure 3. Current-time transients obtained from double pulse experiments.

Single and double potential step experiments on all three of the single crystals yielded relatively fast rising *i-t* transients of the same shape, once a certain characteristic overpotential had been overcome, Fig. 4.a, b. and c.

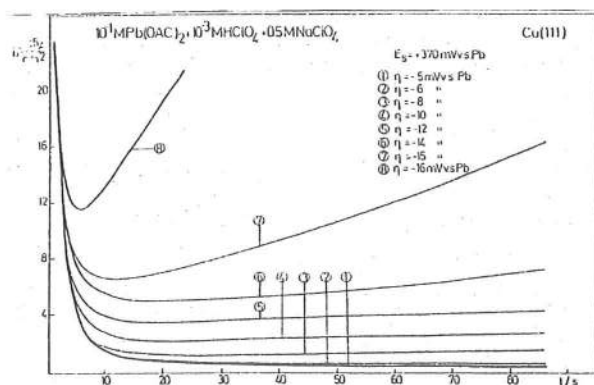


Figure 4.a. Current-time transients for single potential steps.

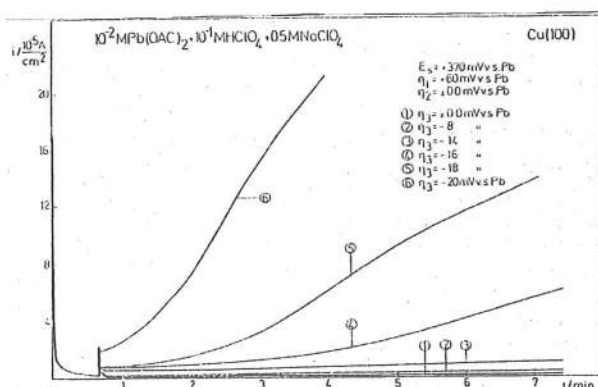


Figure 4.b. Current-time transients for triple potential steps.

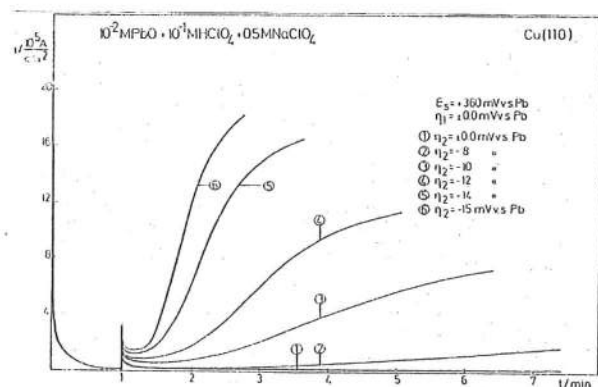


Figure 4.c. Current-time transients for double potential steps.

When the current-time relationships for long overpotential deposition pulses were recorded on a more sensitive current setting, they revealed that the bulk deposition commences at very low overpotentials²⁴⁻²⁸ on all three copper substrates (-4 to -6 mV vs. Pb), Fig. 5.a, b. and c.

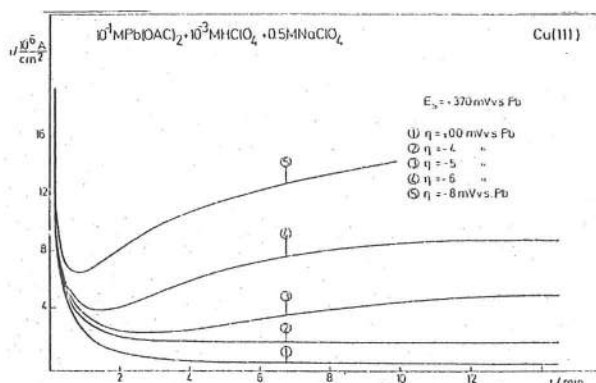


Figure 5.a. Current-time transients for single potential steps.

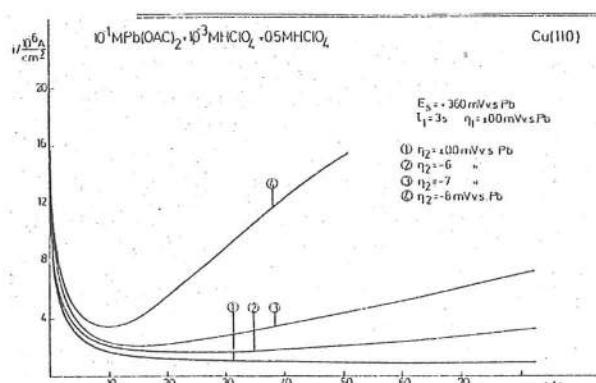


Figure 5.b. Current-time transients for double potential steps.

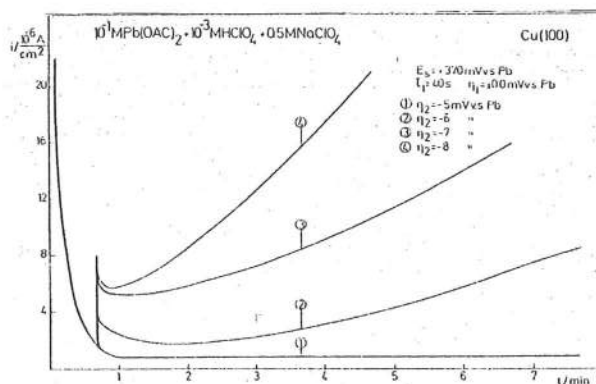


Figure 5.c. Current-time transients for double potential steps.

The triple potential step experiments strengthened this conclusion. On the (111) and (100) oriented substrates a nucleation pulse $\eta_{2(111)} = -8$ mV vs. Pb and $\eta_{2(100)} = -10$ mV vs. Pb lasting $\tau_{1(111)} = 0.3$ s and $\tau_{1(100)} = 0.3$ s, were enough to enable the formation of small number of nuclei capable of growing further at only $\eta_{3(111)} = -3$ mV vs. Pb and $\eta_{3(100)} = -4$ mV vs. Pb (Fig. 6.a. and b.). At the same time, a nucleation overpotential $\eta_{2(110)} = -10$ mV vs. Pb for only a slightly longer time, $\tau_{1(110)} = 1$ s, was needed to produce the same effect for a growth pulse $\eta_{3(110)} = -5$ mV vs. Pb on the (110) oriented copper substrate, Fig. 6.c.

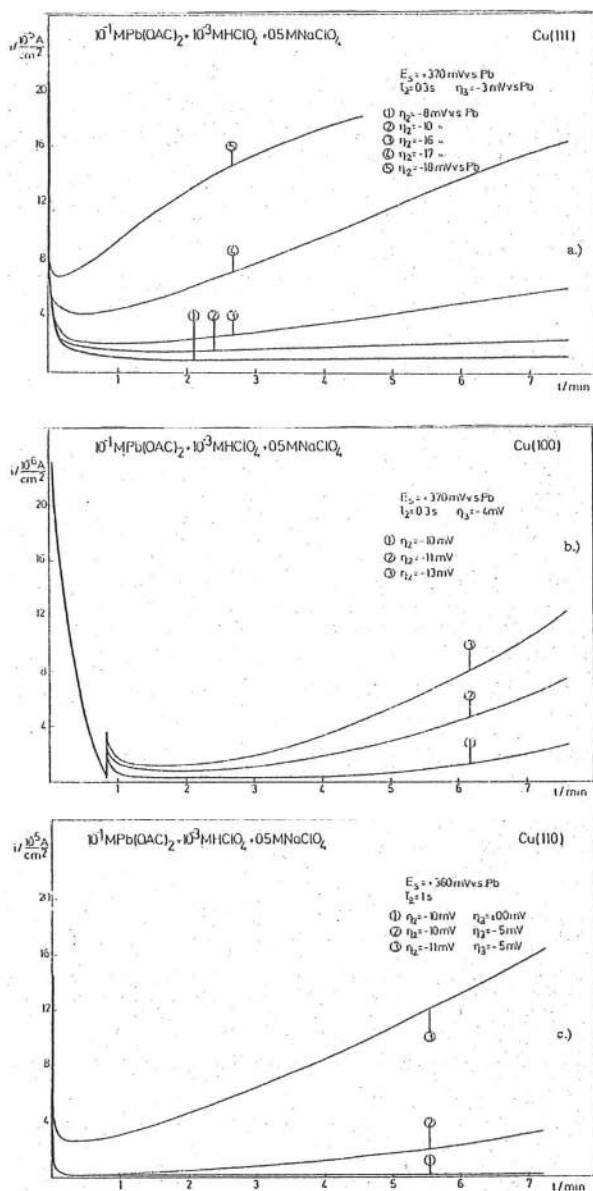


Figure 6. Current-time transients for triple potential steps.

At a constant value of the nucleation pulse amplitude, τ_1 , an increase in its duration, η_1 , produced an increase in the growth currents, Fig. 7. As did an increase in the growth potential.

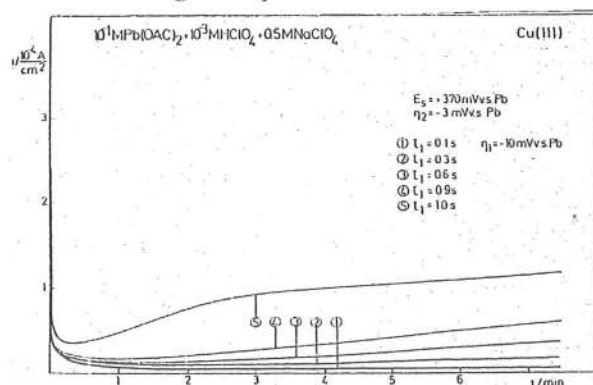


Figure 7. Current-time transients for triple potential steps when the duration of the nucleation pulse (τ_1) was changed.

Generally speaking, with overpotential values ranging between zero and the nucleation overpotential characteristic of each surface examined, a small finite background current could be observed, but this did not rise with time within the observation period (up to 60 min).

All current-time transients were found to be very sensitive to small changes in overpotential: an increase of 1 mV in overpotential causes the gradient to increase by factor of 2-3, 5 and 8 for (100), (111) and (110) oriented substrates, respectively.

Indication of a rising i - t transient reflecting bulk lead deposition on Cu(111) were usually observed at $\eta = -6$ mV vs Pb, Fig. 4.a., although some carefully prepared experiments revealed that overpotentials of $\eta = -4$ mV vs Pb and $\eta = -5$ mV vs Pb could produce the same results.

In the case of the Cu(100) electrode, it was found that $\eta = -6$ mV vs Pb is usually a sufficiently high overpotential to provoke lead bulk deposition, Fig. 5.c., while an overpotential of $\eta = -6$ mV vs Pb was needed for similar effects on Cu(110), Fig. 5.b.

DISCUSSION

The analysis of the i - t transients due to single and double potential steps, Fig. 2. to Fig. 4., yielded linear plots for i vs. t^2 , Fig. 8.a. and b. The same type of linearity was obtained for the current-time responses to triple pulse experiments, Fig. 9. a., b. and c.

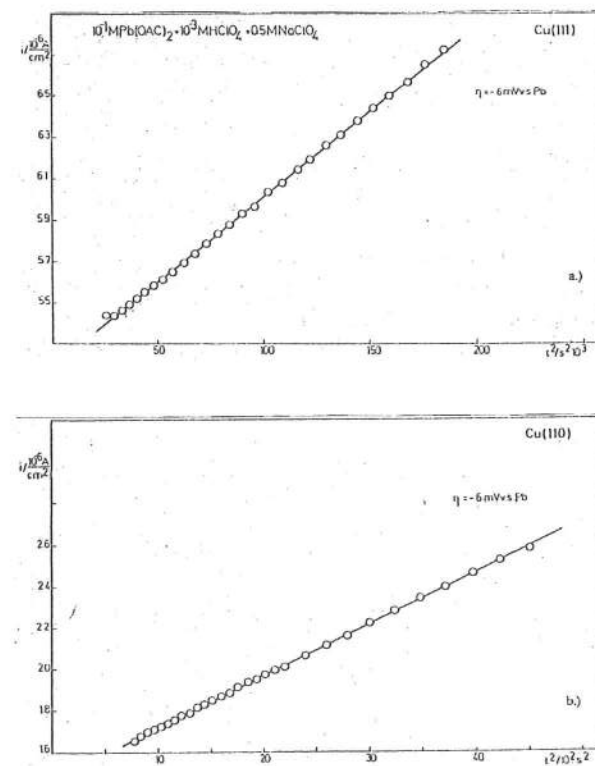


Figure 8. The i vs t^2 relationship obtained from the experimental current-time transients in Figure 5.a. and 5.b., respectively.

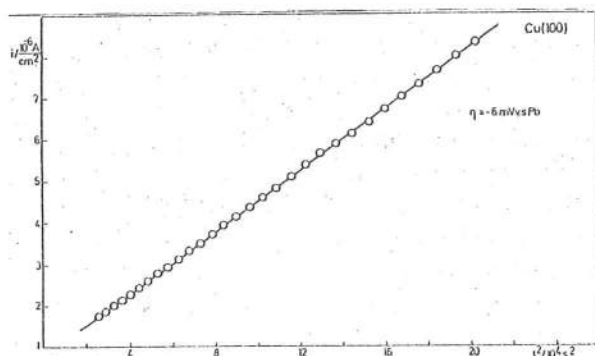


Figure 8. The i vs t^2 relationship obtained from the experimental current-time transients in Figure 5.c.

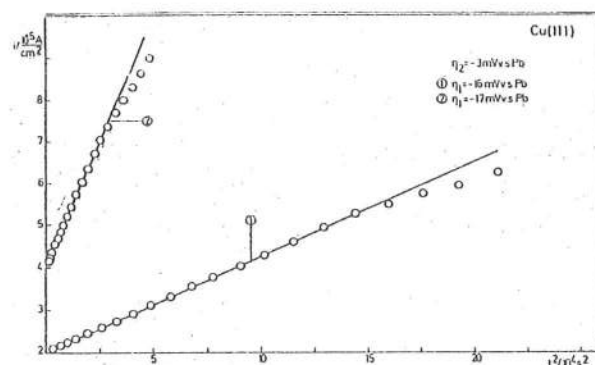


Figure 9.a. The i vs t^2 relationship obtained from the experimental current-time transients in Figure 6.a.

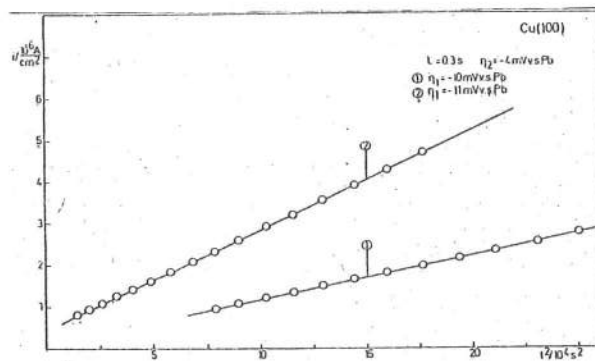
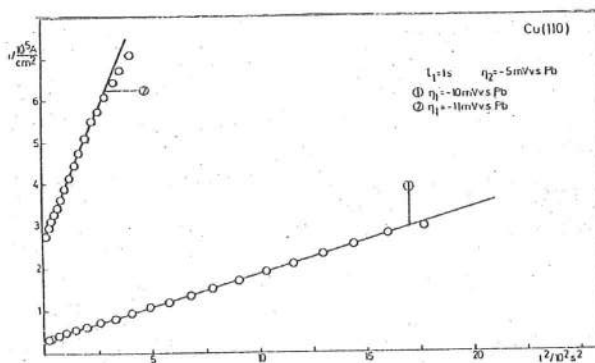


Figure 9. The i vs t^2 relationship obtained from the experimental current-time transients in Figure 6.b. and c. respectively.

The results presented and particularly the i vs. t^2 relationships, could arise from^{4,5} either 3D instantaneous nucleation and growth, or 2D progressive nucleation and growth (charge transfer controlled and the rate determining step being the rate of incorporation of material at the edge of the growth centres).

In the case of 2D nucleation and growth, at least one peak would be expected to appear in the transients, containing approximately a monolayer amount of charge. No such effect was seen among the recorded current-time transients in the present cases.

Therefore, it must be concluded that the observed i vs. t^2 linearity corresponds to 3D instantaneous nucleation of lead on top of the previously formed UPD monolayers and the further growth of the 3D centres.

The equation describing this process at the beginning^{4,5} is:

$$i = \frac{2zF\pi M^2 N_0 k^3 t^2}{\rho^2} \quad (1)$$

The deviation from the i vs. t^2 relationship at longer times observed for all the transients obtained is most probably due to the overlap of the growing centres, and usually the current approaches a limiting value.

However, ultimately the current runs into diffusion control and after reaching a maximum starts to decrease with time eventually settling at the value dictated by the mass transfer laws, Fig. 2.a. and Fig. 3.b.

From the gradient of the i vs. t^2 plots it is possible to determine $N_0 k^3$, which in the present cases show extreme potential dependence. This could arise from a highly potentially dependent k or N_0 , or both. Since the variation of k with overpotential for a simple electron transfer process at small cathodic values would be given by:

$$k \approx k_0 \left(\exp \frac{\alpha z F \eta}{RT} - \exp \frac{-(1-\alpha) z F \eta}{RT} \right) \quad (2)$$

it is difficult to predict such large potential dependence as found experimentally. It seems more probable therefore, that the variation of N_0 , clearly indicated to be appreciable by the increase of the very initial currents, with increasing overpotential, would be responsible for the observed behaviour.

Indeed, this is exactly that could be expected for instantaneous nucleation and growth at very small overpotentials at which all active sites for nucleation in the underlying substrate have not yet been used by the process, and in the example given in Fig. 6.a., b. and c. and Fig. 7. Where amounts of the deposit rarely exceed 10 lead monolayers.

It has already been stated that the results show no appreciable 3D nucleation occurring until the monolayer is completed (similar conclusions were

reached in other cases²⁶) and the very small 3D nucleation overpotentials recorded in the present case varying in the order $\eta_{(111)} \leq \eta_{(100)} \leq \eta_{(110)}$ must be due to the influence of these layers.

In the case of lead UPD on the Cu(111) oriented substrate, the monolayer is the least dense crystallographic structure, compared to the monolayers obtained in the other two copper orientations^{20-24,29-31}. Therefore it seems reasonable to assume that although it is probably the least distorted by the underlying crystallographic structure of the substrate, this monolayer is the least successful in covering active nucleation sites (e.g. dislocations), originally offered by the initial substrate-copper. This will, by the very nature of the process, favor instantaneous rather than progressive nucleation.

Being at the same time crystal metal-like structure, this monolayer must be in character closer to the bulk lead than it was to copper, and therefore it inevitably changes the surface conditions in such an way as to decrease the free energy for 3D nucleation^{32,33}. In such a case the change in free surface energy will be primarily at the interphase nucleus-lead UPD monolayer and it is likely to be of a sort that would, at very small overpotentials, decrease the work of formation of 3D nuclei³⁴⁻⁴¹. This would be facilitated by the existence of the distorted closest-packed epitaxial monolayer structure, enabling a wider choice of possible crystallographic (hkl) orientation for nuclei to be formed.

This is supported by the results obtained on Cu(110). The lead UPD monolayer on this substrate is a close-packed crystalline lattice and therefore the densest of all the three examined^{20-24,29-31}. Although it will be somewhat distorted by the original substrate, such a layer would still most successfully mask dislocations in the surface. Of course, not to the extent of providing the change from instantaneous to progressive nucleation, but well enough to decrease the nucleation overpotentials as observed. On the other hand, the more perfect structure of this lead UPD monolayer narrows the choice of the crystallographic orientation of the nucleus to be formed, most probably to those for which the work of formation is somewhat higher than was the case on Cu(111).

The density of the lead UPD closest-packed epitaxial monolayer on Cu(100) is higher than on Cu(111) but not as high as on Cu(110), therefore in view of what was said above it is not surprising to find that the overpotential for 3D nucleation and the minimum growth potential value are in between those observed for the other cases.

CONCLUSIONS

The characteristics of the *i-t* responses to the potential step regimes applied did not change significantly when different anions were used.

The charge corresponding to the UPD monolayer of lead ($\approx 280 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(111), $\approx 340 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(110) and $\approx 300 \cdot 10^{-6} \text{ As cm}^{-2}$ for Cu(100) oriented substrate) was observed under the very initial fall-off seen on the current-time transients obtained at very short times, preceding the current-time relationships for the overpotential deposition.

Indication of a rising *i-t* transient reflecting bulk lead deposition on Cu(111) were usually observed at $\eta = -6 \text{ mV vs. Pb}$ (some carefully prepared experiments revealed that overpotentials of $\eta = -4 \text{ mV vs. Pb}$ and $\eta = -5 \text{ mV vs. Pb}$ could produce the same results), in the case of the Cu(100) electrode, it was $\eta_2 = -6 \text{ mV vs. Pb}$, while an overpotential of $\eta_2 = -6 \text{ mV vs. Pb}$ was needed for similar effects on Cu(110).

The observed *i* vs. *t*² linearity corresponds to 3D instantaneous nucleation of lead on top of the previously formed UPD monolayers and the further growth of the 3D centres. The results show no appreciable 3D nucleation occurring until the monolayer is completed. The very small 3D nucleation overpotentials recorded, varying in the order $\eta_{(111)} \leq \eta_{(100)} \leq \eta_{(110)}$ must be due to the influence of these layers.

Being at the same time crystal metal-like structure, these monolayers must be in character closer to the bulk lead than to copper, and therefore inevitably change the surface conditions in such an way as to decrease the free energy for 3D nucleation. In such a case the change in free surface energy occurs primarily at the interphase nucleus-lead UPD monolayer and it is likely to be of a sort that would, at very small overpotentials, decrease the work of formation of 3D nuclei. This would be facilitated by the existence of the distorted closest-packed epitaxial monolayer structure, enabling a wider choice of possible crystallographic (hkl) orientation for nuclei to be formed.

The density of the lead UPD closest-packed epitaxial monolayer on Cu(100) is higher than on Cu(111) but not as high as on Cu(110), therefore in view of what was said above it is not surprising to find that the overpotential for 3D nucleation and the minimum growth potential value are in between those observed for the other cases.

The UPD lead monolayer formation, in the case of copper (111), (110) and (100) substrates, is an essential precursor to thicker deposits; its influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

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REFERENCES

- 1.-Faraday, M.: Phil. Trans. Roy. Soc. London, 124 (1834) 77.
- 2.-Raub, E., Muller, K.: "Fundamentals of metal deposition", Elsevier Publishing Co., Amsterdam-New York (1967).
- 3.-Bockris, J.O'M., Despic, A.R.: Vol IX-B, Ch.7, p.p.611, "Physical Chemistry", ed. Eyring, Henderson, Jost, Academic Press, London-New York (1970).
- 4.- Harrison, J.A., Thirsk, H.R.: Vol.5, p.p.67, "Electroanalytical Chemistry", ed. Bard, A.J., Marcela Decker Inc., New York (1971).
- 5.-Fleischmann, M., Thirsk, H.R.: Vol. 3, "Advances in electrochemistry and electrochemical engineering", ed. Delahay, P. and Tobias, C.W., Interscience, London (1963).
- 6.- Despic, A., Popov, K.: Vol. 7, "Modern aspects of electrochemistry", ed. Bockris, J.O'M. and Conway, B.E., Plenum Press, New York (1972).
- 7.-Conway, B.E., Bockris, J.O'M.: Electrochim. Acta, 3, (1966) 340.
- 8.-Budevski, E.: Electrochimica Metallorum, 2 (1966) 131.
- 9.-Fleischmann, M., Rangarajan, S.K., Thirsk, H.R.: parts I, II, III Trans.Faraday Soc., 63 (1967) 1241.
- 10.-Sheludko, A., Bliznakov, G.: Izv. Bul. Akadem. Nauk, Ser. Phys., 2 (1951) 239
- 11.-Erdey-Gruz, T.: "Kinetics of electrode processes", Adam Higher Ltd., London (1972).
- 12.-Bockris, J.O'M., Reddy, K.N.: Vol.2, "Modern electrochemistry", Plenum Press, Rosetta edition, New York (1970).
- 13.-Markus, R.A.: Electrochim. Acta, 13 (1968) 995.
- 14.-Fleischmann, M., Thirsk, H.R.: Electrochim. Acta, 2 (1960) 22, Electrochim. Acta, 9 (1964) 757.
- 15.- Garner, W.E.: Disc. Faraday Soc., 5 (1949)
- 16.-Burton, W.K., Cabrera, N.: Disc. Faraday Soc., 5 (1949).
- 17.-Bransom, S.H., Dunning, W.J., Millard, B.: Disc. Faraday Soc., 5 (1949)
- 18.-Meites, L.: "Polarographic Techniques", 2nd edition, Interscience, New York (1965).
- 19.-Pinner, R., Electroplating, October and November (1953) 360, 401.
- 20.- Jovičević, J.N., Ph.D. Thesis, University of Southampton 1978.
- 21.-Jovičević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.
- 22.-Jovičević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.
- 23.-Jovičević, J.N., Bewick, A., Univ. Thought, Vol.IV(2), in press, (1997) Pristina.
- 24.-Jovičević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 25.-Astley, D.J., Harrison, J.A., Thirsk, H.R., J. Electroanal. Chem., 19 (1968) 325.
- 26.-Thomas, B., Ph.D. Thesis, University of Southampton 1976.
- 27.- Harrison, J.A., J.Electroanal. Chem., 12(1972) 71.
- 28.- Davison, W., Harrison, J.A., Thompson, J., Faraday Disc. Chem. Soc., 56 (1973) 71.
- 29.- Jovičević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 30.- Jovičević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 31.-Jovičević, J.N., Bewick, A., Univ. Thought, accepted for publication, (1998) Pristina.
- 32.-Bewick, A., Fleischmann, M., Thirsk, H.R., Trans. Faraday Soc., 58 (1962) 2200.
- 33.-Vermilyea, D.A., "Advances in Electrochemistry and Electrochemical Engineering", ed. P.Delahay, Vol.3., Interscience, New York (1975).
- 34.-Pangarov, N.A., Phys. Stat. Sol., 20 (1967) 365.
- 35.- Pangarov, N.A., Zash. Metalov, 5 (1969) 467.
- 36.- Pangarov, N.A., Electrichim. Acta, 7 (1962) 139.
- 37.- Pangarov, N.A., Electrochim. Acta, 9 (1969) 721.
- 38.- Pangarov, N.A., Vitkova, S.D., Electrochim. Acta, 11 (1966) 1733.
- 39.- Pangarov, N.A., Velinov, V., Electrochim. Acta, 11 (1966) 1753.
- 40.- Pangarov, N.A., Vitkova, S.D., Electrochim. Acta, 11 (1966) 1719.
- 41.- Pangarov, N.A., Uvarov, L.A., Vagramyan, A.T., Electrochim. Acta, 13 (1968) 1905.
- 42.-Sillen, G., "Stability Constants of Metal Ion Complexes", Chem. Soc., Special publication No.25, (1971).

REZIME

STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA OLOVA NA BAKRU - VII DIO
 REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTROTALOŽENJE PRI KATODNIM PRENAPETOSTIMA NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (111), (110) I (100)

Jovan N. JOVIČEVIĆ¹, Alan BEWICK

Chemistry Department, Southampton University, UK, SO9 5NH

¹Sadašnja adresa: Odsek za hemiju, PMF, Univerzitet u Prištini, 38000 Priština, Jugoslavija

Ovo je sedmi iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja olova (iz acetatnih, nitratnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru.

Rad predstavlja rezultate dobijene potenciostatikom metodom jednostrukog, dvostrukog i trostrukog pulsa na monokristalnim elektrodama površinske kris-

talografke orijentacije (111), (110) i (100) u području potencijala negativnijih od reverzibilnog potencijala olova u datoj sredini.

Karakteristike odgovora struje-vrijeme na primjenjene režime potencijalnih impulsa nisu se značajnije razlikovale s obzirom na različite anjone u izabranim rastvorima.

Početni opadajući dio i-t krive (odražavajući $\approx 280 \cdot 10^{-6} \text{ As cm}^{-2}$ za Cu(111); $\approx 340 \cdot 10^{-6} \text{ As cm}^{-2}$ za Cu(110) i $\approx 300 \cdot 10^{-6} \text{ As cm}^{-2}$ za Cu(100) podlogu) redovno je predhodio naknadnim djelovima i-t krive koji su odražavali elektrotaloženje olova pri katodnoj prenapetosti.

Rastuće i-t krive, koje odražavaju elektrotaloženje masivnog olova, na Cu(111) podlozi javljaju se pri $\eta = -5 \text{ mV vs. Pb}$, na Cu(100) podlozi pri $\eta_2 = -6 \text{ mV vs. Pb}$, a na Cu(110) pri $\eta_2 = -6 \text{ mV vs. Pb}$.

Zapažena linearnost funkcija $i = f(t^2)$ odražava trodimenzionu trenutnu nukleaciju i dalji rast stvorenih centara olova na predhodno formiranom monosloju nastalom pri potencijalima pozitivnijim od reverzibilnog potencijala olova. Dobijeni rezultati ne pokazuju da dolazi do značajnije trodimenzione nukleacije olova prije nego što se u potpunosti ne formira rečeni monosloj. Činjenica da je nukleaciona prenapetost olova na ispitivanim bakarnim površinama ($\eta_{(111)} \leq \eta_{(100)} \leq \eta_{(110)}$) tako mala mora biti rezultat uticaja tih monoslojeva.

Kako su monoslojevi dobijeni pri potencijalima pozitivnijim od reverzibilnog po karakteru kristalne

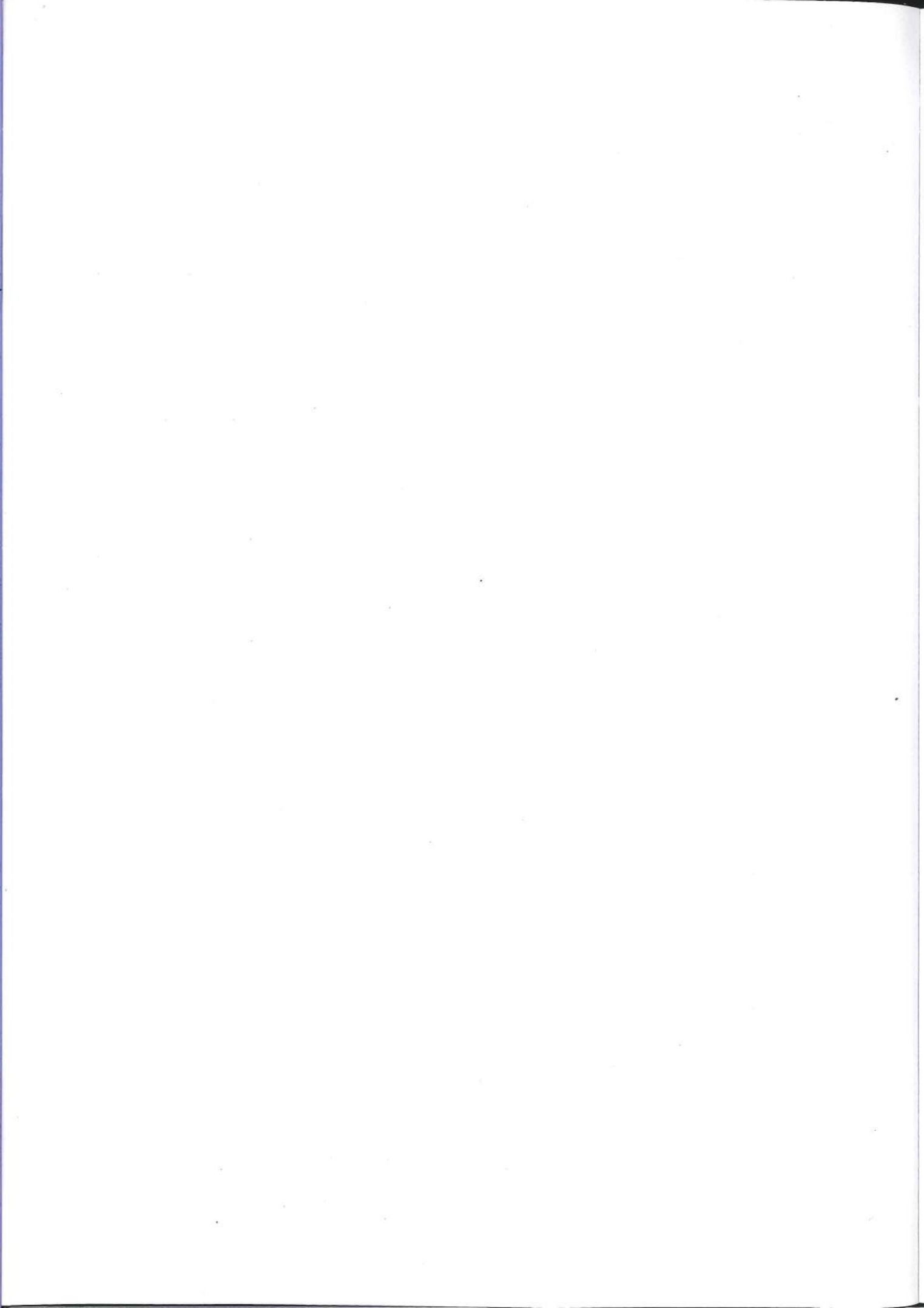
metalnu slične strukture po osobinama bliže olovu nego bakru, njihovo prisustvo neminovno mijenja površinske uslove u pravcu smanjivanja slobodne energije trodimenzione nukleacije. Do promjene slobodne površinske energije trodimenzione nukleacije dolazi najvećim dijelom na granici faza nukleus-olovni monosloj i kao posljedicu ima smanjenje potrebnog rada formiranja 3D nukleusa. Ovo smanjenje rada potrebnog za formiranje nukleusa, nadalje je olakšano i postojanjem poremećene strukture epitaksijalnog gustopakovanog monosloja, što omogućava veći izbor mogućih kristalografskih orijentacija nukleusa (hkl) koji se formiraju.

Gustina olovnog gustopakovanog epitaksijalnog monosloja nastalog pri potencijalima pozitivnijim od reverzibilnog na Cu(100) je veća nego na Cu(111), ali ne tolika koliko na Cu(110), zato nije iznenađujuće da se prenapetosti 3D nukleacije i minimalne prenapetosti rasta međusobno razlikuju na zapaženi način.

Formiranje monosloja olova pri potencijalima pozitivnijim od reverzibilnoga, u slučaju Cu(111), Cu(110) i Cu(100) podloge predstavlja neophodnu predhodnicu debljim olovnim talozima, a njihov uticaj na započinjanje i mehanizam rasta olova pri potencijalima negativnijim od reverzibilnog pokazao se značajnim.

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AMMONIZATION OF OXIDIZED LIGNITE

Milena M. PETROVIĆ¹, PALIĆ M. Radoslav², PETROVIĆ R. Petar³ and MILIĆEVIĆ M. Zoran³

¹Faculty of Science, Priština, ²Faculty of Philosophy, Niš

³Faculty of Economics, Priština

ABSTRACT

We have examined parameters of lignite ammonization (influence of ammonia concentration, temperature, period of ammonization, coal / ammonia ratio). The lignite was previously oxidized by nitric acid in order ammonium-nitro-humat with greater nitrogen content to be

obtained. It has been stated that the maximal nitrogen content in ammonium-nitro-humat (6,26%) is achieved during ammonization of 10 g oxidized lignite in 125 ml of 20% ammonium-hydroxide solution at temperature of 20 °C in period of 16 hours.

Key words: Ammonization, ammonium-nitro-humat, humic acid

INTRODUCTION

The proved varied positive role of humic substances in soil / plant system shows that for modern intensive agricultural production it is necessary besides artificial fertilizer, organic fertilizer to be added to soil since reserves of humus in soil are decreasing. Application of organic fertilizers would be of special importance for soil poor in humus substances. Coal which positively affect soil-plant system is the one used for coal based production of fertilizers. Advantage is given to naturally oxidized coal which contains 40-80 % of humic acids. Although the recent types of coals containing less quantity of humic acids, by oxidation procedure can be easily enriched in humic acids. In such a way enriched coal in humic acids - through ammonization procedure i.e. treatment of coal by ammonia solution gives ammonium-humat, the product soluble in water and accessible to plants for adoption.

Technological procedure to produce ammonium-humat can be different (Fuentes and Alvares, 1981; Dorneanu et al. 1990, Aleksandrov et al. 1992; Xiaoyon, 1994.) and before all depends on type of coal, humic acid content, coal carbonification level and ammonization parameters: temperature, pressure, quantity of ammonia etc.

In reference with the above said the purpose of this paper is to examine ammonization of lignite which is oxidized by nitric acid in order to obtain ammonium-nitro-humat which could be applied for growth and development of plants. Ammonization conditions of oxidized lignite (influence of ammonia concentration, temperature, period of ammonization, coal / ammonia ratio) would be particularly examined to obtain a product with greater gain and nitrogen content.

MATERIAL AND METHODS

We have taken Kosovo lignite from surface excavation site "Dobro selo" for our examination. The lignite was previously oxidized by nitric acid and containing 73,15 % of humic acids.

For the purpose of producing ammonium-nitro-humat, ammonization of oxidated lignite was followed in functions of concentrations of ammonium-hydroxide solution, reaction temperature, period of ammonization and quantity of ammonium-hydroxide solution.

a) Influence of ammonia concentration. Ammonization of oxidized lignite (10 g) was performed by 5%, 10%, 15%, 20% and 25% of ammonium-hydroxide solution. Experiments were made under the same conditions at temperature of 20 °C in period of 16 hours and the volume of ammonium-hydroxide solution was 125 ml.

b) Influence of temperature. Examination of temperature influence to ammonization of oxidized lignite (10 g) was performed at 20, 40, 60, 80 and 100 °C while other parameters (ammonia concentration, ammonization period, volume of ammonium-hydroxide) were constant (125 ml 20 % NH₄OH 16 hours).

c) Influence of ammonization. In the third series ammonization of oxidated lignite (10 g) was performed in function of reaction period duration (0,5, 4,8 and 16 hours) while other parameters were kept constant (125 ml 20% NH₄OH at 20 °C).

d) Influence of ammonium-hydroxide volume. During these examinations ammonization of oxidated lignite (10 g) was performed in function of ammonium-hydroxide quantity (25, 75, 125, 225 and 325 ml) and other parameters were kept constant (20 % solution NH₄OH, 16 hours, 20 °C).

After ammonization was finished the solution was steamed at water bath and then ammonium-nitro-humat was dried at 105 °C. Gain of ammonium-nitro-humat was calculated in relation to lignite without

Table 1. Influence of ammonium-hydroxide concentration to ammonization of oxidated lignite

NH ₄ OH %	ANH %	N %
5	105,83	5,74
10	105,24	5,34
15	107,08	5,58
20	109,09	6,26
25	113,48	5,30

Table 2. Influence of temperature to ammonization of oxidated lignite

Temperature °C	ANH %	N %
20	107,08	5,58
40	114,26	5,83
60	106,48	5,82
80	115,17	5,76
100	114,66	5,68

Table 3. Influence of time duration to ammonization of oxidated lignite

Period h	ANH %	N %
0,5	113,46	5,95
4	114,17	5,31
8	107,89	6,01
12	111,93	5,74
16	107,08	5,58

Table 4. Influence of volume of ammonium-hydroxide to ammonization of oxidated lignite

NH ₄ OH ml	ANH %	N %
25	112,72	5,26
75	115,44	4,20
125	107,08	5,58
175	114,16	5,95
225	231,47	5,18
275	117,59	5,11

humidity and ash. In all samples of ammonium-nitro-humat nitrogen content was determined by Dumas method.

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RESULTS AND DISCUSSION

Ammonization of coal in order produce ammonium-humat and stimulative effect of ammonium-humat preparation to plants growth still are the subject of study to many of the researches.

Our task was to find the most optimal conditions under which ammonium-nitro-humats with the greatest nitrogen content in their structure can be obtained.

Ammonization of oxidated lignite was followed in function of concentration of ammonium-hydroxide solution, reaction temperature, ammonization time duration and in relation of coal to ammonium-hydroxide solution.

Studying the influence of ammonium-hydroxide concentration to ammonization of oxidated lignite we have noticed (Tab. 1) that with increase of ammonium-hydroxide concentration the gain of ammonium-nitro-humat also increases.

Quantity of total nitrogen in the sample of ammonium-nitro-humat ranges from 5,30 to 6,26 %. The least nitrogen content was found in the oxidated lignite sample which was ammoniated with 25 % of ammonium-hydroxide and the greatest nitrogen content was found in the sample which was ammoniated with 20 % of ammonium-hydroxide.

Examinations regarding influence of temperature to ammonization to ammonization of oxidated lignite (Tab. 2) show that the least gain of ammonium-nitro-humat is obtained at temperature of 60 °C and the greatest at ammonization temperature of 80 °C.

Content of total nitrogen in the obtained products ranges from 5,58 to 5,83 %. Change of temperature did not essentially influenced to the change of total nitrogen content. Nevertheless it can be stated that when ammonization temperature increases nitrogen content in ammoniated samples slightly decreases.

Results of influence of time duration to ammonization of oxidated lignite (Tab. 3) show that maximal gain of ammonium-nitro-humat is obtained during four hours period of ammonization of oxidated lignite. Nitrogen content in ammonium-nitro-humats ranges from 5,31 to 6,01 %. The greatest nitrogen content in the samples of oxidated lignite is obtained during ammonization of lignite of 8 hours period. Either shorter or longer ammonization period nitrogen content in the ammoniated samples decreases.

During examination of influence of ammonium-hydroxide volume to gain ammonium-nitro-humat (Tab. 4) it was noticed that maximal gain of ammonium-nitro-humat is obtained when ammonization of oxidated lignite is performed with 225 ml of ammonium-hydroxide solution.

Nitrogen content in ammoniated samples of oxidated lignite ranges from 4,20 to 5,95%. Regarding nitrogen linkage to oxidated lignite the best effect is achieved during ammonization of lignite (10 g) in 175 ml of 20% ammonium-hydroxide solution at 20 °C in 16 hours period.

CONCLUSIONS

When parameters of ammonization of oxidated lignite were examined in order ammonium-nitro-humat to be obtained we have come to the following conclusions:

1. With growth of ammonium-hydroxide concentration gain of ammonium-nitro-humat also increases. The greatest nitrogen content in ammonium-nitro-humat is obtained during ammonization of oxidated lignite with 20% ammonium-hydroxide.
2. Changes of ammonization temperature have not essentially influenced to change of total nitrogen although with ammonization temperature growth nitrogen content in ammoniated samples decreases.
3. The greatest nitrogen content in the samples of ammonium-nitro-humat is obtained during ammonization of oxidated lignite for period of 8 hours. Either shorter or longer ammonization period nitrogen content in ammoniated samples decreases.
4. Change of ammonium-hydroxide volume has influence to ammonization of oxidated lignite and to nitrogen content in ammonium-nitro-humat.
5. Maximal nitrogen content in ammonium-nitro-humat (6,26%) is achieved during ammonization of oxidated lignite (10 g) in 125 ml of 20% ammonium-hydroxide solution at temperature of 20 °C in period of 16 hours.

REFERENCES

- Aleksandrov, V., Kandelaki, I., Zafirova, N., Vazhova, A. (1992): Khim. Tverd. Topl., Moskva.
- Dorneanu, A. et all. (1990): cit po Chem. Abstr. 116, 58157 m.
- Fuertes A., Alvares, R. (1981): Fertilizer production from coal Cong. Mediter. Ing. Anim. Barcelona
- Xiaoyon, L. (1994): cit po Chem. Abstr. 123, 32203 t.

REZIME**AMONIZACIJA OKSIDOVANOG LIGNITA**

Milena M. PETROVIĆ¹, PALIĆ M. Radoslav², PETROVIĆ R. Petar³ and MILIĆEVIĆ M. Zoran³

¹Prirodno-matematički fakultet, Vidovdanska bb, Priština

²Filozofski fakultet, Ćirila i Metodija 2, Niš

³Ekonomski fakultet, Cara Dušana bb, Priština

Ispitana je amonizacija lignita, koji je prethodno oksidovan azotnom kiselinom, u cilju dobijanja amonijum-nitro humata koji bi mogao imati primenu za rast

i razvoj biljaka. Posebno su ispitani uslovi amonizacije oksidovanog lignita (uticaj koncentracije amonijaka, temperature, dužine vremena amonizacije, količine amonijaka) kako bi se dobio proizvod sa većim sadržajem azota.

Konstatovano je da se maksimalan sadržaj azota u amonijum-nitro-humatu (6,26%) postiže pri amonizaciji 10 g oksidovanog lignita sa 125 ml 20% rastvora amonijum-hidroksida na temperaturi od 20 °C i u vremenu od 16 časova.

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PROFESSOR MIŠKOVIĆ'S SUNDIAL

The Sundial of the Belgrade Astronomic Observatory

TADIĆ Milutin

Geography Department of Faculty of Natural Sciences of The University of Pristina

ABSTRACT

The paper deals with the horizontal sundial set, in 1932, in the meridian of then newly built Belgrade Astronomic Observatory. It is a rudimentary sundial and for that reason it is not very important. What is really important is the fact that its constructor was the manager of the Ob-

servatory, Professor Vojislav V. Mišković. Despite all his scientific and teaching obligations, Mišković had time to engage himself in the history of astronomy and in that way in gnomonics, which he defined as "a scientific entertainment".

Key words: gnomonics, sundial, Professor Vojislav V. Mišković, the Belgrade Astronomic Observatory.

INTRODUCTION

Gnomonics is a scientific discipline which deals with the theory and construction of sundials - or shortly - *gnomonics is the art of constructing sundials*. Nowadays, gnomonics is still actual despite the fact that its main product has been replaced with modern instruments. Without discussing the longevity of sundials we may say that science started with astronomy and astronomy with gnomonics.

The essential development of gnomonics has always been within astronomy, and long after the Middle Ages and the first mechanical clocks astronomers were obliged to have knowledge of gnomonics. Because of their complexity sundials are the subject of interest of different kinds of researchers (archeologists, architects, historians of arts...), but among them the first place always belongs to an astronomer.

Every old sundial is important, but the sundials especially important for the history of astronomy are those constructed by astronomers themselves. When we talk about old stationary sundials (those constructed before World War II), only one of this kind is known to us and that is the sundial constructed by a professional astronomer. This sundial is, in fact, the horizontal sundial of the Belgrade Astronomic Observatory.

The Sundial of the Belgrade Astronomic Observatory

The sundial is within the area of the Belgrade Astronomic Observatory. In the middle of the path that connects the pavilions of the big and small refractors (Fig.1) there is the horizontal sundial out of function for a long time (Fig.2). It was constructed in 1932 by Professor, PhD Vojislav V. Mišković (1892-1976), the manager of then newly built Observatory on Veliki Vračar.

The base of the sundial is a square marble slab with its sides 50cm each (Fig.3). There are two concen-



Fig.1-A photograph taken from a plane of the Belgrade Astronomic Observatory in the time when Professor Mišković was its manager. The sundial is marked with an arrow. The pavilion of the big refractor (1), the school pavilion (2) and the small refractor (3) are marked with numbers.

Sl.1.-Avionski snimak Astronomske opservatorije iz vremena kada je profesor Mišković bio njen upravnik. Strelicom je označeno mjesto sunčanika. Brojevima su označeni paviljon velikog refraktora (1), školski paviljon (2) i mali refraktor (3).

tric squares chiselled in the slab with their sides parallel to the slab sides at a distance of 2cm and 7cm. It is the space between these squares where a dial in the range of 5a.m. to 7p.m. is chiselled and represented by Roman numerals with their size of 20-22cm. The lines for full hours are drawn from almost the half of the sundial to the internal frame of the dial, while the lines for halves stretch from the same frame to a hypothetical circle drawn from the centre of the slab 25cm in radius. There is no polos. There are only the remains of its supporters, 89mm far away from each other. Taking into consideration the fact that then measured latitude of the Observatory was $\varphi = 44^{\circ}48'08''$, the supporters of the polos must have been 31.3mm and 88.4mm high, and a rod not longer than 228.6mm (Fig.3).

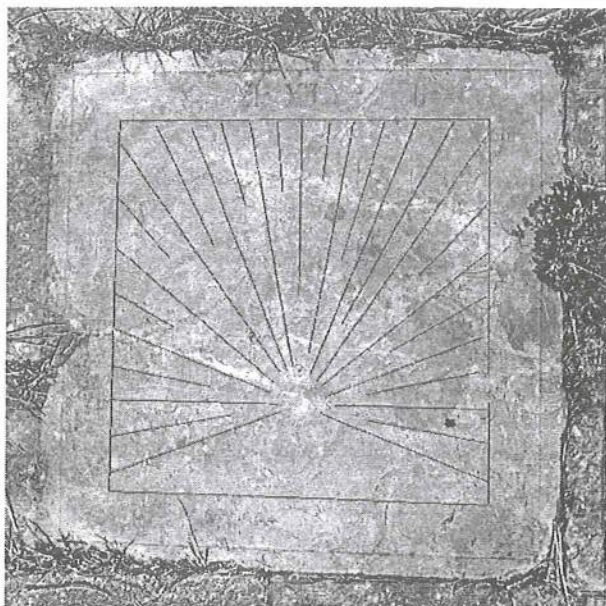


Fig.2-The marble slab of the horizontal sundial of the Belgrade Astronomic Observatory.

Sl.2. Mermerna ploča horizontalnog sunčanika Astronomске opservatorije u Beogradu.

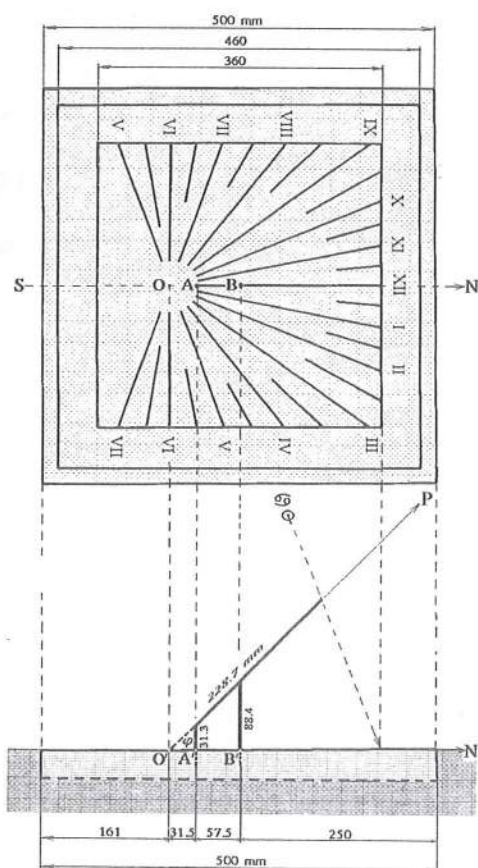


Fig.3-The plan of the horizontal sundial of the Belgrade Astronomic Observatory.

Sl.3.-Nacrt horizontalnog sunčanika Astronomске opservatorije u Beogradu

The sundial was set on the path - in the meridian of the Observatory (then measured $\lambda = 20^{\circ}30'57''$) - which was very busy even at nights, so it is possible that the polos was broken, somebody could have simply stumbled over it. Apart from this, we must not forget that the Observatory was a battle field during World War II.

The lines of the sundial are chiselled with geometrical and stonemason's precision. The sundial was chiselled by Avanti Bertoto¹, a Belgrade stonemason, according to Professor Mišković's plan of course (then measured latitude of the Observatory was $\phi = 44^{\circ}48'08''$). There is neither ornamental nor unnecessary detail on the sundial. It is a typical rudimentary one.

The sundial is constructed to show apparent solar time (T_p). A moment read from the sundial can be converted into Central-European time (T_{SE}) according to the formula $T_{SE}=T_p+22^m3.8s+e$, where e represents a time difference which Mišković for the first time in Serbian called "vremensko izjednačenje" (equation of time) in "Godišnjak našeg neba za godinu 1931"² ("The Almanac of Our Sky - for the year 1931").

The setting of the sundial was preceded by the article "O sunčanim časovnicima" ("On Sundials"), published in "Godišnjak našeg neba za godinu 1931" and completely edited by Professor Mišković.

Mišković: "O sunčanim časovnicima" ("On Sundials")

The article has 17 pages (p.178-195), 9 illustrations and a table. It consists of 5 sections: On Gnomon; On Cadran Solaires; What Does a Cadran Solaire Consist of?; General Instructions: Material, Shape, Dimensions of a Cadran; Appendix to the Previous Explanations.

The article gives a set of instructions and advice for everybody to construct a sundial. In the introduction the author says that he does not want to write about theory because he might lose a great number of readers in that case, and after all, the theory is not quite necessary for constructing elementary sundials. The section "On Gnomon" is a historical introduction about a gnomon - when it was used for the first time by the ancient civilization and for what purpose: for measuring the height of the sun, for determining the direction of the meridian, for measuring latitude and for determining the apparent noon. What Professor Mišković states precisely about the use of a gnomon is the following: **"...for observing and measuring heights and determining only that what could be derived from them"**.

In the footnote of the original it is noted that the historical introduction was done according to: G.Bigourdan, *Gnomonique*. And that is all. In fact, it

¹ Datum: Professor, PhD Milorad Protić

² In the article "O merenju i računanju vremena" ("On the Time Measuring and Calculating"), published in "Godišnjak našeg neba za godinu 1932", p.51.

is *Gnomonique ou traite theorique et pratique de la construction des cadrans solaires* (Paris, 1922) considered as one of the most important papers on gnomonics (Aked 1997).

In the introduction of the next section ("On Cad-rans Solaires") it is stated that "a gnomon is a kind of sundials" and pointed out that the turning of a gnomon into the sky axis represents the main reason for the gnomon to become a sundial³. The author points out the skill of the ancient Greeks and their followers Arabic astronomers as well as that the literature on the theory on sundials and their constructing was especially rich in the Middle Ages. The title of the next section "What Does a Cadrans Solaire Consist of?" completely says what this section is about. It gives not only the parts of a sundial, but also different kinds of sundials: equatorial, horizontal, vertical. In "General Instructions..." marble is recommended as the most appropriate material for constructing sundials and optimal dimensions of rectangular slab that are recommended here are 1-1.5m, maximum 2m, and minimum 10-15cm. A reader is advised to read the latitude of a place from the map before starting work as well as to determine the direction of the meridian by means of gnomon - by means of the method of equal heights, and the best time to do that is around solstice. What follows in the section is a set of very clear and detailed instructions for a geometrical construction of hour lines on a rectangular slab with dimension 60x40cm by means of what we can call "Direr's method". In order to be easy for every reader to construct a sundial and to be spare of any measuring and plotting angles, a table is given on the page 190. In the last section "Appendix..." it is said that sundials show the apparent time, and in order to know the civil time "one has to know a little astronomy". At the end of the article the author says that what follows in the next number of "Godišnjak našeg neba" is the continuation of this article.

Really, the continuation of Mišković's article "On Sundials" was published in "Godišnjak našeg neba za godinu 1933". It has 10 pages, 10 illustrations and a table. It deals with constructing vertical sundials in our latitudes in the same way as the previous article - without discussing theory. This paper gives a set of detailed instructions not only about constructing hour lines of vertical sundials of different orientations, but also some advice on the choice of material, the proportion of dimensions, the way of rod fixing and line drawing. At the end readers are informed that they may expect the article on constructing other kinds of sundials in one of the following numbers of "Godišnjak" ("The Almanac").

In both articles Mišković states only one, already mentioned book source. It is interesting that he does not inform a reader about the book "Opredeljenje časa

pomoću sunčanika" ("An Hour Determination by means of a Sundial"), published in 1902 by Mišković's predecessor Milan Nedeljković (1857 - 1950), who was the founder and the first manager of the Belgrade Astronomic and Meteorological Observatory as well as a professor of astronomy and meteorology at the University. This book (Fig.4) has 130 pages and tables of sunrises and sunsets in 1903 on the last 13 pages. It is divided into 3 chapters: 1-Time (hour), 2-Sundial, 3-Clock.



Fig.4-The front page of Nedeljković's book.
Sl.4.-Naslovna strana Nedeljkovićeve knjige

In the first chapter the author explains the basic terms - apparent and mean solar time and gives two tables to show the way of converting one to another. At the end of the chapter he notifies the aim of the book, and that is to explain the construction of a sundial which would be used in meteorological stations for checking clock correctness. In the second chapter it is stated that it should be the sundial by which one can determine the noon with a mistake not bigger than "a few seconds". The same chapter consists of detailed instructions for determining the noon line by means of the method of equal heights of the sun, and a very important note that in two moments symmetrical to the noon the shadows are not symmetrical to the noon line. The sundial work is described very precisely: material, dimensions, the way of constructing and fitting a sundial...everything. From the very beginning a reader may find reading the book very hard, but after that he starts to admire Nedeljković's patience in describing all details, exactly predicting everything that would be confusing for readers who

³ In fact, it is not exactly the point. A gnomon could be a polos of a sundial as well. It is clear that the author simplifies the instructions in order to be understandable to everyone.

are "not at home" in astronomy. Concerning gnomonics the third chapter is not interesting, it is about checking mechanical clocks according to already constructed sundial.

Nedeljković's instructions are, in fact, about the construction of a gnomon and its use in determining the noon line and the apparent noon. It could be said that it is a noon sundial. This is only the first step in constructing a sundial, what is clearly and concisely written in "Appendix" on the page VII, where Nedeljković states that in constructing a real sundial one should draw hour lines considering the top of a gnomon as *"the top of a hypothetical rod that slopes at the angle of the latitude of a place"*.

Nedeljković and Mišković were both French disciples. From time to time Nedeljković was staying in Paris (Sorbonne, College de France, the Paris Observatory) where one could find about 100 stationary sundials. He went to Paris in 1879, and in Sorbonne 3 years before that a meridian wall sundial had been restored, constructed by Jacques Picard (1620-1682), a French astronomer. In old Sorbonne Picard constructed two vertical sundials as well (Gotteland 1983), the eastern and the western one. The first one was restored and as a gift of Paris taken to the Nice Observatory. In this Observatory Mišković worked as an astronomer since 1922. In the period of 1919-1925, besides Nice, Mišković visited Marseille and Montpellier as well, where one could find 350 sundials⁴. So, during their professional travellings to France both Nedeljković and Mišković learned a lot about sundials and the literature on gnomonics.

The terms one can find in the mentioned works are the most important ones for the history of our gnomonics. Keeping in mind the purpose of their articles, both Nedeljković and Mišković completely avoid the astronomic terms. Nedeljković uses the term *"sunčanik"* (a sundial) for a sundial, and gives its definition, that is *"a device which shows either the solar noon only or particular hours of the apparent solar time as well"*. A sundial consists of *stub (postolje)* (a post (a base)), *ploča* (a slab), *šipka* (a rod) and *kazaljka sunčanika* (a sundial hand). It is interesting that according to Nedeljković *"kazaljka sunčanika"* represents a cut on the flat end of the rod. On the other hand, Mišković uses a Serbian-French compound *"sunčani kadran"* (a cadran solaire). The base of a sundial is called *"tabla"* (a board), the polos is *"kadranova osočina"* (a cadran axis) and the exact point it is fixed in is called *"središte kadrana"* (a cadran centre). According to the board position Mišković divides sundials into *horizontalni* (horizontal), *ekvatorijalni* (equatorial) and *vertikalni* (vertical). The vertical ones are divided into those *"bez skretanja"* (without turning) and those *"koji skreću"* (which turn). The first group includes vertical sundials which lie in the

first vertical level (*sjeverni i južni*) (the northern and the southern) and those which lie in the meridian level (*istočni i zapadni*) (the eastern and the western). The second group includes other vertical sundials with the noon shadow which does not fall vertically on the board of a normal stick, and these sundials are divided into those *"koji skreću ka istoku"* (which turn towards the east) and those *"koji skreću ka zapadu"* (which turn towards the west).

Gnomonics itself is defined by Mišković as *"a science of sundials"*, and later as *"a scientific entertainment"* what is maybe the most appropriate description of the modern status of this ancient art.

Mišković's Motive for Constructing the Sundial

In the astronomic observatories and planetariums over the world there are not only a lot of old sundials, but newly constructed ones as well. The Belgrade Observatory is not an exception. So, we cannot accept a very frequent statement that since the second half of the 19th century sundials have been only traditional ornaments on churches or plastics in city parks. We can agree that sundials have an aesthetic function, but that is not all. They are not only ornaments...and this is best explained by Mišković in his preface of *"Godišnjak našeg neba za godinu 1931"* by making comments on a letter of a village school principle who asked for instructions about constructing sundials:

"What would we praise more the pedagogical intention and the idea of this principle or his love towards science and towards his pupils? There is no doubt that the children will learn much more and more easily in this way than by means of books and many other methods".

By these words Mišković clearly explains not only his motive for constructing the sundial within the area of the Belgrade Observatory, but a general motive for constructing sundials nowadays.

REFERENCE

- Aked C.K: 1997, An Opusculum of Dialing References, Copyright Exposition.
- Dimitrijević M.S.: 1997, 110 godina Astronomske opservatorije, Publikacije Astronomske opservatorije u Beogradu, Beograd, p.9-20.
- Gotteland A., 1983, Les cadrans solaires de l'abbé Picard a la Sorbone, L'Astronomie, SAF, str.429-436
- Nedeljković M.: 1902, Opredeljenje časa pomoću sunčanika, Opservatorija, Beograd.
- Mišković V.: 1930, O sunčanim časovnicima, Godišnjak našeg neba za 1931, Beograd, p.179-195.
- Mišković V.: 1930, O sunčanim časovnicima, Godišnjak našeg neba za 1933, Beograd, p.274-285.

4 Repartition departementale des cadrans francais, fiches a la SAF, 1988.

REZIME

SUNČANIK PROFESORA MIŠKOVIĆA
SUNČANIK BEOGRADSKE ASTRONOMSKE OPSERVATORIJE

TADIĆ Milutin

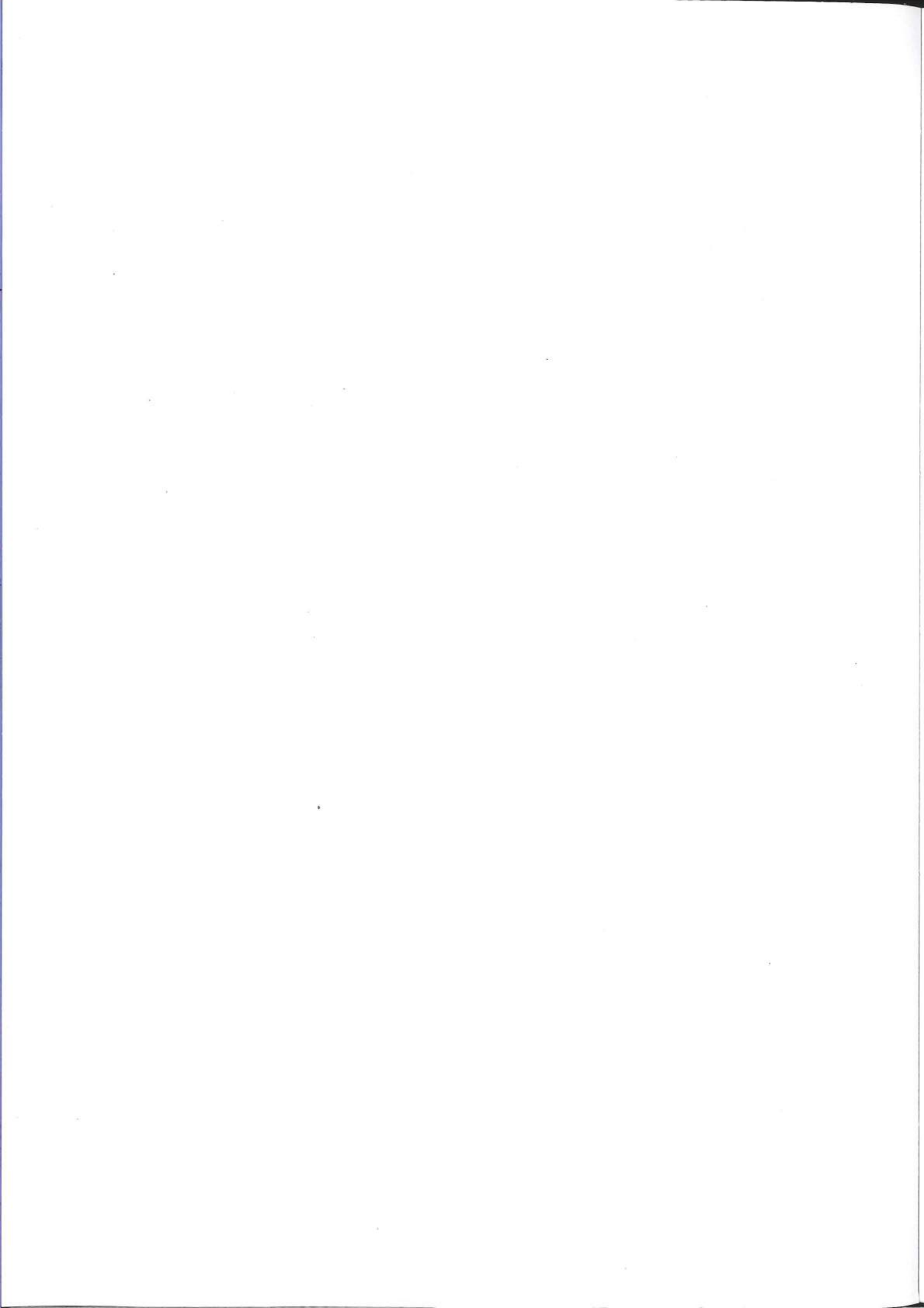
PMF, Odsek za geografiju, Vidovdanska bb, 38000
Priština, Jugoslavija

U krugu Astronomske opservatorije u Beogradu nalazi se kvadratna mermerna ploča (50 x 50 cm) horizontalnog sunčanika, bez bacača sjenke (Sl.2). Sunčanik je postavljen 1932.g. u meridijan ($\lambda = 20^{\circ}30'57''$) tek sagrađene opservatorije na Velikom Vračaru (Sl.1). Sunčanik je konstruisao (Sl.3) sam upravnik opservatorije, Vojislav V. Mišković (1892-1976), profesor Beogradskog Univerziteta. Konstrukciji sunčanika prethodio je Miškovićev članak "O

sunčanim časovnicima" u "Godišnjaku našeg neba za 1931", čiji je drugi dio objavljen u narednom broju istog godišnjaka. Mišković se pored intezivnog naučno-nastavnog rada bavio i istorijom astronomije, i usput gnomonikom. U ovim Miškovićevim radovima, i u navedenom radu (Sl.4) njegovog prethodnika, profesora Milana G. Nedeljkovića (1857-1950), osnovača Astronomske i meteorološke opservatorije u Beogradu, nalazimo na srpskom jeziku prvi put jasno definisane pojmove iz gnomonike. Mišković je gnomoniku nazivao "naučnom zabavom", što je, možda, njeno najprimjerenije savremeno određenje.

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Floristic composition of weed communities in wheat, maize and soybean crops after liming

Radomir OGNJANOVIĆ, Nebojša DELETIĆ
Faculty of Agriculture, Priština.

ABSTRACT

The use of calcium (the "Njival Ca" fertilizer) improved physical, chemical and biological properties of the soil (vertisol). The changes observed in this soil caused some changes in floristic composition of wheat, maize, and soybean agrophytocenoses. Number of acidophilic weeds decreased with the simultaneous increase of cal-

ciphilic ones. The total weediness also diminished, as well as number of individuals per m², and these changes were followed by the decrease of raw and air-dry weed biomass. The dominant species of the mentioned agrophytocenoses have been established.

Key words: calcium, liming, maize, soybean, wheat, weeds.

INTRODUCTION

Rinsing down of calcium and its going out of soil by yields, intensive crop production, use of physiologically acid fertilizers and pesticides, heavy machines and making of soil anaerobe conditions, root system secretions, acid rainfall, etc., influence soil acidification more and more. About 50-60% of the total agricultural land in Serbia is acid (Stevanović, 1991; 1995). Soil acidification (the change of pH value) has a significant influence on macro and micro flora and fauna, especially on floristic composition of grown crops agrophytocenoses. We can, therefore, estimate approximate soil pH value on the basis of present weed species, because weed plants are good indicators of resident conditions (Gračanin, 1947; Popović, 1960; Kovačević, 1976; Čalić, 1993; Kojić i Janjić, 1994; Ognjanović *et al.*, 1995; 1996). Acidophilic weeds are prevalent on acid soils, and alkalophilic ones on alkal soils. Zdravković *et al.* (1993), Veljović (1995), Novaković (1995), Ognjanović *et al.* (1995; 1996), established, investigating influence of soil liming when wheat, maize and soybean were grown, that on the plots unfertilized by calcium (control), in all the crops, there was the highest number of species, and that acidophilic weeds were prevalent in the control, whereas in the variants with applied calcium there were some calciphilic (alkalophilic) species too.

MATERIAL AND METHODS

The investigation have been carried out during the six-year period (1989/90-1994/95), at the experimental field of the Centre for Small Grains in Kragujevac, at the stationary three-field trial (wheat, maize, soybean), on the vertisol soil type. Fertilization by NPK fertilizers were the same for all the investigated crops.

The following variants of calcium fertilization and liming were applied:

1. NPK (120 N : 90 P₂O₅ : 90 K₂O), without use of calcium (control);
2. NPK (120 N : 90 P₂O₅ : 90 K₂O) + 0.8 t/ha of "Njival Ca" fertilizer;
3. NPK (120 N : 90 P₂O₅ : 90 K₂O) + 1.6 t/ha of "Njival Ca" fertilizer;
4. NPK (120 N : 90 P₂O₅ : 90 K₂O) + 4.0 t/ha of "Njival Ca" fertilizer;
5. NPK (120 N : 90 P₂O₅ : 90 K₂O) + 8.0 t/ha of "Njival Ca" fertilizer.

As a lime fertilizer was used "Njival Ca" - ground lime of Serbian Glass Factory at Paraćin, obtained from the "Plana" mines on the Baba mount. It contained at least 98.5% of CaCO₃. Size of the elementary plot was 100 m² (10x10 m). Variant 1 (control without Ca) was involved in the study because in production of the mentioned crops (wheat, maize, soybean) NPK fertilizers were regularly used, and these conditions were similar to the production ones. Variants 2 and 3 were the variants of calcium fertilization usually used every year, and the variants 4 and 5 were the liming variants usually applied periodically every five years.

Weed determination was carried out according to the handbook of Čanak *et al.* (1978). We also used scientific and popular literature references (Behrend *et al.*, 1979; Javorka *et al.*, 1979; Hanf, 1980; Kojić, 1981; 1986; Šarić, 1978; Fisjunov, 1984; Tatić *et al.*, 1984).

The weed flora and vegetation have been studied by the method of testing area (control squares). We determined weediness, as well as the total raw and air-dry biomass. Determination of weediness was carried out during waxy ripeness in the wheat agrophyto-

Table 1. Life forms and number of weeds in wheat, maize, and soybean crops (individuals/m²)

L.F.*	Weed species	Wheat		Maize		Soybean		Mean	
		var. 1	var 2-5	var. 1	var 2-5	var. 1	var 2-5	var. 1	var 2-5
T	<i>Abutilon theophrasti</i> Med.	1.00	0.05	1.50	0.80	1.10	0.40	1.20	0.42
T	<i>Anthemis arvensis</i> L.	0.20	0.05	0.10	--	--	--	0.10	0.02
T	<i>Agrostemma githago</i> L.	0.50	0.05	--	--	--	--	0.20	0.02
T	<i>Amaranthus albus</i> L.	--	--	0.80	--	1.00	0.10	0.60	0.03
T	<i>Amaranthus retroflexus</i> L.	--	--	1.20	0.20	1.00	0.20	0.70	0.13
T	<i>Adonis aestivalis</i> L.	0.20	1.40	--	--	--	--	0.07	0.35
T	<i>Anthemis cotula</i> L.	1.10	0.20	--	--	--	--	0.35	0.07
T	<i>Apera spica-venti</i> (L.) P.B.	0.60	0.05	--	--	--	--	0.20	0.02
T	<i>Atriplex patula</i> L.	0.70	1.20	1.20	2.40	2.20	2.60	1.36	2.07
T	<i>Avena fatua</i> L.	1.00	0.05	--	--	0.10	--	0.36	0.02
T	<i>Bifora radians</i> M.B.	0.80	0.60	--	--	--	--	0.26	0.20
T	<i>Brasica campestris</i> L.	0.60	0.05	--	--	--	--	0.02	0.02
H	<i>Cardaria draba</i> L.	--	--	0.20	0.35	--	--	0.06	0.12
T	<i>Centaurea cyanus</i> L.	1.70	0.10	--	--	--	--	0.60	0.03
H	<i>Cicorium intubus</i> L.	0.40	0.60	--	--	--	--	0.13	0.20
G	<i>Cirsium arvense</i> (L.) Scop.	0.80	0.05	--	--	--	--	0.26	0.02
G	<i>Convolvulus arvensis</i> L.	1.20	1.65	0.80	1.25	2.30	2.50	1.43	1.80
G	<i>Cinodon dactylon</i> (L.) Pers.	0.05	--	0.15	--	0.10	--	0.10	--
T	<i>Delphinium consolida</i> L.	0.80	3.20	--	--	--	--	0.26	1.66
T	<i>Digitaria sanguinalis</i> (L.) Scop.	--	--	2.65	0.60	3.15	0.50	1.90	0.36
G	<i>Equisetum arvense</i> L.	--	--	0.60	0.05	0.80	--	0.67	0.02
H	<i>Eryngium campestre</i> L.	--	--	--	--	--	0.05	--	0.02
T	<i>Euphorbia falcata</i> L.	--	--	--	0.05	--	--	--	0.02
T	<i>Eragrostis major</i> Host.	--	--	0.20	--	0.20	0.05	0.13	0.02
G	<i>Gagea arvensis</i> (Pers.) Dum.	--	0.20	--	--	--	0.05	--	0.08
T	<i>Galeopsis tetrahit</i> L.	0.50	--	0.65	--	0.40	--	0.52	--
T	<i>Galium tricornue</i> Stock.	--	0.10	--	0.10	--	0.20	--	0.13
T	<i>Gipsophila muralis</i> L.	0.20	--	--	--	--	--	0.06	--
T	<i>Helianthus annuus</i> L.	--	--	0.10	--	--	0.05	0.03	0.02
T	<i>Hibiscus trionum</i> L.	--	--	0.20	0.50	0.10	0.50	0.01	0.33
T	<i>Heliotropium europaeum</i> L.	0.05	--	--	--	--	--	0.01	--
H	<i>Holcus lanatus</i> L.	0.10	--	--	--	0.10	--	0.02	--
H	<i>Inula salicina</i> L.	--	--	--	--	--	--	0.06	0.02
T	<i>Lactuca saligna</i>	0.05	0.15	--	--	0.10	0.05	0.05	0.05
T	<i>Lamium amplexicaule</i> L.	--	0.10	--	--	--	--	--	0.02

T	<i>Lathyrus aphaca</i> L.	0.05	0.50	--	--	--	--	--	0.02	0.17
T	<i>Lathyrus hirsutus</i> L.	--	0.05	--	--	--	--	--	--	0.02
T	<i>Lathyrus nissolia</i> L.	--	0.10	--	--	--	--	--	--	0.02
H	<i>Lathyrus tuberosus</i> L.	0.10	--	0.10	--	--	--	0.07	0.02	0.02
T	<i>Myagrurn perfoliatum</i> L.	--	0.10	--	0.15	0.15	0.15	--	--	0.13
T	<i>Panicum crus-galli</i> L.	--	--	0.80	1.10	1.20	1.60	0.69	0.90	0.90
T	<i>Polygonum convolvulus</i> L.	1.20	1.50	0.60	0.80	0.30	0.50	0.70	0.90	0.90
T	<i>Polygonum lapathifolium</i> L.	--	--	0.30	--	0.15	--	0.15	--	--
T	<i>Portulaca oleracea</i> L.	0.05	--	0.80	--	0.30	--	0.38	--	--
G	<i>Pteridium aquilinum</i> (L.) Kuhn.	--	--	0.10	--	0.05	--	0.05	--	--
T	<i>Ranunculus arvensis</i> L.	--	0.05	--	--	--	--	--	0.02	0.02
T-H	<i>Reseda lutea</i> L.	--	--	--	0.05	--	--	--	--	--
H	<i>Plantago media</i> L.	0.20	--	0.20	--	--	--	0.13	--	--
H	<i>Rumex acetosella</i> L.	--	--	0.20	--	--	--	0.07	--	--
T	<i>Raphanus raphanistrum</i> L.	0.20	--	0.20	--	0.20	--	0.20	--	--
H	<i>Sabia verticillata</i> L.	0.10	--	--	--	0.05	--	0.05	--	--
T	<i>Sinapis arvensis</i> L.	0.50	0.85	0.10	--	--	--	0.20	0.03	0.03
G	<i>Sonchus arvensis</i> L.	0.30	--	0.10	--	0.10	--	0.17	--	--
T	<i>Spergula arvensis</i> L.	0.80	0.05	0.20	--	--	--	0.35	0.02	0.02
T	<i>Stachys annua</i> L.	--	0.10	--	0.10	--	--	--	0.07	0.07
H	<i>Syphytum officinale</i> L.	0.20	--	0.20	--	0.10	--	0.17	--	--
H	<i>Veronica officinalis</i> L.	--	0.20	0.10	--	--	--	--	0.10	0.10
T	<i>Veronica bederifolia</i> L.	0.45	1.20	--	--	--	--	0.15	0.40	0.40
T	<i>Vicia tetrasperma</i> (L.) Schreb.	0.20	--	0.10	--	--	--	0.10	--	--
T	<i>Vicia panonica</i> Grantz.	0.30	--	--	--	--	--	0.10	--	--
T	<i>Vicia hirsuta</i> (L.) Gray.	--	--	--	--	--	--	0.03	--	--
T	<i>Viola arvensis</i> Murr.	0.10	0.05	0.10	--	--	--	0.07	--	--
T	<i>Xanthium strumarium</i> L.	2.10	0.30	3.20	0.50	2.80	0.40	2.70	0.40	0.40
Number of species		37	32	31	16	25	17	31.00	21.60	21.60
Number of weeds per m ²		19.40	14.30	17.75	9.00	18.00	10.10	19.18	10.03	10.03
Raw mass (g/m ²)		53.50	48.15	59.60	38.75	39.66	28.00	50.92	38.30	38.30
Air-dry mass (g/m ²)		17.50	12.60	21.45	12.95	12.60	9.05	17.18	11.53	11.53
Air-dry mass (%)		33.00	26.00	36.00	33.00	32.00	32.00	33.60	30.30	30.30

*L.F. = Life form

Table 2. Life spectar in weed communities of the investigated agrophytocenoses

Life forms	Variant - crop			
	wheat 1		wheat 2-5	
	No of sp.	%	No of sp.	%
<i>Terraphyta (T)</i>	27	73.0	27	84.3
<i>Hemicryptophyta (H)</i>	6	16.2	2	6.3
<i>Geophyta (G)</i>	4	10.8	3	9.4
Total	37	100.0	32	100.0
Life forms	maize 1		maize 2-5	
	No of sp.	%	No of sp.	%
	No of sp.	%	No of sp.	%
<i>Terraphyta (T)</i>	20	64.5	12	75.0
<i>Hemicryptophyta (H)</i>	6	19.3	1	6.3
<i>Geophyta (G)</i>	5	16.2	2	12.4
<i>Terro-hemicryptophyta (T-H)</i>	--	--	1	6.3
Total	31	100.0	16	100.0
Life forms	soybean 1		soybean 2-5	
	No of sp.	%	No of sp.	%
	No of sp.	%	No of sp.	%
<i>Terraphyta (T)</i>	17	68.0	13	76.4
<i>Hemicryptophyta (H)</i>	3	12.0	2	11.8
<i>Geophyta (G)</i>	5	20.0	2	11.8
Total	25	100.0	17	100.0
Life forms	total			
	No of sp.	%		
	No of sp.	%		
<i>Terraphyta (T)</i>	44	69.84		
<i>Hemicryptophyta (H)</i>	11	17.46		
<i>Geophyta (G)</i>	7	11.11		
<i>Terro-hemicryptophyta (T-H)</i>	1	1.59		
Total	63	100.0		

cenose, during earing in maize, and during flowering in the soybean crop. Herbicides were not used at the experimental field many years ago.

For the better clearness, changes of the weed flora and other observed parameters are given as the six-year mean of the crops, separately for the control (var. 1), and joint for the variants with applied calcium (var. 2-5) (tables 1 i 2).

RESULTS AND DISCUSSION

The most of crops request a slightly acid, neutral, or slightly alkal soil. Thus, alfalfa requests soil pH value of 7-8, barley 7-8, wheat and maize 6-7, sugar beet 6.5-7.5, onion 6.5-7.8, etc. A little higher tolerance to acid environment is shown by buckwheat, grapevine, strawberry, tomato, vetch, rhubarb, cucumber, Timothy's grass, and much higher tolerance by forage pea, lupine, millet, oats, potato, rye, and watermelon (Popović, 1960; Ognjanović et al., 1996). Stevanović (1991) stated that is very difficult to product biologically worthy and quality food because of higher content and mobility of some harmful elements (Al, Cd, Cu, Cr, Ni, Pb, NO₂), that could, except their phytotoxic effect, pollute plant fruits and vegetative organs. According to the same investigator, application of lime fertilizers (ground CaCO₃ and similar) through acidity decrease significantly decreases solubility of the harmful elements in soil, and so their higher accumulation in plants.

Weed plants have a similar behavior with crops. So Ognjanović (1987), by the study of some mineral matters outcoming, found out that dominant wheat and maize weeds contained 1.99% and 1.34% of Ca respectively, and Ca coming out of soil under wheat and maize was 9101 kgCa/ha and 8799 kgCa/ha respectively.

The same researcher consider *Stachys annua* L. and *Sonchus arvensis* L. as acidophilic weed plants. He also found out that mechanical weed replacement (weeding), when they had been replaced out of a crop, accelerated soil acidification, because significant calcium amounts came out of crop by weeds.

Some weed species tolerate an acid environment (*Spergula arvensis* L., *Rumex acetosella* L., *Equisetum arvense* L., *Holcus lanatus* L., *Deschampsia flexuosa* (L.) Trin., *Calluna vulgaris* (L.) Hull., *Lathyrus montanus* L., *Potentilla tormentilla* L., *Arnica montana* L., *Nardus stricta* L., *Blechnum spicant* L., *Juncus trifidus* L.), and some a neutral and slightly alkal (*Salvia pratensis* L., *Plantago media* L., *Teucrium montanum* L., *Centaurea scabiosa* Neck., *Deschampsia caespitosa* (L.) Beauv., *Cirsium oleraceum* (L.) Scop., *Angelica sylvestris* L., *Tussilago farfara* L., *Agrostis alba* L., etc.).

We observed in total, during six years of the investigation and in all three agrophytocenoses, 63 weed species, of which 46 in wheat, 36 in maize, and 31 in soybean. There were 13 species (20.63%) observed in all the agrophytocenoses. There were eight species of Monocotyledonae (12.70%), 53 of Dicotyledonae (84.12%), and two species were Pteridophytes (3.18%).

According to life form the most of weeds were terraptyta (T in tab. 1) with 44 species (69.84%), then hemicryptophyta (H) with 11 species (17.46%), geophyta (G) with seven species (11.11%), and one species was terro-hemicryptophyta (T-H) which was 1.59% of the total number. Such life spectar of the communities was caused by the intensive agrotechnique applied in the investigated crops production (crop rotation, cultivation, fertilization, protection, etc).

The dominant weed group in the wheat agrophytocenose were *Delphinium consolida* L., *Convolvulus arvensis* L., *Centaurea cyanus* L., *Anthemis arvensis* L., *Polygonum convolvulus* L., *Avena fatua* L. i *Xanthium strumarium* L. In maize crop the following species were dominant: *Abutilon theophrasti* Med., *Amaranthus retroflexus* L., *Atriplex patula* L., *Convolvulus arvensis* L., *Digitaria sanguinalis* (L) Scop., *Panicum crus-galli* L. i *Xanthium strumarium* L., and in soybean agrophytocenose *Abutilon theophrasti* Med., *Amaranthus albus* L., *Amaranthus retroflexus* L., *Atriplex patula* L., *Convolvulus arvensis* L., *Digitaria sanguinalis* (L) Scop., *Panicum crus-galli* L. i *Xanthium strumarium* L.

It might be seen that weed communities of maize and soybean were typical for crops with a lower density and alike each other (tab. 1). It also can be seen that the weed community of wheat was typical for small grains. In all three agrophytocenoses was observed a higher number of individuals and species per m² on the control without calcium, in comparision with the limed variants. That difference in wheat agrophytocenose amounted five species, in maize 15, and eight species in soybean. The highest difference was observed in maize agrophytocenose because, among others, maize phytomicroclimate (lower density) gave more opportunities for appearing and development of weed plants comparing with wheat and soybean crops, which had a higher density and their phytomicroclimate was more "closed", so the grown plant prevented higher weed infestation by competition. This lower species number in all three agrophytocenoses was followed by lower individuals number per m², as well as by lower raw and air-dry biomass in the variants fertilized by "Njival Ca" fertilizer.

It can be seen in table 1, according to the value of ecological index for soil pH (R; Kojić i Janjić, 1994), that in the control plots (without Ca) were observed the species tolerant to acid soils (R1- a plant living on very acid soils, pH = 3.0-4.5 and R2- a plant living on acid soils when pH is, 3.5-5.5) *Anthemis arvensis* L., *Apera spica-venti* (L) P.B., *Gypsophila muralis* L., *Pteridium aquilinum* (L) Kuhn., *Rumex acetosella* L., *Spergula arvensis* L., *Vicia tetrasperma* (L) Schreb., etc. On the other hand, in the variants of lime fertilization and liming we observed, among others, species with higher values of ecological index for soil acidity (R3- a plant living on slightly acid and neutral soils, R4- a plant

living mainly on alkal soils when pH is 5.5-8.0, and R5- a plant obligately living on alkal soils) such were *Sonchus arvensis* L., *Atriplex patula* L., *Convolvulus arvensis* L., *Galium tricornne* Stock., *Lathyrus tuberosus* L., *Myagrum perfoliatum* L., *Plantago media* L., *Salvia verticillata* L., *Stachys annua* L., *Delphinium consolida* L., and other species demanding a lower soil acidity. Similar results were found by Ognjanović et al. (1995; 1996). As is seen, application of the lime fertilizer ("Njival Ca") significantly decreased weediness, which decreased the need for use of herbicides and other weed control measures. It is very important for environmental protection and economical production of grown crops.

Number of geophyta and hemicryptophyta (G, H) was lower on the control plots. It can be explained by the presence of a robust root system in two-year and perennial species, that can use mineral matters from deeper layers of the control plots, despite significantly higher pH and less-favourable life conditions (Ognjanović, 1987). We could state that the geophyte species *Convolvulus arvensis* L. demands a less-acid environment, because number of *Convolvulus* plants per m² was significantly higher in the variants with applied calcium. This might be seen better in the terraptyta species *Atriplex patula* L., *Panicum crus-galli* L., *Polygonum convolvulus* L., *Hibiscus trionum* L., which was confirmed by the values of ecological index for soil acidity (Kojić i Janjić, 1994). However, significantly higher number of *Digitaria sanguinalis* (L) Scop., *Amaranthus retroflexus* L. etc., was observed in the maize and soybean control plots, as well as of *Abutilon theophrasti* Med. in the wheat agrophytocenose. It means these species tolerate well soils with lower pH, regardless their R3 ecological index for soil acidity (living on slightly acid and neutral soils). We can state, therefore, they are able to adapt to ecological conditions (significantly lower pH) of the control.

Antropogenous factors are very important, and in some cases crucial for appearing, growth and development of weed plants, as well as for weed communities forming (Kojić i Janjić, 1994). The mentioned influence can be seen in life forms change, so between agrophytocenoses, as between variants fertilized and unfertilized by calcium (tab. 2).

We found out four life forms. The domination of terraptyta is visible in all the agrophytocenoses, as in control variants as in the calcium fertilized ones. Depending of agrophytocenose, their percent on the control was from 64.5% (maize) to 73.0% (wheat) or 68.5% in average, and on the variants fertilized by calcium (var. 2-5) from 75.0% (maize) to 84.3% (wheat) or 78.5% in average.

Life forms change in the variants fertilized by calcium was observed in every weed community. One can see (tab. 2) that man's intervention (application of calcium) caused an increase of terraptyta percent, meanly by 10%. That occurred because of decreased

percent of geophyta and hemicryptophyta life forms in the variants of calcium fertilization and liming (2-5), comparing with the control (1), and reason for that was the improvement of physical, biological, and especially chemical soil properties, not only soil acidity (pH), but also other traits favourable for terraphyta (Ognjanović *et al.*, 1995), which expelled geophyta and hemicryptophyta from weed community.

A little higher number of geophyta and hemicryptophyta in maize and soybean agrophytocenoses, in general, was caused by the sowing term, but also by the other agrotechnique measures usually applied in the production of spring crops with lower crop density. The application of calcium improved above mentioned soil properties; as first soil acidity decreased, which caused appearing of a higher number of terraphyta species (tab. 2), mainly those with higher value of ecological index for soil pH.

CONCLUSION

The use of the "Njival Ca" fertilizer decreased number of acidophilic weeds with the simultaneous increase of calciphilic ones. Also decreased the total weediness, number of species and individuals per m², as well as raw and air-dry weed mass per m². It is very important for environmental protection and economical production of grown crops.

We also observed some changes in weed communities life spectar. At the variants of calcium fertilization and liming number of terraphyta increased, and number of geophyta and hemicryptophyta decreased.

The dominant weed group in the wheat agrophytocenose were *Delphinium consolida* L., *Convolvulus arvensis* L., *Centaurea cyanus* L., *Anthemis arvensis* L., *Polygonum convolvulus* L., *Avena fatua* L. i *Xanthium strumarium* L. In maize crop the following species were dominant: *Abutilon theophrasti* Med., *Amaranthus retroflexus* L., *Atriplex patula* L., *Convolvulus arvensis* L., *Digitaria sanguinalis* (L) Scop., *Panicum crus-galli* L. i *Xanthium strumarium* L., and in soybean agrophytocenose *Abutilon theophrasti* Med., *Amaranthus albus* L., *Amaranthus retroflexus* L., *Atriplex patula* L., *Convolvulus arvensis* L., *Digitaria sanguinalis* (L) Scop., *Panicum crus-galli* L. i *Xanthium strumarium* L.

REFERENCES

- Behrend, M., Haf, M. (1979): Trave - korovi na oranicama (prevod sa nemačkog). BSF, Ludwigshafen. Zagreb.
- Čalić, P. (1993): Kalcifikacija - popravka zemljišta unošenjem kreča. Srpska fabrika stakla, Paraćin.
- Čanak, M., Parabućski, S., Kojić, M. (1978): Ilustrovana korovska flora Jugoslavije. Matica srpska, Novi Sad.
- Fisjunov, A.V. (1984): Sornie rastenja. "Kolos", Moskva.
- Gračanin, M. (1947): Kalcifikacija tala. Nakladni zavod, Zagreb.
- Hanf, M. (1980): La erbe infestanti e le loro piante. Milano.
- Javorka, S., Csapody, V. (1979): Ikonografie der flora des Sudostlichen Mitteleuropa. Akademiai Kiado, Budapest.
- Kojić, M. (1981): Određivanje korova. "Nolit", Beograd.
- Kojić, M. (1986): Mala korovska flora. "Naučna knjiga", Beograd.
- Kojić, M., Janjić, V. (1994): Osnovi herbologije. "Nauka", Institut za istraživanja u poljoprivredi "Srbija", Beograd.
- Kovačević, J. (1976): Korovi u poljoprivredi. "Znanje", Zagreb.
- Novaković, J. (1995): Uticaj različitih količina NPK i Ca đubriva na broj i biomasu korova u pšenici. Prirodno-matematički fakultet, Kragujevac.
- Ognjanović, R. (1987): Uticaj načina primene i količina mineralnih đubriva i načina obrade zemljišta na strukturu i dinamiku korovskih sinuzija u pšenici i kukuruzu. Doktorska disertacija. Poljoprivredni fakultet, Sarajevo.
- Ognjanović, R. (1990a): The influence of method of application and rates of fertilizers on structure and dynamics of weed communities in wheat. Review of research works, No. 10, p5-72. Institute for Small Grains, Kragujevac.
- Ognjanović, R. (1990b): Uticaj načina primene i količine mineralnih đubriva na strukturu i dinamiku korovskih sinuzija u kukuruzu. Radovi Poljoprivrednog fakulteta Univerziteta u Sarajevu, No. 42, p27-60.
- Ognjanović, R., Božić, D., Milovanović, M. (1996): Uticaj đubrenja kalcijumom i kalcizacije na zakorovljenost pšenice, kukuruza i soje. V kongres o korovima, Zbornik radova, p432-440, Banja Koviljača.
- Ognjanović, R., Božić, D., Zdravković, L. (1995): The effect of "Njival Ca" on the weed flora and vegetation in crop and environment. Savetovanje "Popravka kiselih zemljišta Srbije primenom krečnog đubriva 'Njival Ca', SFS, Paraćin.
- Ognjanović, R., Kostić, M., Đokić, D., Jelić, M., Jelenković, R. (1994): Changes of certain soil properties after application of calcium fertilizer "Njival Ca" and cropping agricultural species. Zemljište i biljka. Vol. 43, No. 3, p195-202.
- Ognjanović, R., Lomović, S., Đokić, D., Jelić, M. (1994): The effect of calcium fertilization and liming on the soil improvement and grain yield of wheat, corn and soybean. Fertilizers and Environment, 51-54, Netherlands.
- Popović, Ž. (1960): Agrohemijska. Poljoprivredni fakultet, Sarajevo.
- Stevanović, D. (1991): Značaj kalcifikacije kiselih zemljišta u proizvodnji kvalitetne i biološki vredne

hrane. *Ekonomika poljoprivrede*, Vol. 38, No. 6-8, p391-397.

Stevanović, D., Jakovljević, M., Martinović, Lj. (1995): Rešavanje problema kiselih zemljišta Srbije - preduslov povećanja proizvodnje hrane i zaštite zemljišta. Savetovanje "Popravka kiselih zemljišta Srbije primenom krečnog đubriva 'Njival Ca', Zbornik radova p7-21, Paraćin.

Šarić, T., (1978): Atlas korova. NIŠRO "Svjetlost", Sarajevo.

Tatić, B., Petković, B. (1984): Praktikum iz sistematike i filogenije viših biljaka. Univerzitet u Beogradu, Beograd.

Veljović, S. (1995): Uticaj đubrenja kalcijumom i kalcifikacije na popravku zemljišta, prinos pšenice (*Triticum vulgare*) i korovsku vegetaciju. Prirodno-matematički fakultet, p1-42, Kragujevac.

Zdravković, L., Ognjanović, R., Lomović, S. (1994): The effect of ground limestone on the weed flora and vegetation in crop and environment. SMIS '94, p371-377, Faculty of Agriculture, Zemun.

REZIME

FLORISTIČKI SASTAV USEVA PŠENICE, KUKURUZA I SOJE POSLE KALCIZACIJE

Radomir OGNJANOVIĆ, Nebojša DELETIĆ

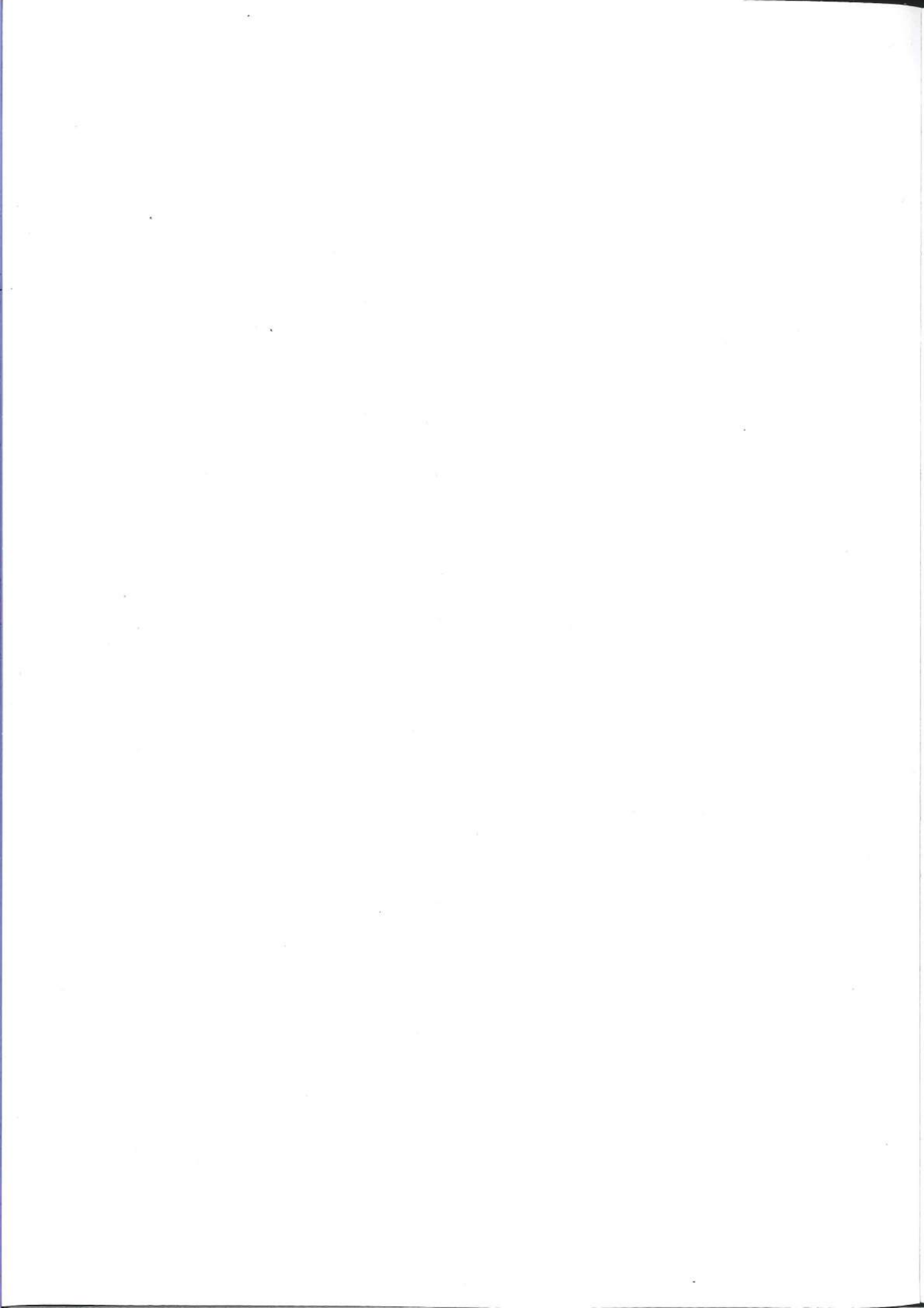
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Ispitivanja su izvršena u šestogodišnjem razdoblju (1989/90-1994/95), na oglednom polju Centra za strna žita u Kragujevcu, na tropskom stacionarnom ogledu (pšenica, kukuruz, soja), na zemljištu tipa smonica (vertisol). Proučavan je uticaj đubrenja kalcijumom i kalcizacije na floristički sastav agrofitoracena pšenice kukuruza i soje.

Upotrebom kalcijuma (đubrivo "Njival Ca") poboljšana su fizička, hemijska i biološka svojstva zemljišta (smonica). Promene koje su se dogodile u ovom zemljištu su dovele do izvesnih promena u florističkom sastavu agrofitoracena pšenice, kukuruza i soje. Smanjena je brojnost acidofilnih korova uz istovremeno povećanje broja kalcifilnih vrsta. Takođe, smanjena je i ukupna zakorovljenost, kao i ukupna sveža i vazdušno suva biomasa korova. Došlo je i do određenih promena u životnim formama proučavanih agrofitoracena uslovljenih primenom kalcijuma. Izdvojene su i dominantne grupe korova agrofitoracena pšenice, kukuruza i soje.

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A SUPPLEMENT TO THE KNOWLEDGE OF ALGAE OF THE TWO WATER ECO-SYSTEMS IN THE NEDZINAT CIRCUE

Violeta UROSEVIC

FNS, Biology Department, Vidovdanska street No.--, 38000 Pristina, Yugoslavia

ABSTRACT

The paper presents the results of algological analysis (July 1997) of the two water eco-systems in the Nedzinat circue on Prokletije Mountains. Some 42 taxa were found in Dreljsko Lake, while 16 were found in the spring that lays isolated below the lake. Total composition of both communities was presented with 54 taxa: *Cyanophyta* - 4, *Chrysophyta* - 1, *Bacillariophyta* - 44, *Euglenophyta* - 1 and *Chlorophyta* - 4. The representatives of *Bacillariophyta* community, pre-

sented with 78.5%, 87.4% respectively, were the most numerous in both of the systems examined. A quantitative domination of *Phormidium autumnale* (*Cyanophyta*) species was determined in the spring. The water quality determined on the basis of indicator's values of types of algae (25) was good (1.36, 1.43 respectively) indicating the affiliation to oligo-beta-mezzo-saprobic degree, or to the 1st and 2nd quality class.

Key words: Peryplithon algae, indicator's species, Prokletije Mountains, Dreljsko lake, spring.

INTRODUCTION

High-mountain lakes of Prokletije are relatively less researched from the algological aspect. Up to now, we could have only got, literature data of the lakes on Visitor and Bogicevica (Petkovic Smiljka and Petkovic St., 1971), then, the algae of Ridsko, Visitorsko, Plavsko and Rikavacko lakes (Petkovic Sm., 1975), as well as, a supplement to the knowledge of Plavsko lake algae (Petkovic Sm. and Petkovic St., 1982). We have also given a supplement to the knowledge of algae of the water eco-systems on Djeravica (Urosevic, 1997). Finally, the algae of the spring and the creek of Velika Podina on the saddle of Nedzinat and Zuti Kamen were researched too.

Dreljsko lake and the spring are settled in the circue that is oriented in the direction of southeast - northwest with its face starting from the saddle mentioned between the spurs of Nedzinat and Zuti Kamen (2,522 m a/s/l). Water currents are short and periodical in higher zones of the circue, due to karstic terrain. The first larger accumulation, in which, the water from the surrounding slopes are collected is Dreljsko Lake, situated at an altitude of 1,820-m (Figure 1). The lake is of pear-like form. The water, which flows off the lake, sinks. At some 2 km downstream (1,160 m), the arm of the lake river merges with the river arm of the neighboring Kucisko lake and both together make up Nedzinat creek, that is the right-side tributary of Pecka Bistrica.

Dreljsko lake is some 130-m long and some 75-m wide, and we have estimated the depth to be some 2.0-m in its deepest part, during the sampling day. It dries intensively during summer months, which is indicated by the shoreline that is far from the water surface. The lake is situated in the lakebed whose

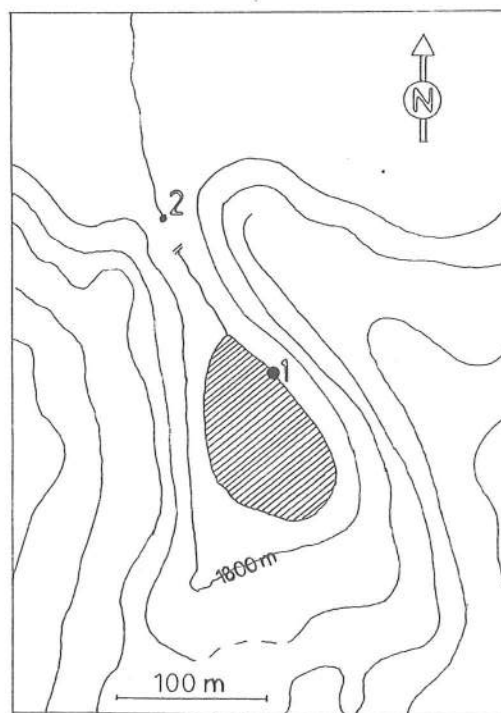


Figure 1. The position of Dreljsko Lake in Nedzinat circue with the sampling spot indicated (1) and the position of the spring below the lake (2)

shore is built up of the rocky blocks and large gravel. It is surrounded by dense coniferous forest. The spring below the lake has no physical connection with it, but, probably, the lake water feeds it.

Pedological-geologic ground of the whole complex is a shallow brown soil on compact limestone.

Table 1. Systematic census of overgrowing algae, frequency and presence of indicating species in Dreljsko Lake (1) and the spring below the lake (2).

TAXONS	1	2	INDEX OF SAPROBITY
CYANOPHYTA			
<i>Calothryx parietina</i> Thuret	1		o
<i>Merismopedia punctata</i> Meyen	1		
<i>Microcystis elabens</i> (Menegh) Kütz	1		
<i>Phormidium autumnale</i> (Ag.) Gom.	1	5	b - a
CHRYSTOPHYTA			
<i>Hydrurus foetidus</i> (Vill.) Trev.		3	x - o
BACILLARIOPHYTA			
<i>Achnantes lanceolata</i> (Bréb.) Grun.		1	x - o
<i>Achnantes lanceolata</i> var. <i>lanceolata</i> f. <i>ventricosa</i> Hust.		1	
<i>Amphora ovalis</i> var. <i>gracilis</i> Ehr.	1		
<i>Anomoeoneis serians</i> (Bréb.) Cl.	1		
<i>Anomoeoneis serians</i> var. <i>brachysira</i> (Bréb.) Cl.	1		x
<i>Caloneis alpestris</i> Cl.	1		x
<i>Caloneis schumaniana</i> (Grun.) Cl.	1		o - b
<i>Caloneis silicula</i> (Ehr.) Cl.	1		o - b
<i>Cyclotella bodanica</i> Eulens.	1	1	o
<i>Cyclotella comta</i> (Ehr.) Kütz.	1	1	o
<i>Cymbella aequalis</i> W. Sm.		1	
<i>Cymbella affinis</i> Kütz	1	1	o - b
<i>Cymbella cistula</i> var. <i>gibbosa</i> Brun.	1		
<i>Cymbella hauckii</i> V.H.	1		
<i>Cymbella hebridica</i> (Greg.) Grun.	1		
<i>Cymbella lanceolata</i> (Ehr.) V.H.		1	b
<i>Denticula tenuis</i> Kütz	1		x
<i>Denticula tenuis</i> var. <i>crassula</i> (Näg.) Hust.	1		
<i>Diatoma hiemale</i> var. <i>mesodon</i> (Ehr.) Grun.	1		x
<i>Diatome vulgare</i> var. <i>productum</i> Grun.		1	
<i>Diploneis parma</i> Cl.		1	
<i>Fragilaria pinnata</i> Ehr.	1		
<i>Frustulia rhomboides</i> var. <i>saxonica</i> f. <i>undulata</i> Hust.	1		
<i>Gomphonema angustatum</i> (Kütz.) Rabenh.		1	o
<i>Gomphonema angustatum</i> var. <i>productum</i> Grun.		1	b - a
<i>Gomphonema angustatum</i> var. <i>undulatum</i> Grun.		1	
<i>Hantzschia amphioxys</i> f. <i>capitata</i> O. Müll.	1		
<i>Melosira italica</i> (Ehr.) Kütz.	1		o
<i>Meridion circulare</i> Ag.		1	x
<i>Navicula cuspidata</i> var. <i>heribrandii</i> Perag.	1		
<i>Navicula pupula</i> var. <i>rectangularis</i> (Greb.) Grun.	1		

<i>Navicula radiosa</i> Kütz.	1		<i>o - b</i>
<i>Navicula viridula</i> Kütz.	1		<i>a</i>
<i>Neidium affine</i> var. <i>amphirhynchus</i> (Ehr.) Cl.	1		
<i>Neidium iridis</i> var. <i>amphigomphus</i> (Ehr.) Cl.	1		
<i>Nitzschia thermalis</i> var. <i>minor</i> Hilse.	1		
<i>Nitzschia vermicularis</i> (Kütz.) Grun.	1		<i>b</i>
<i>Pinnularia divergens</i> var. <i>elliptica</i> Grun.	1		
<i>Pinnularia episcopalis</i> var. <i>brevis</i> Cl.	1		
<i>Stauroneis anceps</i> f. <i>gracilis</i> (Ehr.) Cl.	1		
<i>Stauroneis fluminea</i> Patr. & Freese	1		
<i>Surirella linearis</i> W. Sm.	1		<i>b</i>
<i>Surirella linearis</i> var. <i>helvetica</i> (Brun.) Meist.	1		
<i>Synedra ulna</i> var. <i>biceps</i> (Kütz.) Schonf.	1		<i>b</i>
EUGLENOPHYTA			
<i>Trachelomonas volvocina</i> var. <i>subglubosa</i> Lemm.	1		
CHLOROPHYTA			
<i>Oedogonium</i> sp.	1		
<i>Pediastrum boryanum</i> (Turp.) Menegh.	1		<i>b</i>
<i>Scenedesmus dispar</i> Bréb.	1		
<i>Staurostrum punctulatum</i> Bréb.	1		<i>o</i>

MATERIAL AND METHODS

The water temperature recordings and the algae sampling were done July 1997 in Dreljsko lake and the spring laying below (Fig. 1). The alcohol lab thermometer (scale from -20°C to 50°C) was used to record the water temperature. The samples for the algological analysis were collected by scratching the submerged stones and by squeezing the moss. The fixing was done in a 4% solution of Phoraldehide. The microscope analysis was made by the "Ergeval" (Zeiss, Jena) microscope in the laboratory of the Biology Department of the FNS in Pristina.

The keys and handbooks were used for the determination of the systematic taxon affiliation: Cvijan & Blaženčić (1996), Dedusenko et al. (1959), Gollerbach et al. (1953), Hustedt (1930), Hustedt (1961 - 1965), Hindak et al. (1975), Komarenko et al. (1975), Lazar (1969), Patrick - Reimer (1966), Pascher (1925), Vodenicharov et al. (1971), Zabelina et al. (1951), Popova (1966), Palmar-Mondviceva (1982). Indicators of water saprobity were established according to Sladeček (1973). Saprobity index was determined according to Pantle and Buck (1955).

RESULTS AND DISCUSSION

The Dreljsko lakeshore is rocky and its water (16.0°C) is probably enriched with lime content (chemical recordings were not made). As a proof to the respective is that the limestone layer is visible in the jar

with the sample collected. Regarding the respective and other ecological-geographic factors prevailing in the area researched, a specific algae community, presented with 42 taxa, was determined (Table 1, Fig. 2). All of the taxa were found in quite rare, individual samples. Among these, the representatives of *Bacillariophyta* community were the most numerous with 33 taxa (78.5%). Subdominant communities of *Cyanophyta* and *Chlorophyta* participated with 4 taxa each (9.5%), while the representatives of *Euglenophyta* indicated their presence only with the taxon of *Trachelomonas volvocina* var. *subglubosa* (2.5%).

A spring with fast water flow (10.0°C) lays isolated below Dreljsko Lake. Its poor community of algae was presented by 16 taxa only, dispersed on small-submerged stones and rare moss at the bottom of the spring. *Cyanophyta* (6.3%) with a massively frequent species of *Phormidium autumnale*, *Chrysophyta* (6.3%) with well frequent species of *Hydrurus foetidus* and *Bacillariophyta* (87.4%) with 14 individually presented taxa (Table 1, Figure 2) indicated their presence in the composition of the spring community. A massive presence of *Phormidium autumnale* species could be connected with a complex action of ecological factors, but it is most probable that the moss present, through the process of mineralization, provides nitrogen, easily attainable for a strong development of nitrogen-fixing species of *Phormidium autumnale* (Gecen, 1990).

June 1, 1997, the analysis of overgrowing algae determined 54 taxa in Dreljsko Lake and the spring located near by the lake, as follows: *Cyanophyta* - 4,

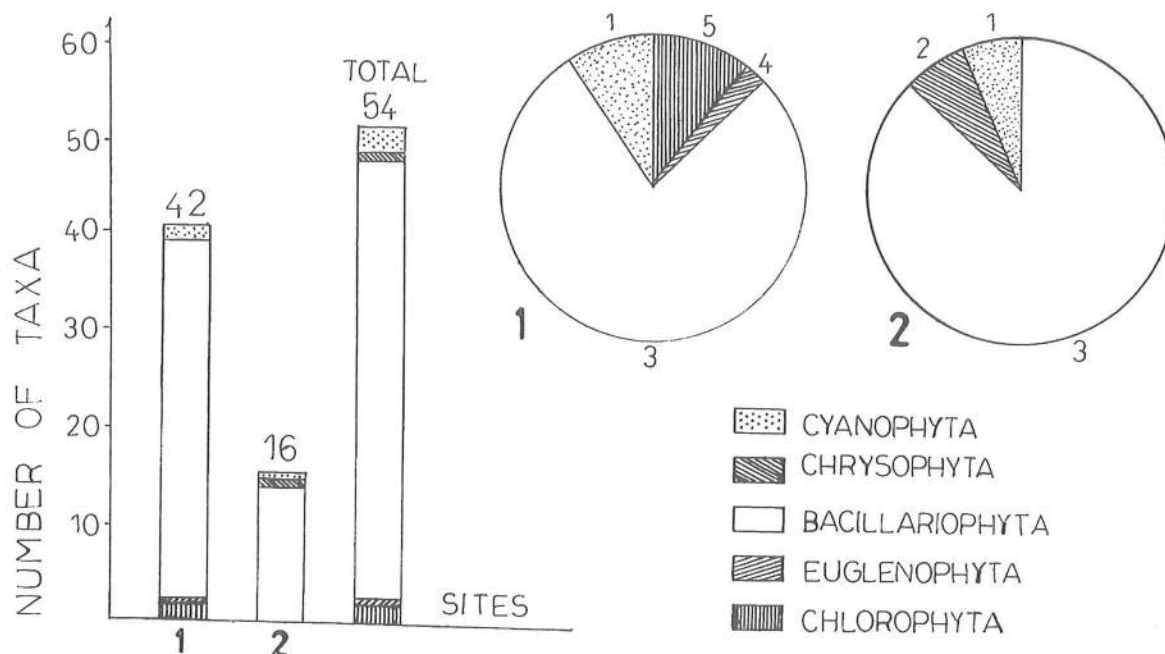


Figure 2. The number of overgrowing species of algae in Dreljsko Lake (1) and the spring below the lake (2) July 1996

Chrysophyta - 1, *Bacillariophyta* - 44, *Euglenophyta* - 1, and *Chlorophyta* - 4.

The complexity of both communities researched is reflected in the systematic characteristics of the taxa determined (54), as well as in the taxon affiliation to a large number of various genera (31). Accordingly, an emphasis is given that the richest genera of *Cymbella* and *Navicula* had only 4 taxa each.

Although Dreljsko Lake and in the spring below the lake represent two different eco-systems, insignificantly remote one from another, the presence of 4 mutual species were determined, as follows: *Phormidium autumnale* (*Cyanophyta*), *Cyclotella bodanica*, *C. compta* and *Cymbella affinis* (*Bacillariophyta*). Table 1 indicates that the qualitative algological analysis in Dreljsko Lake and in the spring below, determined total (54 taxa) 25 species indicators of water saprobity. The presence of an alpha-mezzo-saprobe species (*Navicula viridula*) and higher presence of oligo-saprobe (10 species, or 40.0%) and xeno-saprobe (7 species, or 28.0%) compared to beta-mezzo-saprobe indicator species (7, or 28.0%), witness the purity of water tested. The respective is also confirmed by the results obtained on the basis of calculated low index values of water saprobity (1.36, 1.43 respectively) and v.v., - high water bonus (Class 1 to Class 2) for both water system examined.

The algae of various eco-systems: lakes, river arms, springs were examined on the mountain massif of Prokletije (Urosevic, 1997, 1998). The algae residences were examined individually, but also within the complex that considers the action of the same climatic factors, geologic and pedological ground, as well as, an insignificant distance of the localities. A mosaic diversity of floral and vegetation structure of

each algae residence remained unexplained from the ecological point. The above is confirmed by the presence of an insignificant number of common species in, at present, researched ecosystems, as follows: within the complex of Djeravicka lakes (2 lakes) and river arms (3 river arms) only 3 common species were determined out of total 239 species. At the locality of Velika Podina on Nedzinat saddle in 2 springs and the creek formed by the two spring arms, out of 73 taxa, common species were not determined, while between the right spring (30 taxa) and the creek (47 taxa), 12 common species were determined, and between the left spring (11 taxa) and the creek, only 3 common species were found.

Taxonomic complexity is also reflected in the presence of an insignificant number, but, probably, more tolerant species, as follows: *Phormidium autumnale* (*Cyanophyta*), *Cyclotella bodanica*, *Gomphonema angustatum*, *Neidium iridis* var. *amphigomphus*, *Nitzschia thermalis* var. *minor* (*Bacillariophyta*) and *Trachelomonas voivocina* var. *subglubosa* (*Euglenophyta*), as these are frequently found in the Prokletije eco-systems examined.

REFERENCES

- Braune W., Leman A. und Taubert H., 1982. Pflanzenanatomisches Praktikum II. Gustav Fischer Verlag. Stuttgart.
- Blaženčić J. & Cvijan M., 1996. Flora algi Srbije. Cyanophyta. Naučna knjiga. Beograd.
- Dedusenko-Ščegoleva A.M., Matvivenko L.A. Škorbatov, 1959. Chlorophyta. Opređel. presnov. vodorosli SSSR, 8: 1-230, Moskva - Leningrad.

Gecen M.V., 1990. Vodorosli kak konstitucionaja osnova žizni vjisokoširotnih ekosistema. Botaničeskij žurnal, 75(12): 1641-1646.

Golerbah M.M., E.K. Kosinkaja, V.I. Poljanskij, 1953. Sinzelenije vodorosli. Opredel. presnov. vodorosli SSSR, 2: 1-652.

Golerbah M.M., 1977. Vodorosli. Tom treći, Prosvešćenije. Moskva.

Hindak F., J. Komarek, P. Marvin, J. Ružička, 1975. Ključ na určovanie vytrsných rastlin. I. diel. Ri-asu. Slovenske pedagogiske nakladateľstvo. Bratislava.

Hustedt, F., 1930. Bacillariophyta. Subwasserflora Deutschlands. Helf 10, 2. Aufl., 23.

Hustedt F., 1961 - 1965. Rabenhorst Krypt., Fl. Die Kieselalgen, 3. Teil.

Komarenko L.E., I.I. Vasiljeva, 1975. Presnovodnie diatomov i sinzelenie vodorosli vodemov Jakuti. Izdatel'stvo Nauka, Moskva.

Lazar, J., 1969. Alge Slovenije. Slovenska Akademija znanosti in umetnosti., Ljubljana.

Palmar G.M.-Mondviceva, 1982. Opredel. presnov. vodorosli. Zelenie vodorosli. Vjip. 11(2), Conjugatophyceae, Desmidiaceae. Nauka. Leningrad.

Pantle R., Buck H., 1955. Die Biologische Überwachung der Gewässer und die Darstellung der Ergebnisse besondere Mitteilungen Z. Deut. Gewässerkunde, 12: 135-143.

Pascher A., 1925. Süsswasser-flora Deutschlands, Österreich und der Schweiz., Cyanophyceae, Helf 12. Prag.

Patrik R.W., E.C. Reimer, 1966. The Diatoms of the United States. Acad. Nat. Sci. of Philadelphia. Monograph no. 13, Philadelphia.

Petković Smiljka i Petković S., Sastav i karakter planktonskih zajednica dva mala visokoplaninska glacialna jezera na planini Visitoru i Bogičevici u Crnoj Gori. Poljoprivreda i šumarstvo, 17(3): 3-30. Titograd.

Petković Smiljka, 1975. Prilog poznavanju taksonomije i distribucije Bacillariophyceae u slatkim vodama Crne Gore. Poljoprivreda i šumarstvo, 21(2): 33-56. Titograd.

Petković Smiljka i Petković S., 1982. Prilog poznavanju planktona Plavskog jezera. Poljoprivreda i šumarstvo, XXVIII(2): 29-53. Titograd.

Popova T.G., 1966. Euglenovije vodorosli. Vjip. 1. Euglenophyta. Izdatel'stvo Nauka. Moskva.

Proškina-Lavrenko, A.I., 1974. Diatomovije vodorosli SSSR. In: Gleser S.I. (ed.) Diatomei ozer. Izdatel'stvo Nauka, Leningrad.

Sladeček V., 1973. System of water quality from biological point of view. Archiv für Hydrobiologie. Beih 7, Ergebnisse der limnologie, e. Schweizerartsche verlagbuchhandlung (Nagel und Obermiller), Stuttgart.

Urošević Violeta, 1997. Periphyton Algae in the System of Djeravica Lakes on the Spring Branch of Erenik. Univ. Thought, Nat. Sci., III(2): 11-21, Pristina.

Vodeničarov D., S.T. Draganov, D. Temniskova, 1971. Flora na Bolgaria. Narodna prosveta. Sofija.

Zabelina M.M., Kiseleva L.A., Proškina-Lovrenko A.I., V.C. Šešukova, 1951. Opredel. Presnov. vodorosli SSSR, Vjip. 4. Diatomovije vodorosli, Akademia nauka SSSR, Leningrad.

REZIME

PRILOG POZNAVANJU ALGI DVA VODENA EKOSISTEMA U NEDŽINATSKOM CIRKU

UROŠEVIĆ Violeta

PMF, Odsek za biologiju, Vidovdanska bb, 38000 Pristina

Dreljsko jezero (1820 m) i izvor koji izolovano leži ispod jezera (Prokletije) ispitivani su sa algološkog aspekta jula 1997. godine. Analizom obraštaja utvrđeno je ukupno 54 taksona: *Cyanophyta* - 4, *Chrysophyta* - 1, *Bacillariophyta* - 44, *Euglenophyta* - 1 i *Chlorophyta* - 4.

Predstavnici zajednice *Bacillariophyta* imali su najveću brojnost taksona (78,5 odnosno 87,4%) na oba ispitana lokaliteta (Tabla 1, Figura 2).

Dreljsko jezero je u vreme ispitivanja predstavljeno sa 42 taksona. Svi taksoni su nadjeni u vrlo retkim, pojedinačnim primercima. Reakcija na kvantitativnu selektivnost taksona može se dovesti u vezu sa ekološkim faktorima sredine, od kojih najvažnijim smatramo sadržaj kreča u vodi, čije su naslage jasno vidljive u teglici sakupljenog uzorka.

U odnosu na Dreljsko jezero izvor je imao siromašniju zajednicu algi, predstavljenu sa 16 taksona, ali i kvantitativnu dominaciju vrste *Phormidium autumnale* (*Cyanophyta*). Masovni razvoj ove vrste verovatno je u funkcionalnoj vezi sa mahovinama naseljenim u izvoru.

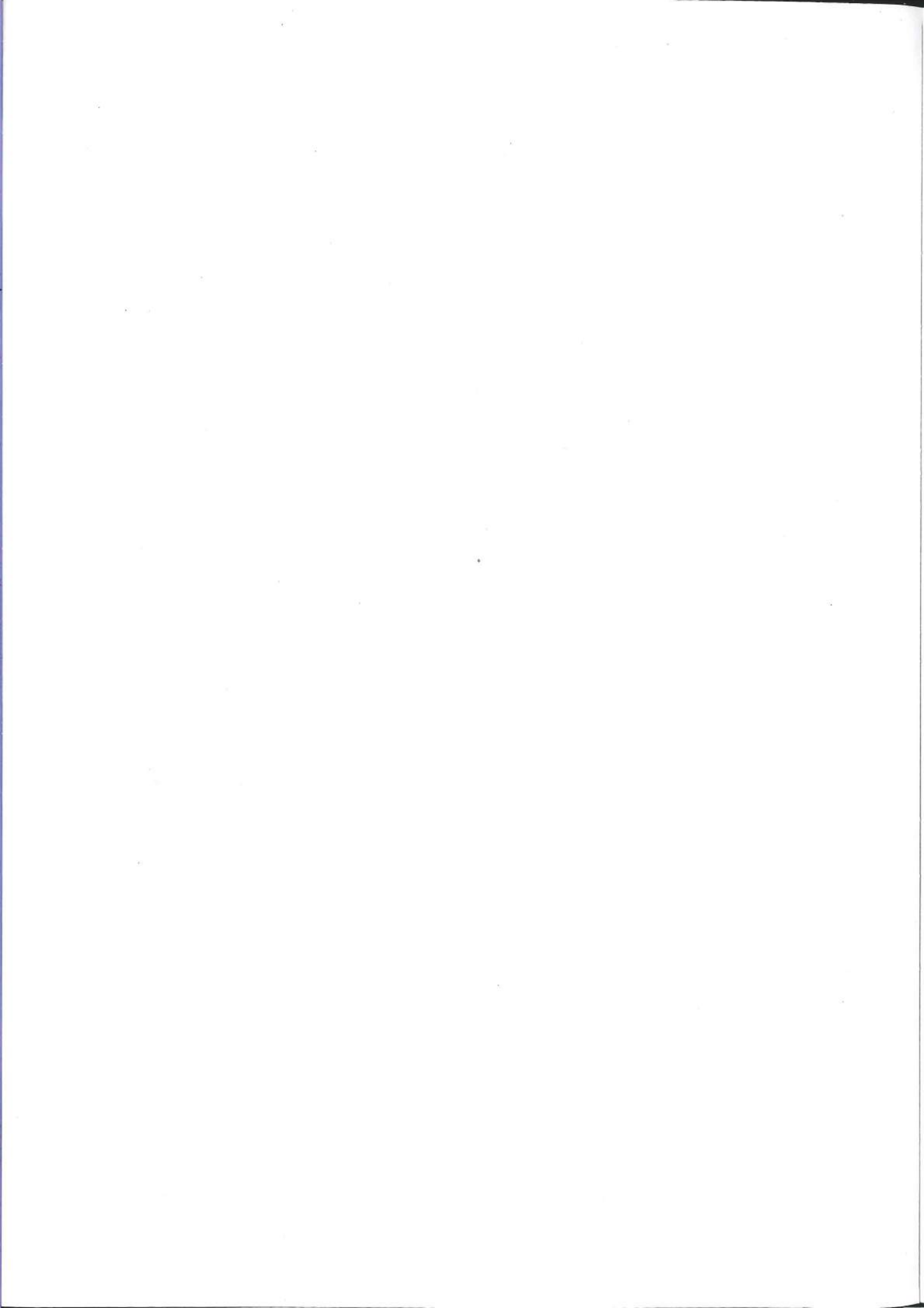
Taksonomska složenost ispitanih fitocenoza ogleda se i u pripadnosti taksona (54) velikom broju rodova (31): *Cymbella* i *Navicula* kao najbrojnije, imale su samo po 4 taksona.

Iako su ispitivana dva različita vodena ekosistema, svaka zajednica algi pojedinačno, imala je jedinstven sastav, ali i 4 zajedničke vrste: *Phormidium autumnale* (*Cyanophyta*), *Cyclotella bodanica*, *Cyclotella comta* i *Cymbella affinis* (*Bacillariophyta*).

U Dreljskom jezeru i izvoru utvrđeno je ukupno (54 taksona) 25 vrsta algi indikatora saprobnosti vode: ksenosaprobnih - 7 (28,0%), oligosaprobnih - 10 (40,0%), betamezosaprobnih - 7 (28,0%) i alfamezosaprobnih - 1 (4,0%). Izračunata vrednost indeksa saprobnosti u oba ispitana staništa algi bila je (1,36 odnosno 1,43) u granicama oligobetamezosaprobnog stupnja, tj., pripadnost I - II klase boniteta vode.

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Flora and Vegetation of High-mountain Peat-bogs of Mt. Šar-planina

Vladimir RANDJELOVIĆ¹, Bojan ZLATKOVIĆ², Lidija AMIDŽIĆ³

¹Faculty of Technology Leskovac, University of Niš

²Biological Society "Dr Sava Petrović" Niš

³The Institute of Nature Conservation of Serbia, Priština

ABSTRACT

Flora and Vegetation of high-mountain peat-bogs of Mt. Šar-planina.

In this paper results of investigation of flora and vegetation of high-mountains peat-bogs of serbian part of Mt. Šar-planina are presented. On

peat-bogs of Mt. Šar-planina 8 species of mosses and 80 species of vascular plants are found. Peat-bog's vegetation belong to classis Scheuchzerio-Caricetea fuscae and its are presented with 8 association from 2 orders and 4 alliances.

Key words: peat-bogs, flora, vegetation, Mt. Šar-planina

INTRODUCTION

In phytogeographical sense massif of Mt. Šar-planina is located in the north of Scardo-Pindic floristical province of the Central European floristical region, and her highest peaks belongs to the Central-South-European mountain floristical region. Change of different rocks in the substrate, often and on a small space, and jagged terrain caused various flora and vegetation. Special sel to floristical diversity of Mt. Šar-planina gives high-mountain peat-bogs, which had preserved many elements of tertiary endemic flora. Except endemic species, on peaat-bogs, after the last period of glaciation, shelter have found and many representatives of boreal flora, which had caused forming of specific plant cover.

Peaat-bogs vegetation of Mt. Šar-planina is till now very little explored. Košanin (1913) on peat-bogs of this mountain massif finds and describes species *Narthecium scardicum*, the most significant species of high-mountain peat-bogs of Balkan peninsula.

Some floristical characteristics of peat-bogs of Mt. Šar-planina had shown Horvat (1935, 1936) in works which are related to former Vardar regional unit. The area that he had explored partly reached and Kosovo-Metohian part of Mt. Šar planina and that the part in which peat-bogs takes up the biggest surface (Šutman and Vraca). Except a few characteristic species for peat-bogs vegetation, horvat cites two peat-bogs associations, *Cariceto-Narthecietum scardici* and *Caricetum macedonicum*, but without phytocenological tables.

Data about distribution of peat-bogs plant species can be found in some floristical works (Horvat, 1953, Stevanović, Janković, 1984, Randjelović et al., 1997).

MATERIAL AND METHODS

Exploring flora and vegetation of peat-bogs of Mt. Šar-planina, which results had been shown in this work, was carried in the period from 1995 to 1997. The peat-bogs were detaily explored in glacial cirque Durlav potok, on Šutman and in the foothill of Vraca, and material was collected on the spring of Prizrenska Bistrica river.

Determination and nomenclature of mosses was done according to Pavletić (1968) and Petrov (1975), while for determination and nomenclature of vascular plants "Flora Europaea, 1-5" was used (Tutin et al. (ed.), 1964-1980). For taxa that have not been described so far, the other sources have been consulted (Josifović (ed.), 1970-1977; Sarić (ed.), 1986).

The grouping of floristic elements into area groups and area types was performed on the basis of the definitions by Stevanović (1992).

The vegetation was studied according to the Braun-Blanquet approach (Braun-Blanquet 1964, Mueller-Dombois & Ellenberg 1974). Abundance, coverage, sociability and the presence of each species was measured by means of the Braun-Blanquet scale.

The herbarium material of shown taxons is in the private herbarium collection "Herbarium Moesiicum" in Doljevac (HMD).

HIGH-MOUNTAINS PEAT-BOGS OF MT. ŠAR-PLANINA

High-mountain peat-bogs of the Southeastern Europe belongs to eutrophic-mesotrophic low peat-bogs, which were formed on impermeable silicate substrate in glacial forms of relief (Milić & Gigov, 1974). Florogenesis of this peat-bogs had began in tertiary (Lakušić, 1968), and today's characteristics of peat-bogs flora are result of changing different climate con-

ditions on this area. Peat-bogs are developed fragmentary around springs of mountain brooks and on the places where water longer retains. Continuous stagnation of water on this cold mountain residences had caused dense development of specific hydrophilic vegetation, and also made anaerobic conditions in substrate which had brought to slowly process of disassembling of dead plant parts, because of this they were accumulated in the form of weak disassembled organic masses called peat. This substrate is distinguished by characteristic and only typical for it peat vegetation, which presents perfect isolated and in definite measure "conservative environment" in which were saved many elements of tertiary and boreal flora. Presence of tertiary endemic plant species refers to relict character of the vegetation, and also disables their regard as identical with Central and North-European peat-bogs.

Peat-bogs of Mt. Šar-planina can be divided conditional on glacial lake peat-bogs and high-mountain spring and brook peat-bogs.

The biggest peat-bog is "Tija voda", which is located in foothill of peak Velika Vraca. It had become by overgrowing of former glacial lake. It extends on around 6 ha surface, with extending direction NW-SE. Depth of peat layers are to 150 cm (Tešić et al., 1979). Peat is exceptionally acid reaction (pH around 4), and is built mostly of Sphagnum and partly of Caricetum-peat. On several places in this peat-bog big holes of free water are noticed.

Big surface takes up Veljinbeška peat-bog, too. Its located in the foothill of peak Mala Vraca. According by characteristics of the plant cover this peat-bog is very heterogenous. By its edge is developed a great number of little spring peat-bogs, but the biggest middle part presents a lake peat-bog. Peat is exceptionally acid reaction, and on some parts of peat-pH is 3.5.

On Šutman are a few little peat-bogs originated by overgrowing of glacial lakes. South of "Šutman" farm is peat-bog "Šutman lake", which takes up area about 50 ares. Peat is deep to 80 cm and is built of Sphagnum and Caricetum-peat exceptionally acid reaction (Tešić et al. 1979). Not far from it is one more peat-bog ("Little Šutman lake"), which is completely overgrown with vegetation of type Hygronardetum, which is the last stage in succession of peat-bogs vegetation.

Spring and brook peat-bogs can be found by almost any spring and brook on silicate massives of Mt. Šar-planina. This peat-bogs are built mostly of Caricetum-peat temperate acid reaction. By this exploring are included spring peat-bogs Šutman, Čelepinsko vrelo and Durlov potok.

On places where on impermeable silicate substrate from the depth is coming out water rich with carbonate are developed alkalifilous peat-bog discovered on the spring of Prizrenska Bistrica.

FLORA OF HIGH-MOUNTAIN PEAT-BOGS OF MT. ŠAR-PLANINA

Floristical investigation of peat-bogs of Mt. Šar-planina are carried out mostly from Veljinbeški Rid in the foothill of Vraca to Čelepinsko vrelo on the foothill of peak Čelepinski Vrh. On this place are the biggest surfaces under peat-bogs vegetation on Mt. Šar-planina. Except that, in floristical list are included plant species discovered on little peat-bog surfaces in cirque Durlov potok and around spring of Prizrenska Bistrica.

On explored peat-bog are noted 8 species of mosses (collected only dominant species of mosses) and 80 species of vascular plants. Considering that by this exploring are not included all high-mountain peat-bogs, no them could be expected much bigger number of plant species.

Basic characteristic of flora of high-mountain peat-bogs of Mt. Šar-planina gives tertiary endemics *Narthecium scardicum*, *Leucorchis frivaldi*, *Silene astartias*, *Calicocorsus stipitatus*, *Barbarea balcana*, *Carduus kernerii* ssp. *scardicus*, *Cirsium heterotrichum*, *Dactylorhiza cordygera* ssp. *bosniaca*, *Rumex balcanicus*, *Pedicularis brachyodontha* and *Phyteuma pseudorbiculare*. From mountain peat-bogs of Central Balkan high-mountain peat-bogs of Mt. Šar-planina are differentiating by bigger representation of species of the Central-South-European area-group (13.7%) and Arcto-Alpine area-type (7.7%) as well as minor presence of boreal elements of flora (5.0%).

Table 1. Review of taxons

MOSES (BRYOPHYTA)
<i>Bryum schleicheri</i> (Hedw.) Turm. (1, 3, 5)
<i>Climacium dendroides</i> (L.) Web. et Mohr. (2)
<i>Conocephalum conicum</i> (L.) Dum. (1)
<i>Cratoneuron commutatum</i> (Hedw.) Roth. (5)
<i>C. commutatum</i> var. <i>falcatum</i> (Brid.) Moenkem (1)
<i>Drepanocladus exannulatus</i> (B.S.G.) Warnst. (1, 2, 6)
<i>Marchantia polymorpha</i> L. (1, 6)
<i>Philonotis seriata</i> Mitt. (1-7)
<i>Sphagnum nemoreum</i> Scop. (1, 2, 3)
VASCULAR PLANTS
<i>Agrostis alba</i> L. (1)
<i>A. canina</i> L. (1, 2, 3)
<i>Alchemilla crinita</i> Buser (4)
<i>A. glabra</i> Neugeb. (3)
<i>Allium sibiricum</i> L. (3, 6)
<i>Angelica paniculata</i> Vand. (3)
<i>Anthoxanthum odoratum</i> L. (3)
<i>Barbarea balcana</i> Pančić (1, 3)
<i>B. stricta</i> Andr. (3)
<i>Blysmus compressus</i> (L.) Panz. (1, 5)
<i>Brickenthalia spiculifolia</i> Rehb. (3)
<i>Calicocorsus stipitatus</i> (Jacq.) Rausch. (1, 3, 6)
<i>Calla palustris</i> L. (1, 3)
<i>Campanula abietina</i> Gris. et Sch. (1, 2)
<i>C. scheuchzeri</i> Vill. (1)
<i>Cardamine glauca</i> Sprengel (5)
<i>C. pratensis</i> L. (1, 2, 3, 7)
<i>C. rapanifolia</i> Pourret (1, 2, 5)
<i>Carduus kernerii</i> Simenk. (1, 4)

Carex canescens L. (1-7)
C. davalliana Sm. (5)
C. echinata Murr. (1-7)
C. elongata L. (6)
C. ferruginea Scop. (6)
C. flava L. (1-7)
C. lepidocarpa Tausch (1, 2, 3)
C. nigra (L.) Reich. (1, 2, 3)
C. nigra (L.) Reich.
 var. *macedonica* nom. nud. (4, 6)
C. rostrata Stokes in With. (1, 2, 3)
C. sempervirens Vill. (1)
Cerastium cerastoides (L.) Britton (1, 2, 3)
Cirsium heterotrichum Pančić (1, 3)
Dactylorhiza cordigera (Fries) Soo
 ssp. *bosniaca* (Beck) Soo (1)
Deschampsia caespitosa (L.) P.B. (1, 2, 3)
D. flexuosa (L.) Trin. (2)
Dianthus superbus L. (1)
Eleocharis acicularis (L.) R.Br. (2, 3)
E. palustris (L.) R. Br. (3)
Epilobium alsinifolium Vill. (1)
Epilobium palustre L. (1, 2, 3)
Equisetum palustris L. (1)
Eriophorum angustifolium Roth. (1-7)
Eriophorum vaginatum L. (2, 3)
Festuca rubra L. (1)
Galium palustre L. (1)
Geum coccineum Sibth. et Sm. (1, 3, 6)
Hieracium alpicola Schleicher ex Gaudin
 ssp. *alpicola* (4)
Juncus alpinus Vill. (1, 4)
J. triglumis L. (4)
Leontodon autumnalis L. (1, 2, 3)
Leucorchis frivaldii (Hampe) Schlechter (1-7)
Ligusticum mutellina (L.) Crantz (1, 3)
Lusula campestris (L.) Lam. et DC.
 ssp. *multiflora* (Ehr.) A. et G. (1)
L. sudetica (Willd.) DC. (3)
Nardus stricta L. (1-7)
Narthecium scardicum Košanin (4, 5, 6)
Parnassia palustris L. (1-7)
Pedicularis verticillata L. (1)
Pedicularis brachyodonta Schlosser & Vuk. (6)
Pinguicula balcanica Casper (1-7)
Phleum alpinum L.
 var. *commutatum* (Gaud.) Boiss. (1, 2, 3)
Phyteuma pseudorbiculare Pant. (3)
Plantago gentianoides Sibth. et Smith (1, 3, 5)
Poa pratensis L. (1, 2, 3)
P. trivialis L. (1)
P. violacea Bell. (2)
Polygonum bistorta L. (1-7)
Potentilla palustris (L.) Scop. (1)
Primula balleri Gmel. (4)
Prunella vulgaris L. (1)
Ranunculus montanus Willd. (1)
Rumex balcanicus Rech. (1, 3)
Sanguisorba officinalis L. (1)
Saxifraga aizoides L. (5)
Selaginella sellaginoides (L.) Link (4)
Scleranthus neglectus Roch. (4)
Silene asterias Griseb. (1)
Tozzia alpina L. (3)
Trifolium badii Schreb. (1-7)
T. pratense L. var. *pilosum* Griseb. (1)
Veratrum album L. (1-7)
Veronica beccabunga L. (1)
V. serpyllifolia L. (1)

- 1 - Veljinbeški Rid
- 2 - Tija voda
- 3 - Šutman
- 4 - spring of Šutmanska river
- 5 - spring of Prizrenska Bistrica
- 6 - Durlov potok
- 7 - Čelepinski vrelo
- 1-7 - on all peat-bogs

VEGETATION OF HIGH-MOUNTAIN PEATBOGS OF MT. ŠAR-PLANINA

Plant cover of peat-bogs of Mt. Šar-planina is presented by mosaic arranged associations of peat-bogs plants. Peat-bogs vegetation is the most developed on plateaus which were once glacial lakes, while around springs and upbrooks takes up just a little surfaces. Floristical structure and arrangement of this associations depends of ecological influences on peat-bog residances had caused appearing of 7 different associations, which are on explored area divided in 2 ordos and 4 alliances. All associations belongs to classis Scheuchzerio-Caricetea fuscae. Together with peat-bogs associations on spring are developing vegetation of classis Montio-Cardaminetea, which presents transitional stage in development of spring peat-bogs. (Table 2)

Table 2. Review of plant communities

SCHEUCHZERIO-CARICETEA FUSCAE (Nordh. 1936) R. Tx. 1937

CARICETALIA FUSCAE W. Koch 1926 em. Nordh. 1937

Caricion cannescentis-nigrae Nordh. 1937

Sphagno nemorei-*Caricetum rostratae*

V. Randj., ass. nova

Eriophoro-*Caricetum echinatae* V. Randj., ass. nova

Carici ferruginei-*Eriophoretum angustifoliae*

V. Randj., prov

Caricetum nigrae scardicum V. Randj., prov.

Narthecion scardicae (Horvat 1960) Lakušić 1966

Calicocorso stipitatae-*Caricetum nigrae* Lakušić 1964

Carici-Narthecietum scardicae Horvat 1935

Carici-Nardion V. Randj. all. nova (*Hygromardetum* s. l.)

Carici-Nardetum strictae V. Randj. prov.

caricetosum nigrae

caricetosum macedonicae

CARICETALIA DAVALLIANAE Br. Bl. 1949

Caricion davallianae Klika 1934

Pinguiculo balcanicae-*Caricetum davallianae*

V. Randj. et B. Zlat. prov.

MONTIO-CARDAMINETEA Br.-Bl. et Tx. 1943

MONTIO-CARDAMINETALIA Pawl. 1928

Cardamino-Montion Br.-Bl. 1925

Bryetum schleicheri Br.-Bl. (1921) 1926

Rumicion balcanici Lakušić 1965

Barbareo-Rumicetum balcanici V. Randj. prov.

Cratoneurion commutati W. Koch 1928

Saxifragetum aizoides Horvat 1935

Table 3. Association *Sphagno-Caricetum rostratae* V. Randj., ass. nova (1, 2 - Veljinbeški Rid, 3, 4 - Tija voda, 5 - Šutmansko Lake)

	1	2*	3	4	5
Character arten of association					
<i>Carex rostrata</i>	5.5	3.2	5.5	5.5	5.5
<i>Sphagnum nemoreum</i>	1.3	3.3	+3	1.3	+2
Char. arten of alliance, ordo and classis					
<i>Carex nigra</i>	.	1.2	1.2	1.2	.
<i>Carex canescens</i>	+2	1.2	+2	.	.
<i>Potentilla palustris</i>	1.1	+	.	.	.
<i>Drepanocladus exannulatus</i>	.	3.3	.	.	.
<i>Eriophorum angustifolium</i>	.	1.2	.	.	.
<i>Carex echinata</i>	.	1.2	.	.	.
<i>Cerastium cerastioides</i>	.	+	.	.	.
<i>Calicocorsus stipitatus</i>	.	+	.	.	.
<i>Eriophorum vaginatum</i>	+2
<i>Cardamine pratensis</i>	.	.	.	+	.
<i>Epilobium palustre</i>	.	+	.	.	.

* Nomenclature type

Table 4. Association *Eriophoro-Caricetum echinatae* V. Randj., ass. nova (1, 2 - Veljinbeški Rid, 3, 4 - Tija voda, 5 - Šutmansko Lake)

	1	2	3*	4	5
Character arten of association					
<i>Carex echinata</i>	4.4	3.3	3.3	3.3	4.4
<i>Eriophorum angustifolium</i>	2.2	2.2	2.2	2.2	2.2
<i>Eriophorum vaginatum</i>	.	.	1.1	+2	+2
Char. arten of alliance, ordo and classis					
<i>Sphagnum nemoreum</i>	1.3	2.3	3.3	2.3	2.3
<i>Drepanocladus exannulatus</i>	2.3	1.3	1.3	1.3	2.3
<i>Carex nigra</i>	2.2	1.2	1.2	1.2	1.2
<i>Parnasia palustris</i>	1.1	1.1	1.1	1.1	+
<i>Carex flava</i>	1.2	1.2	+2	1.2	+2
<i>Leontodon autumnalis</i>	1.1	1.1	+	+	1.1
<i>Pinguicula balcanica</i>	1.1	1.1	1.1	+	+
<i>Trifolium badium</i>	+	1.1	1.1	+	+
<i>Agrostis canina</i>	+2	+2	1.2	+2	1.2
<i>Alchemilla glabra</i>	1.1	+	+	+	+
<i>Leucorchis frivaldi</i>	+	1.1	1.1	+	.
<i>Philonotis seriata</i>	3.3	.	1.3	.	1.3
<i>Carex canescens</i>	.	+2	+2	+2	.
<i>Cardamine pratensis</i>	+	+	+	.	.
<i>Dactylorhiza cordygera</i> ssp. <i>bosniaca</i>	+	+	.	.	.
<i>Dianthus superbus</i>	+
Commons and others species					
<i>Sanguisorba officinalis</i>	+	+	.	.	1.1
<i>Campanula abietina</i>	+	.	+	.	+
<i>Ligusticum mutellina</i>	1.1	+	.	.	.
<i>Phleum alpinum</i> v. <i>commutatum</i>	+	+	.	.	.
<i>Veratrum album</i>	+	.	.	.	+
<i>Deschampsia caespitosa</i>	+2	.	+2	.	.
<i>Lusula campestris</i> ssp. <i>multiflora</i>	+2	+2	.	.	.
<i>Lusula sudetica</i>	+2	.	+2	.	.
<i>Epilobium palustre</i>	+	.	+	.	.
<i>Eleocharis acicularis</i>	.	.	1.2	.	.
<i>Brium schleicheri</i>	+3
<i>Prunella vulgaris</i>	+
<i>Festuca rubra</i>	+2
<i>Poa pratensis</i>	+2
<i>Poa trivialis</i>	+2
<i>Trifolium pratensis</i>	+
<i>Galium palustre</i>	+
<i>Agrostis alba</i>	+2

* Nomenclature type

Table 5. *Caricetum nigrae scardicum* V. Randj. prov.

	1	2	3
Character arten of association			
<i>Carex nigra</i> v. <i>scardicum</i>	5.5	3.3	5.5
<i>Pinguicula balcanica</i>	+	1.1	.
Char. arten of alliance, ordo and classis			
<i>Sphagnum nemoreum</i>	+3	+3	+3
<i>Eriophorum angustifolium</i>	+2	+2	1.2
<i>Drepanocladus exannulatus</i>	1.3	.	2.3
<i>Leontodon autumnale</i>	.	1.1	1.1
<i>Philonotis seriata</i>	.	+3	+3
<i>Deschampsia caespitosa</i>	.	+2	+2
<i>Climacium dendroides</i>	.	1.3	.
<i>Eleocharis acicularis</i>	.	1.2	.
<i>Carex canescens</i>	.	1.2	.
<i>Carex rostrata</i>	.	1.2	.
<i>Trifolium badium</i>	.	1.1	.
<i>Galium palustre</i>	.	1.1	.
<i>Allium sibiricum</i>	.	.	1.1
<i>Carex echinata</i>	.	.	1.2
<i>Eriophorum vaginatum</i>	+2	.	.
<i>Agrostis alba</i>	+2	.	.
<i>Cardamine pratensis</i>	.	+	.
<i>Campanula abietina</i>	.	+	.
<i>Epilobium palustre</i>	+	.	.
<i>Ligusticum mutellina</i>	+	.	.
<i>Sanguisorba officinalis</i>	.	.	+

Table 6. *Carici-Narthecietum scardicae* Horvat 1935 (1, 2 - Šutman, 3 - Durlov potok) and *Calicocorsus stipitatae-Caricetum nigrae* Lakušić 1964 (4 - Veljinbeški Rid)

	1	2	3	4
Char. arten of association and alliance				
<i>Narthecium scardicum</i>	3.3	2.2	2.2	.
<i>Carex nigra</i> v. <i>macedonica</i>	1.2	+2	1.2	.
<i>Pinguicula balcanica</i>	1.1	1.1	1.1	1.1
<i>Leucorchis frivaldi</i>	1.1	+	1.1	1.1
<i>Calicocorsus stipitatus</i>	+	+	+	1.1
<i>Carex nigra</i> v. <i>scardica</i>	.	.	.	2.2
<i>Primula halleri</i>	+	1.1	.	.
<i>Juncus triglumis</i>	+	1.2	.	.
<i>Dactylorhiza cordygera</i> ssp. <i>bosniaca</i>	+	.	+	.
<i>Silene asterias</i>	.	.	.	+
Char. arten of ordo and classis				
<i>Eriophorum angustifolium</i>	1.2	1.2	1.2	1.2
<i>Philonotis seriata</i>	1.3	+3	2.3	+3
<i>Trifolium badium</i>	+	.	+	1.1
<i>Parnasia palustris</i>	+	1.1	.	+
<i>Deschampsia caespitosa</i>	+2	.	+2	+2
<i>Carex lepidocarpa</i>	2.3	1.2	.	.
<i>Eleocharis acicularis</i>	+2	1.2	.	.
<i>Sanguisorba officinalis</i>	+	1.1	.	.
<i>Bruckenthalia spiculifolia</i>	+	1.1	.	.
<i>Eleocharis palustris</i>	+	+	.	.
<i>Juncus alpinus</i>	.	+	.	+
<i>Dianthus superbus</i>	+	+	.	.
<i>Carex flava</i>	.	.	.	1.2
<i>Selaginella selaginoides</i>	.	1.1	.	.

Association *Sphagno nemorei*-*Caricetum rostratae* V. Randj. ass. nova

Association *Sphagno nemorei*-*Caricetum rostratae* presents beginning stage in developing peat-bogs vegetation. In singenetic sense this association traces origin to swamp vegetation of alliance *Magnocaricion* W. Koch 26, exactly from association *Caricetum rostrato-vesicariae* W. Koch 26. Characteristic and dominant species of association are *Carex rostrata* and *Sphagnum nemoreum*. It is developing around free water surfaces and around bigger brooks in the shape of narrow vegetation zone. Further succession of this association unfolds in the direction of the most widest association on peat-bogs of Mt. Šar-planina, *Eriophoro-Caricetum echinatae*. The floristical structure of association is shown in Table 3.

Association *Eriophoro-Caricetum echinata* V. Randj., ass. nova

This association is developed on glacial lake peat-bogs. Physiognomy of association defines the species *Carex echinata* and *Eriophorum angustifolium*, which are characteristic species of association together with *Eriophorum vaginatum*. According to floristical structure association is very similar with association *Eriophoro-Caricetum flavae* V. Randj. et Radak 94 from Vlasina peat-bog (Randelović 1994). Differential species in relation to the quoted association are *Eriophorum vaginatum*, *Sphagnum nemoreum*, *Philonotis seriata*, *Pinguicula balcanica*, *Dactylorhiza cordigera* ssp. *bosniaca* and *Trifolium badium*. Floristical structure of association is shown in Table 4.

Association *Cariceto ferruginei-Eriophoretum angustifoliae* V. Randj., prov.

By high-mountain brooks in cirques of Mt. Šar-planina are developing stands of peat-bogs vegetation characterized by numerous population of species *Eriophorum angustifolium* and different species of the genus *Carex*. Absence of sphagnum mosses and species *Carex echinata* shows that it is about a special association, which is different from the previous and by floristical structure and by morphology. In explored stands on terraces by brook Durlov potok are noted the next vascular plant species: *Carex elongata*, *C. ferruginea*, *C. lepidocarpa*, *C. nigra* ssp. *macedonica*, *Leucorchis frivaldi*, *Pinguicula balcanica*, *Dactylorhiza cordigera* ssp. *bosniaca*, *Calicocorsus stipitatus*, *Trifolium badium*, *Geum coccineum* and others, and mosses *Bryum schleicheri*, *Drepanocladus exanulatus*, *Philonotis seriata* and others.

Association *Caricetum nigrae scardicum* V. Randj. prov.

Association *Caricetum nigrae scardicum* overgrows the edge part of glacial lake peat-bogs. Pure stands of species *Carex nigra* are developing by parts of lake peat-bogs in which water slowly moves. By floristical structure (Tab. 5) is not essentially different from association *Caricetum goodenowii* Penev 1953, which is developing on peat-bogs of Balkan mountains. However, characteristic species of association, *Carex nigra*, from this peat-bogs is in a great part different from the typical representatives of species. It is probably word about some special infraspecific taxon, which is for now under the name *C. nigra* var. *scardica*. Except that, in any stands it is not recorded another characteristic species of association *Caricetum goodenowii*, *Juncus filiformis*.

Alliance *Narhecion scardicae* (Horvat 1960) Lakušić 1966

Endemic Balkan alliance of tertiary-relict origin *Narhecion scardicae* on Mt. Šar-planina is presented by associations *Calicocorsus stipitatae-Caricetum nigrae* and *Carici-Narheciatum scardicae*. First association (Tab. 6) is rare and develops around springs and edges of glacial lake peat-bogs. Characteristic species of this association are *Calicocorsus stipitatus* and *Carex nigra*. Distribution and floristical structure of association on Mt. Šar-planina should be detailed explored.

Second association (Tab. 6) is more spreaded on Mt. Šar-planina and develops around high-mountain brooks. Characteristic and dominant species of association is *Narhecium scardicum*. Except it, in association is reported a great number of species which are - according to Lakušić (1968) - characteristic for alliance: *Carex nigra* v. *macedonica*, *Pinguicula balcanica*, *Leucorchis frivaldi* and *Calicocorsus stipitatus*. In this type of vegetation here are reported *Juncus triglumis* and *Pinguicula balleri*, so they could be designated as local characteristic species of alliance.

Alliance *Carici-Nardion* V. Randj., all. nova

Secondary vegetation which originates by overgrowing and by gradual draining of plane peat-bogs, characterized by domination of species *Nardus stricta* and by participation of peat-bogs elements in building stands, most of authors keeps under provisional name *Higronardetum*. However, vegetation which presents the last stage in overgrowing of plane peat-bogs in mountain and high-mountain zone and in which species *Nardus stricta* appears in a great number, can be divided on great number of associations. On Mt. Šar-planina alliance is presented by association *Carici-Nardetum nigrae*, which is divided on two

subassociations: *caricetosum macedonicae* and *caricetosum scardicae*. Characteristic species of association are *Nardus stricta* and *Carex nigra*. First subassociation is the last stage in overgrowing of plane peat-bogs in which dominates species *Narthecium scardicum*. In it species *Carex nigra* is presented by variety of *macedonica*. Second subassociation is the last stage in overgrowing of glacial lake peat-bogs. *Carex nigra* is presented by variety of *scardica*.

**Asocijacija Pinguiculo-Caricetum
davallianae V. Randj. et B. Zlat. prov.**

On places where on impermeable silicate substrate from the depth is coming out water full of carbonate, develops vegetation of basophilic low peat-bogs, which belongs to ordo *Caricetalia davallianae*. On Mt. Šar-planina hitherto this type of vegetation is found only on spring of Prizrenska Bistrica. It is probably about a new association in which dominates species *Carex davalliana*, but in relation to Central European association *Caricetum davallianae* differentiate by species *Pinguicula balcanica*. In explored stands are noted next species *Blismus compressus*, *Cardamine glauca*, *C. raphanifolia*, *Cratoneuron commutatum* and *Bryum schleicheri*. Together with this association on spring of Prizrenska Bistrica is developing association *Saxifragetum aizoides*.

Ordo Montio-Cardaminetalia Pawl. 1928

Together with peat-bogs associations on spring developing vegetation of classis *Montio-Cardaminetea*. This vegetation on Mt. Šar-planina is presented by alliances *Cardamino-Montion* and *Rumicion balcanici* on silicate springs and *Saxifragetum aizoides* on carbonate springs on impermeable silicate substrate. This type of vegetation deserves a special attention and should be detaily explored.

CONCLUSION

By analysis of flora and vegetation of explored peat-bogs we had came to the conclusion that high-mountain peat-bogs of Mt. Šar-planina is in great measure different not only of peat-bogs of Central and North Europe, and also of mountain peat-bogs of Central Balkan.

Flora of explored high-mountain peat-bogs of Mt. Šar-planina encircles 8 species of mosses (collected only dominant species) and 80 species of vascular plants. Great number of endemic and relict species (*Narthecium scardicum*, *Leucorchis frivaldi*, *Silene asterias*, *Calicocorsus stipitatus*, *Barbarea balcana*, *Carduus kernerii ssp. scardicus*, *Cirsium heterotrichum*, *Dactylorhiza cordygera ssp. bosniaca*, *Rumex balcanicus*, *Pedicularis brachyodontha* and

Phyteuma pseudorbiculare) points that genesis of this peat-bogs had started in tertiary. About strong influence of glaciation on forming peat-bogs flora testifies greater number of species of Arcto-Alpine area-type (7.7%), in relation to boreal elements of flora (5.0%), which were in period of glaciation populated mostly the mountain region. Greater number of species of Central-South-European mountain area-group (13.7%) is the result of the location of this peat-bogs.

Peat-bogs vegetation belong to class *Scheuchzeria-Caricetea fuscae* and it consists of 8 associations from 4 alliances.

On peat-bogs which presents former glacial lakes in overgrowing develops mostly vegetation of alliance *Caricion cannescentis-nigrae*, and the biggest surface of this peat-bogs takes up association *Eriophoro-Caricetum echinatae*.

On peat-bogs around springs and mountain brooks develops vegetation of endemic Balkan alliance of tertiary and relict origin *Narthecion scardicae*. This alliance is presented by associations *Calicocorsus stipitatae-Caricetum nigrae* and *Carici-Narthecietum scardicae*.

On places where on impermeable silicate substrate comes out water full of carbonate develops vegetation of basophilic low peat-bogs, which belongs to ordo *Caricetalia davallianae*. This alliance on Mt. Šar-planina is presented by association *Pinguiculo-Caricetum davallianae*.

The peat-bogs vegetation around springs always follows vegetation of ordo *Montio-Cardaminetalia*.

Presence of great number of endemic species, the specific of plant cover and relict character of vegetation of high-mountain peat-bogs imposes a question of its protection on the whole Mt. Šar-planina. This is especially related to the south-west part of mountain (Rudoka and Vraca) which is not lying on the borders of the National park.

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REFERENCES

- Braun-Blanquet, J. (1964): Pflanzensozologie. Wien-New York.
 Horvat, I. (1935/36): Istraživanje vegetacije planina Vardarske banovine, 1 i 2. Ljetopis JAZU, Zagreb, 47: 142-160, 48: 211-227.
 Horvat, I. (1953): Prilog poznavanju raširenja nekih planinskih biljaka u jugoistočnoj Evropi. Godiš. Biol. Inst. u Sarajevu, 5 (1-2): 199-217.
 Horvat, I. (1960): Planinska vegetacija Makedonije u svijetlu suvremenih istraživanja. Acta Mus. mac. scient. nat. Skopje, 6: 163-203.
 Horvat, I., Glavač, V., Ellenberg, H. (1974): Vegetation Südosteuropas. Gustav Fischer Verlag, Stuttgart. 768 p.

Јорданов, Д. - ед. (1963-1979): Флора на НР Българија, I-VII. Изд. на БАН. Софија.

Josifović, M. - ed. (1970-1977): Flora SR Srbije, I-IX. SANU. Beograd.

Košanin, N. (1913): *Narthecium scardicum* spec. nov. Öst. Bot. Zeit.

Lakušić, R. (1968): Planinska vegetacija jugoistočnih Dinarida. Glasn. republ. zavoda za zašt. prirode, 1: 9-77. Titograd.

Milić, Č. S., Gigov, A. (1974): Tresave i njihovi elementi reljefa. Glas SANU, Odeljenje priro.-mat. nauka, 38: 1-14. Beograd.

Pavletić, Z. (1968): Flora mahovina Jugoslavije. Institut za botaniku Sveučilišta u Zagrebu.

Петров, С. (1975): Определител на мъховете в България. Издателство на БАН, София.

Randjelović, V. (1994): Geobotanička studija Vlasinske tresave. Magistarski rad. Biološki fakultet Beograd.

Randjelović, V., Amidžić, L., Zlatković, B., Pešić, V. (1997): Contribution to the flora of Mt. Šar-planina. The University Thought, 4(1): 23-27. Priština.

Sarić, M., ed. (1986): Flora SR Srbije, 10. SANU. Beograd.

Stevanović, V. (1992): Floristička podela teritorije Srbije sa pregledom viših horiona i odgovarajućih flornih elemenata. In: Flora Srbije, I (2nd ed.) (Sarić, M., ed.), 37-49. SANU, Beograd.

Stevanović, V., Janković, M. (1984): Pregled nekih značajnih endemičnih i reliktnih vrsta visokoplaninske flore kosovskog dela Šar planine. Priroda Kosova, 1: 55-82. Priština.

Tešić, Ž., Gigov, A., Bogdanović, M., Milić, Č. (1979): Tresave Srbije. Zborn. rad. Geografskog inst. "Jovan Cvijić", 31: 19-64. Beograd.

Tutin, T.G., V.H. Heywood, N.A. Burges, D.M. Moore, D.H. Valentine, S.M. Walters & D.A. Webb - eds. (1964-1980): Flora Europaea, I-V. Cambridge University Press. London.

REZIME

FLORA I VEGETACIJA VISOKOPLANINSKIH TRE-SAVA ŠAR PLANINE

Vladimir RANDJELOVIĆ¹, Bojan ZLATKOVIĆ², Lidija AMIDŽIĆ³

¹Tehnološki fakultet Leskovac, Universitet u Nišu

²Biološko društvo "Dr Sava Petrović" Niš

³Zavod za zaštitu prirode Srbije, Priština

Analizom flore i vegetacije istraživanih tresava došli smo do zaključka da se visokoplaninske tresave Šar planine u velikoj meri razlikuju ne samo od tresava srednje i severne Evrope, već i od planinskih tresava centralnog Balkana.

Flora istraživanih visokoplaninskih tresava Šar planine obuhvata 8 vrsta mahovina (sakupljane samo dominantne vrste) i 80 vrsta vaskularnih biljaka. Veliki broj endemo-reliktnih vrsta () ukazuje da je geneza ovih tresava otpočela još u tecijsaru. O jakom uticaju glacijacije na formiranje flore tresava svedoči veća zastupljenost vrsta arкто-alpskog areal tipa (7.5%), u odnosu na borealne elemente flore (5.0%), koji su u periodu glacijacije naseljavali uglavnom planinski region. Velika zastupljenost vrsta srednje-južноевропске planinske areal-grupe (13.7%) posledica je položaja ovih tresava.

Tresavska vegetacija pripada klasi *Scheuchzeria-Caricetea fuscae*, a čini je 8 asocijacija iz četiri sveze i dva reda.

Na tresavama koje predstavljaju nekadašnja glacijalna jezera u zarastanju razvija se uglavnom vegetacija sveze *Caricion cannescentis-nigrae*, a najveću površinu ovih tresava zauzima asocijacija *Eriophoro-Caricetum echinatae*.

Na tresavama oko izvora i planinskih potoka razvija se vegetacija endemitske balkanske sveze terciarno-reliktnog porekla *Narthecion scardicae*. Ova sveza predstavljena je asocijacijama *Calicocorso stipitatae-Caricetum nigrae* i *Carici-Narthecietum scardicae*.

Na mestima gde na nepropustljivoj silikatnoj podlozi izbijaju vode bogate krečnjakom, razvija se vegetacija bazofilnih niskih tresava, koja pripada resu *Caricetalia davallianae*. Sveza je na Šar planini predstavljena asocijacijom *Pinguiculo-Caricetum davallianae*.

Tresavsku vegetaciju oko izvora redovno prati vegetacija reda *Montio-Cardaminetalia*.

Prisustvo velikog broja endemitskih vrsta, specifičnost biljnog pokrivača i reliktni karakter vegetacije visokoplaninskih tresava nameće pitanje njihove zaštite na čitavoj Šar planini. Ovo se posebno odnosi na jugozapadni deo planine (Vraca i Rudoka) koji ne leži u granicama Nacionalnog parka.

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High-mountain Flora of Nedzinat and Zuti Kamen (Prokletije Mt.)

Lidija AMIDŽIĆ¹, Zoran KRIVOŠEJ²

¹The Institute of Nature Protection of Serbia, The Faculty of Mathematics And Natural Sciences - Biology Dept., The University of Pristina

²The Faculty of Mathematics And Natural Sciences - Biology Dept., The University of Pristina

ABSTRACT

The paper provides the results of field research of high-mountain flora of the Prokletije massifs of Nedzinat and Zuti Kamen (Yellow Stone), northwestern range and the highest part of Lumbardske Mt. The herbal material, based on

which, the paper was made, was collected within the period of July 16 - 20, 1997, on this, at present, relatively less researched area of the central part of Yugoslav Prokletije.

Key words: Prokletije, Nedzinat Zuti Kamen, high-mountain flora

INTRODUCTION

The massifs of Nedzinat, Lumbardske Mt., Koprivnik, Streocke Mt. Starac, Zavojska and Cakor with Planinica make up the mid group of Yugoslav, the northwest part of the mountain system of Prokletije, respectively. This group is not presented with long ranges, but is comprised of relatively separated mountains that make specific oro-morphological entitities, as follows: Nedzinatsko-Lumbardska, Koprivnicko-Streocka, Staracko-Zavojska, and Cakorsko-Velicka. Their geologic ground consists of Paleozoic schist, mainly of Permian age, above which lay the Triassic limestone and dolomites (Knezevic, 1995).

The review of our research refers to a part of Nedzinatska-Lumbardska entirety that covers the massifs of Nedzinat and Lumbardske Mt. connected with a vast saddle. More precisely, the evidencing of species of vascular flora mainly, was made along the continuing range of Nedzinat within the height scope from 2,250 to 2,441 m a/s/l, and then, over the saddle (2,344 m a/s/l), and was continued on southeastern and eastern slopes of Zuti Kamen (from 2,344 to 2,522 m a/s/l), that represents the northwestern range and the tallest peak of Lumbardske Mt. The vegetation of turf, rock piles, rocky ground, around firm snow and in rock cracks dominates on the limestone dolomite ground of this part of Prokletije within the condition of severe peri-glacial climate.

MATERIAL AND METHODS

Plant material from Nedzinat and Zuti Kamen was collected and placed in herbarium within the period of July 16 - 20, 1997.

The determination of the material placed in a herbarium was made and checked by respective literature (Hayek, 1927-1933, Javorka et Ksapody, 1934,

Tutin - ed. 1964-1980, Josifovic - ed. 1970-1977, Saric - ed. 1986, Saric - ed. 1992), while the determination of floral elements was made on the basis of Stevanovic's division (1992).

RESULTS AND DISCUSSION

During second half of July, the presence of 176 plant species, distributed into 4 sections (Table 1), was registered in the subject area of Nedzinat and Zuti Kamen within the height scope of 2,250 to 2,522 m a/s/l. Of the species determined, one family belongs to the section of *Lichenophyta*, two families each to the sections of *Pteridophyta* and *Gymnospermae*, while 36 families to the section of *Angiospermae*. Within the section of *Angiospermae*, 31 families were listed in the class of *Dicotyledones*, and 5 families in the class of *Monocotyledones*, respectively. The most presented according to the number of genera were the families of *Asteraceae* (16), *Poaceae* (9), *Caryophyllaceae* (6), *Brassicaceae* and *Rosaceae* (5). The largest number of species was covered by the genera of *Saxifraga* (7), *Gentiana*, *Poa* (5), *Silene*, *Geum*, *Potentilla* and *Hieracium* (4).

The area spectrum of the flora determined of this part of Prokletije indicates the domination of mountain elements. Within the respective, the following could be selected: Mid-South-European Mountainous (MSEM) presented with 25.00%, Mid-European Mountainous (MEM), presented with 22.15%, and South-European Mountainous (SEM) present with 17.05% (Table 2). Large numbers of species, especially those belonging to eastern element (E) of these mountainous groups, represent endemic. Most endemic appear in the frame of eastern South-Euro Mountainous elements (SEM/E), but these could be also found among

Table 1. Review of taxons

Odeljak : LICHENOPHYTA

Fam : Parmeliaceae

1. Rod : Cetraria

1.C . islandica (L .) Ach. (1,2)

ARKT-ALP

2.C . nivalis (L .) Ach. (1,2)

ARKT-ALP

Odeljak : PTERIDOPHYTA

Fam : Ophyoglossaceae

1. Rod : Botrychium

1. B. lunaria (L .)Swartz. (1,2)

CIRKBOR

Fam : Polypodiaceae

1. Rod : Cystopteris

1. C . fragilis (L .)Bernh. (1,2)

CIRCHOL

(arkt-oreotrop)

2. Rod : Polystichum

1. P. lonchitis (L .)Roth (1,2)

CIRCBOR

3. Rod : Dryopteris

1. D. filix - mas (L .)Schott (1,2)

CIRCHOL

(subbor-merid)

4. Rod : Asplenium

1. A. trichomanes L . (1,2)

COSM

(subarkt-merid)

2. A. ruta -muraria L . (1,2)

CIRCHOL

(arkt-merid)

3. A. fissum Kit.Will. (1,2)

SJEP/C-E

SPERMATOPHYTA

Odeljak : GYMNOSPERMAE

Fam : Pinaceae

1. Rod : Pinus

1. P. mugo Turra (1)

SEP/W - E

Fam : Cupressaceae

1.Rod : Juniperus

1. J. sibirica Burgsd. (1,2)

CIRCBOR

Odeljak : ANGIOSPERMAE

Klasa : Dicotyledones

Fam : Ranunculaceae

1.Rod : Ranunculus

1. R. carinthiacus Hoppe (1,2)

SEP/W - E

2. *R. conncinatus* Schott (1,2) SEP/E (ilir-din)
2. Rod : *Aquilegia*
1. *A. bleicicii* Pod. (1) SEP/E (eilir-din)
3. Rod : *Anemone*
1. *A. narcissiflora* L. (1) EAZP
4. Rod : *Trollius*
1. *T. europaeus* L. (1) CIRCBOR
5. Rod : *Caltha*
1. *C. palustris* L. (1) CIRCBOR
- Fam : Caryophyllaceae
1. Rod : *Minuartia*
1. *M. verna* (L.) Hiern.ssp.
ssp.collina (Neilr.) Hall.(1,2) SE/E-POMT/W-SUBM/E
JEP/E (din)
2. *M. bosniaca* (Beck.) K. Maly (1,2)
2. Rod : *Cerastium*
1. *C. decalvans* Sch.et Vuk. ssp
dollineri (Beck)Gaj. (1,2) JEP/E(din-balk/
nspind-z.mez)
ARKT-ALP
2. *C. cerastoides* (L.) Britton (1,2)
3. Rod : *Silene*
1. *S. acaulis* L. (2) ARKT - ALP
2. *S. sendtnerii* Boiss. (1,2) JEP /E(din-balk/
skard-pind-w.mes)
JEP/E
(lok.endem Prokl.)
3. *S. macrantha* (Panč.) Neum.(1,2)
4. *S. pusilla* W.K.
ssp. quadridentata (Murr.) Neum. (1,2) JEP/E (din-balk/pind)
4. Rod : *Paronychia*
1. *P. kapela* (Hacq.) Kern. (1,2) JEP/W-E-AN
5. Rod : *Dianthus*
1. *D. integer* Vis. (1,2) JEP/E(din-balk/skpind)
1. *D. microlepis* Boiss. (1,2) SEP/E(seilir/din-
balk/scpind-mes)
6. Rod : *Arenaria*
1. *A. biflora* L. (1,2) SEP/W-E(din-balk
/scpind-mes)
- Fam : Polygonaceae
1. Rod : *Polygonum*
1. *P. viviparum* L. (1,2) ARKT-ALP
2. Rod : *Rumex*
1. *R. acetosa* L. (1,2) CIRCHOL
(arct-submerid)
- Fam : Plumbaginaceae
1. Rod : *Armeria*
1. *A. canescens* Host. (1,2) JEP/C-E -AN
- Fam : Hypericaceae
1. Rod : *Hypericum*
1. *H. richeri* Vill.

- ssp. *grisebachii* (Boiss.) Nyman (1,2) SJEP/C-E(alp-karp-bal)
- Fam : Violaceae
1. Rod : *Viola*
1. *V. zoysii* Wulf. (1,2) SJEP/C-E(alp-ilir-din)
2. *V. elegantula* Schott.
var. *latisepala* (Wettst.) Beck. (1,2) SJEP(seilir/din-balk/nscpind)
- Fam : Cistaceae
1. Rod : *Helianthemum*
1. *H. oelandicum* (L.) DC
ssp. *alpestre* (Jacq.) Breistr. (1,2) SJEP/W-E
2. *H. nummularium* (L.) Mill.
ssp. *glabrum* (Koch) Wilczek (1,2) SJEP/W-E-KA-AN
- Fam : Brassicaceae
1. Rod : *Arabis*
1. *A. alpina* L.
ssp. *flavescens* (Gris.) Hay. (1,2) SJEP
2. *A. constricta* Gris. (1,2) SJEP/C-E
2. Rod : *Allysum*
1. *A. montanum* L.
ssp. *scardicum* (Wettst.) Hay. (1,2) SJEP/E(din - scpind/w.mes)
3. Rod : *Draba*
1. *D. korabensis* Kumm. et Deg. (1,2) SEP/E(seilir/din -balk/nscpind)
2. *D. lasiocarpa* Rochel (1,2) JEP/W-E
4. Rod : *Thlaspi*
1. *Th. praecox* Wulf. (1,2) SJEP/C-E
5. Rod : *Iberis*
1. *I. sempervirens* L. (1,2) JEP/W-E -AN
- Fam : Salicaceae
1. Rod : *Salix*
1. *S. caprea* L. var. *caprea* (1) EAZ(bor-submerid)
2. *S. retusa* L.
ssp. *serpyllifolia* (Scop.) Arcang. (1,2) SEP/W-E
- Fam : Ericaceae
1. Rod : *Arctostaphylos*
1. *A. uva - ursi* (L.) Spreng. (1) CIRCBOR
- Fam : Vacciniaceae
1. Rod : *Vaccinium*
1. *V. uliginosum* L. (1,2) CIRCBOR
2. *V. myrtillus* L. (1,2) CIRCBOR
- Fam : Primulaceae
1. Rod : *Androsace*
1. *A. villosa* L. (1) SEP/W-E
2. Rod : *Primula*
1. *P. veris* Huds.
ssp. *columnae* (Ten.) Hay. (1,2) SJEP/W-E-AN
2. *P. elatior* (L.) Grufb.

- ssp.intricata (Gren.Godr.)Widm. (1,2) SJEP/W-E
3. Rod : Soldanella
1. S. alpina L . (1,2) SEP/W-E
- Fam : Rosaceae
1. Rod : Rubus
1. R. idaeus L . (1) CIRCBOR
2. Rod : Dryas
1. D. octopetala L . (1) ARKT-ALP
3. Rod : Geum
1. G. bulgaricum Panč. (1,2) JEP/E(eilir/din
-balk/nscpind-wmes)
2. G. montanum L . (1,2) SEP/W-E
3. G . molle Vis. et Panč. (1) JEP/C-E(apen-balk)
4. G. rivale L . (1) CIRCBOR
4. Rod : Potentilla
1. P . crantzii (Crantz)Beck. (1,2) ARKT-ALP
2. P. speciosa Willd. (1,2) JEP/E(eilir/din-
balk/scpind-wmes)-AN
3. P. montenegrina Pant.
f. minor Gajić (1,2) JEP/E(din-balk
/nscpind-wmes)
- 4.P. apenina Ten.(1,2) JEP/E(eilir/din-
scpind-wmes)
5. Rod : Alchemilla
1. A. plicatula Gand. (1,2) SEP/W-E
- Fam : Crassulaceae
1. Rod : Sedum
1. S . hispanicum L . (1,2) SE/C-SMED-WPONT
2. S. acre L . (1,2) EVBOR-SE-PONT-SMED
3. S. album L . SE-SMED/MED
2. Rod : Sempervivum
1. S. kosanini Praeg . (1,2) JEP/E(seilir/din-
balk/nscpind)
3. Rod : Jovibarba
1. J. heuffelii Schott . (1,2) JEP/E(s.karp-din-
balk/scpind-mes)
- Fam : Saxifragaceae
1. Rod : Saxifraga
1. S . adscendens L. ssp. adscendens (1,2) ARKT-ALP
2. S. rotundifolia L . (1,2) SJEP/W-E-KAV-AN
3. S. sempervivum C.Koch. (1,2) JEP/E(eilir/din-
balk/scpind-wmes)
ne-AN
4. S. aizoon Jacq. var.brevifolia Engl. (1,2) ARKT-ALP
5. S. maginata Sternb. (1,2) JEP /E(apen-din
-scpind)
6. S. trydactylites L . (1,2) SE-SMED/MED
7. S. glabella Bertol. (1,2) JEP/C-E(apen-din-
balk/nscpind)
- Fam : Fabaceae

1. Rod : Trifolium
 1. *T. noricum* Wulf. (1,2) SJEP/C-E(e.alp-din-balk/nscpind)
 2. *T. badium* Chreb. (1,2) SJEP/W-E
2. Rod : Lotus
 1. *L. corniculatus* L. (1,2) EAZ (bor-merid)
3. Rod : Anthylls
 1. *A. vulneraria* L.
 ssp. *pulchella* (Vis.)Bornm. (1,2) SJEP/E(din-balk/scpind-mes)
4. Rod : Onobrychis
 1. *O. montana* DC.
 ssp. *scardica* (Gris.)P.W. Ball. (1,2) SJEP/E(din-balk/scpind-mes)
5. Rod : Vicia
 1. *V. cracca* L. ssp. *incana* (Gouan)Rouy (1) SJEP/W-E-AN
6. Rod: Oxytropis
 1. *O. campestris* (L.) DC.
 ssp. *dinarica* Murb. (1,2) SEP/E(din-balk/scpind)
 2. *O. halleri* Bunge ssp. *korabensis* (1,2) SEP/E(seilir/din-balk/nscpind)
- Fam : Linaceae
 1. Rod : Linum
 1. *L. capitatum* Kit. (1,2) SJEP/C-E(apen-din-balk/scpind)
- Fam : Geraniaceae
 1. Rod : Geranium
 1. *G. sanguineum* L. (1,2) SE-PONT
 2. *G. silvaticum* L. (1) EVSIB (bor)
 3. *G. coeruleatum* Schur. (1,2) SJEP/E(karp-din-balc/nscpind w.mes)
- Fam : Polygalaceae
 1. Rod : Polygala
 1. *P. alpestris* Rchb.
 ssp. *croatica* (Chodat)Hay. (1,2) SEP/C (apen)- E (din)
- Fam : Apiaceae
 1. Rod : Trinia
 1. *T. glauca* (L.)Dumort. (1,2) SJEP/C-E(apen-karp-din-balk)
2. Rod : Ligusticum
 1. *L. mutellina* (L.)Cr. (1,2) SEP/C-E(alp-karp- balk)
- Fam : Gentianaceae
 1. Rod : Gentiana
 1. *G. kochiana* Perr. et Song. (1,2) SEP/W-E
 2. *G. verna* L. (1,2) SEP/W-E
 3. *G. punctata* L. (1,2) SEP/C-E(alp-karp- balk)
 4. *G. nivalis* L. (1,2) ARKT-ALP

5. *G. tergestina* Beck. (1,2) SJEP/C-E(apen-
din-scpind)
- Fam : Rubiaceae
1. Rod : *Galium*
1. *G. anisophyllum* Vill. (1,2) SJEP/C-E
2. Rod : *Asperula*
1. *A. cynanchica* L .
- ssp. *montana* (W.K.)Stoj. (1,2) SE/C-SMED- PONT/W
- Fam : Valerianaceae
1. Rod : *Valeriana*
1. *V. montana* L . (1,2) SJEP/W-E
2. *V. pančićii* Hal. et Bald. (1,2) SJEP/E(seilir/din-
nscpind)
- Fam : Boraginaceae
1. Rod : *Myosotis*
1. *M. silvatica* Ehrh.)Hoffm. ssp.
silvatica var. *firma* Cinc .et Koj. (1,2) EAZ (subor-temp)
- Fam : Scrophulariaceae
1. Rod : *Verbascum*
1. *V. nicolai* Rohl. (1) JEP/E(seilir/din-
nscpind)
2. Rod : *Wulfenia*
1. *W. bleicicii* Lak. (1) SJEP/E
(lok.end.Prokl.)
3. Rod : *Pedicularis*
1. *P. brachyodonta* Schloss. et Vuk. (1,2) SJEP/E (ilir-din)
2. *P. verticillata* L . (1,2) ARKT-ALP
4. Rod : *Veronica*
1. *V. orsiniana* Ten. (1,2) SJEP W/E
2. *V. aphylla* L . (1,2) SEP/W-E
3. *V. bellidioides* L . (1,2) SEP/W-E
- Fam : Lentibulariaceae
1. Rod : *Pinguicula*
1. *P. balcanica* Cass.(1,2) SJEP/E(din-
scpind-mez)
- Fam : Globulariaceae
1. Rod : *Globularia*
1. *G. cordifolia* L .
- ssp. *bellidifolia* (Ten.)Wettst. (1,2) JEP/W-E-AN
- Fam : Plantaginaceae
1. Rod : *Plantago*
1. *P. atrata* Hoppe (1,2) SJEP/W-E
- Fam : Lamiaceae
1. Rod : *Acinos*
1. *A. alpinus* (L .)Moench ssp.
alpinus f. *albanica* Kumm.et Jav. (1,2) SJEP/C(alp/apen) -E(din)
2. Rod : *Ajuga*
1. *A. genevensis* L . (1,2) SE-PONTJSIB-KA
3. Rod : *Thymus*

- | | |
|---|---|
| 1. <i>Th. zygiformis</i> (H. Braun)Jalas (1,2) | JEP (apen-din
-skpind/w.mes) |
| 2. <i>Th. longicaulis</i> Presl .(1,2) | SJEP/C-E |
| 4. Rod : <i>Stachys</i> | |
| 1. <i>S. tymphaea</i> Hausskn. (1,2) | SJEP/C-E |
| Fam : Campanulaceae | |
| 1. Rod : <i>Phyteuma</i> | |
| 1. <i>Ph. orbiculare</i> L . (1,2) | SEP/C-E |
| 2. <i>Ph. confusum</i> A. Kern.(1,2) | SEP/C-E |
| 3. <i>Ph. pseudorbiculare</i> Pant. (1,2) | SEP/E(din-scpind) |
| 2. Rod : <i>Edraianthus</i> | |
| 1. <i>E. montenegrinus</i> Horak. et Lak.(1,2) | JEP/E (din) |
| 2. <i>E. graminifolius</i> (L.)DC
var. <i>alpinus</i> (Wettst.)Janh. (1,2) | JEP C-E(apen)-E (din-balk/
skpind-w.mes) |
| 1. Rod : <i>Jasione</i> | |
| 1. <i>J. laevis</i> Lamm. ssp. <i>orbiculata</i> Gris. (1,2) | SJEP/C-E(apen-
karp-din-balk) |
| Fam : Asteraceae | |
| 1. Rod : <i>Aster</i> | |
| 1. <i>A. alpinus</i> L . f. <i>dolomiticus</i>
(Beck.)Mor. et Nyardy (1,2) | ARKT-ALP |
| 2. Rod : <i>Antennaria</i> | |
| 1. <i>A. dioica</i> (L.)Gaertn.
var. <i>australis</i> Gris. (1,2) | CIRCBOR |
| 3. Rod : <i>Anthemis</i> | |
| 1. <i>A. montana</i> L .
var. <i>cronia</i> (Boiss.etHeldr.)Boiss. (1,2) | SJEP/W-E |
| 4. Rod : <i>Achillea</i> | |
| 1. <i>A. lingulata</i> W.K. (1,2) | SJEP/E(karp-balk) |
| 2. <i>A. abrotanoides</i> Vis. (1,2) | SJEP/E(din-
scpind) |
| 3. <i>A. clavenae</i> L . (1,2) | SJEP/C-E(alp-din) |
| 5. Rod : <i>Doronicum</i> | |
| 1. <i>D. columnae</i> Ten. (1,2) | SJEP/C-E-KAV-AN |
| 6. Rod : <i>Amphoricarpus</i> | |
| 1. <i>A. neumayeri</i> Vis . (1) | JEP/E(seilir/din) |
| 7. <i>Taraxacum</i> | |
| 1. <i>T. officinale</i> Web.
ssp. <i>nigricans</i> (Kit.)Hegi (1,2) | SEP/C (alp)-E(din-
balk-karp) |
| 8. Rod : <i>Crepis</i> | |
| 1. <i>C. incarnata</i> (Wulf.)Tausch.
ssp. <i>dinarica</i> (Beck.)Hay. (1,2) | SEP/C(ealp)-E(din) |
| 8. Rod : <i>Hieracium</i> | |
| 1. <i>H. bauhini</i> Bess. (1,2) | SE-KA |
| 2. <i>H. murorum</i> L . (1,2) | SE-BOR(evr) |
| 3. <i>H. villosum</i> Jacq. (1,2) | SEP/C-E |

4. *H. piliferum* Hoppe (1,2) SEP /W-E(din-karp)
9. Rod : Homogyne
1. *H. alpina*(L.)Cass. (1,2) SEP/W-E
10. Rod : Erigeron
1. *E. polymorphus* Scop. L. (1,2) SEP/W-E
11. Rod : Scorzonera
1. *S. rosea* W.K. (1) SJEP/C-E
12. Rod : Senecio
1. *S. abrotanoides* ssp. *carpaticus* Herb. (1,2) SEP/E(karp-balk)
13. Rod : Carduus
1. *C. carduelis* (L.)Kern.(1,2) SEP/C(ealp)-E(din)
14. Rod : Leontodon
1. *L. montanus* Lam. ssp.
montaneormis (Widder)Finch&P.D. (1,2) SEP/C (alp-apen)E(din)
15. Rod : Gnaphalium
1. *G. supinum* L. (1,2) ARKT-ALP
16. Rod : Campanula
1. *C. rotundifolia* L. (1,2) CIRCBOR

Klasa : Monocotyledones

Fam : Iridaceae

1. Rod : Crocus
1. *C. veluchensis* Herb. (1,2) JEP /E

Fam : Liliaceae

1. Rod : Veratrum
1. *V. album* L. ssp *loblium*(1,2) EAZ (arkt-temp)
2. Rod : Lilium
1. *L. albanicum* Gris. (1) SJEP/E
3. Rod : Fritillaria
1. *F. messenensis* ssp. *gracilis* (1) JEP/C(apen)-E(din)
4. Rod : Scilla
1. *S. bifolia* L. (1,2) SE

Fam : Orchidaceae

1. Rod : Nigritella
1. *N. nigra* (L.)Rchb. (1,2) ARKT-ALP
2. Rod : Leucorchis
1. *L. albida* E. Mey. (1,2) ARKT-ALP (evr)
3. Rod : Gymnadenia
1. *G. conopsea* (L.)R.Br. (1,2) EAZ (bor-temp)

Fam : Juncaceae

1. Rod : Luzula
1. *L. sudetica* (Willd.)DC (1,2) ARKT-ALP
2. *L. luzuloides* (Lam.)Dandy et Wil. (1,2) SE
3. *L. campestris* (L.)Lam. (1,2) SE/C-E-BOR/WSIB
2. Rod : Carex
1. *C. laevis* Kit. (1,2) SJEP/C(apen)-E
(din-balk/scpind-w.mes)

2. <i>C. pallescens</i> L. (1,2)	SE - KA - CAZ
3. <i>C. ornithopoda</i> Willd. (1,2)	ARKT-BOR - SEP/W-E
4. <i>C. sempervirens</i> Vill. (1,2)	SEP/W-E
Fam : Poaceae	
1. Rod : Anthoxanthum	
1. <i>A. odoratum</i> L. (1,2)	EAZ/W-C
2. Rod : Phleum	
1. <i>Ph. michelii</i> All.	
var. <i>subincrassatum</i> Gris. (1,2)	SJEP/C-E - KAV -AN
2. <i>Ph. alpinum</i> L. var. <i>alpinum</i> (1,2)	SEP/W-E
3. Rod : Bromus	
1. <i>B. erectus</i> Huds.	
var. <i>transilvanicus</i> (Strnd.)Beck. (1,2)	SE
4. Rod : Poa	
1. <i>P. bulbosa</i> L. f. <i>vivipara</i> Koch. (1,2)	EAZ/W-C
2. <i>P. alpina</i> L. f. <i>vivipara</i> L. (1,2)	ARKT-ALP
3. <i>P. ursina</i> Vel. (1,2)	SEP/E(karp-balk)
4. <i>P. pumila</i> Host. (1,2)	SEP/C-E(karp-din-balk)
5. <i>P. supina</i> Schr. (1,2)	BOR(Scand-wsib-SEP/W-E
5. Rod : Festuca	
1. <i>F. violaceae</i> Gaud. (1,2)	SEP/C(alp-apen)
	E(din-balk)
2. <i>F. rubra</i> L. (1,2)	EAZ/W-C(bor-submerid)
3. <i>F. halleri</i> All. ssp.	
<i>scardica</i> (Gris.)Markgr.-Dannenb.(1,2)	SEP/E(din-scpind)
6. Rod : Nardus	
1. <i>N. stricta</i> L. (1,2)	BOR-SE(evr)
7. Rod : Sesleria	
1. <i>S. nitida</i> Ten. (1,2)	JEP/E(din-
balk/nscpind)	
2. <i>S. coerulans</i> Friv. (1,2)	JEP/E (karp-balk)
8. Rod : Avenula	
1. <i>A. versicolor</i> Vill. Lainz. (1,2)	SEP
9. Rod : Alopecurus	
1. <i>A. gerardi</i> Vill. (1,2)	SJEP/W-E-KAV-AN

-
1. Nedžinat
 2. Žuti kamen
-

Table 2. Floral elements of plant species registered in the high-mountain zone of Nedzimat and Zuti Kamen.

Elementi flore	broj vrsta	%
SJEP / C - E	17	9,66
SJEP / E	11	6.25
SJEP / W - E	7	3.98
SJEP / W - E - KAV - AN	3	1.71
SJEP / W - E - AN	2	1.14
SJEP	2	1.14
SJEP / C - E - KAV - AN	2	1.14
SJEP	44	25.00
JEP/W - E	15	8.53
JEP/C - E	12	6.82
JEP/ E	9	5.12
JEP	2	1.14
JEP/ W - E - AN	1	0.57
JEP	30	17.05
ARKT-ALP	17	9.96
SE	3	1.71
SE/ SMED - MED	2	1.14
SE/ C - SMED-WPONT	2	1.14
SE/E-PONT / W - SUBM /E	1	0.57
SE- PONT	1	0.57
SE - PONTJIS - KA	1	0.57
SE / C-E-BOR / WSIB	1	0.57
SE - BOR	1	0.57
SE - KA - CAZ	1	0.57
SE - KA	1	0.57
SE	14	7,95
EAZ	5	2.84
EAZ/ W - C	3	1.71
EAZP	1	0.57
EAZ	9	5.11
EVSIB	1	0.57
EV RBOR-SE-PONT-SMED	1	0.57
CIRCBOR	12	6.84
BOR - SEP	1	0.57
BOR-SEP / W - E	1	0.57
CIRCHOL	4	2.27
COSM	1	0.57

Abbreviations:

AN - Anatolian

Arct-Alp - Arctic-Alpine

Bor - Boreal

CIRCHOL - Circum-Hole-Arctic

EAS(EAZ) - Euro-Asian

EASM(EAZP) - Euro-Asian Mountainous

EUSIB(EVSIB) - Euro-Siberian

SEM(JEP) - South-European Mt.

E - Eastern C - Central

MEM(SEP)-Mid-European Mountainous

MSEM(SJEP) - Mid-South-European Mt.

CAU - Caucasian

Scand - Scandinavian

Ill/Din - Illyrian Dinaric

Balk - Balkan

SCPIND - Scardus - Pindus

Mes - Messian

W - Western

eastern Mid-European Mountainous (E/MEM) and eastern Mid-South-European Mountainous (MSEM/E) elements. Primarily representing the continuity of ancient Tertiary flora, these elements appear as the combination of Illyrian - Dinaric (Ilir-Din), Messian (Mes), Scardo-Pindus (ScPind), or Balkan (Balk) endemic of western (w), eastern (e), or central (C) dispersion. Of the total of 176 registered species, 33, 18.75% respectively, are the endemic of narrower dispersion that, together with sub-endemic species, present at narrower space of Alpine - Carpathian - Balkan - Apennine entirety, make up 35.23% of endemic flora. The local endemic of Prokletije, *Wulfenia bleicii* and *Silene macrantha*, as well as, the Dinaric endemic of *Ranunculus oreophilus*, *Aquilegia bleicii*, *Minuartia bosniaca*, *Pedicularis brachyodonta* and *Edrianthus montenegrinus*.

In addition to the mountain elements of South and Mid Europe of various origin and age, large number of glacial species of Arctic - Alpine dispersion (Arct-Alp - 9.96%) appear on this part of Prokletije, joined by the Circum-Boreal species (CircBor - 6.81%). This indicates that Pleistocene glaciation strongly affected the flora of Prokletije, not only with regard to its poverty in oro-Mediterranean species, but also regarding simultaneous enrichment of glacial newcomers from the Arctic, or northern parts of European taiga.

The presence of Circum-hole-Arctic elements (CIRPOL - 2.24%), as well as, of highly heterogeneous groups of Mid-European (ME - 7.95%) and Euro-Asian (EA - 5.11%) area types of various photo-genesis and dispersion direction, made floral genetic structure of high-mountain area of Nedžinat and Zuti Kamen more complex.

CONCLUSION

Some 176 plant species, listed into 41 families and 4 sections, as follows: *Lichenophyta*, *Pteridophyta*, *Gymnospermae* and *Angiospermae* were registered in the high-mountain region of the Prokletije massifs of Nedžinat and Zuti Kamen during second half of July 1997. According to the number of families and species, the most present section is Angiospermae presented with 31 families in the frame of Dicotyledones and with 5 families in the frame of class of Monocotyledones.

The Mid-European Mountainous (MEM), Mid-South-European Mountainous (MSEM), South-European Mountainous (SEM) and Arctic-Alpine (Arct-Alp) elements predominate in the area spectrum of the species determined, indicating that present flora of this part of Prokletije primarily represents the continuity of tertiary oro-Mediterranean flora, enriched by glacial newcomers of Arctic-Alpine origin.

REFERENCES

- Amidžić, L. (1997): Pinetum mughi - Geum bulgaricum, New Association of the Mountain Pine (Pinus mugo Turra) on Prokletije Mountain. The University Thought, Publication in Natural Sciences. Vol.4, No 2 : 89 - 95. University of Priština.
- Hayek, A. (1927 - 1933): Prodromus Florae Peninsulae Balcanicae. Berlin - Dahlem.
- Javorka, S. et Ksapody, V. (1934): Magyar Flora Kepegen (Iconographia) Florae Hungaricae. Budapest.
- Јорданов, Д. - ед. (1963-1979): Флора на НР Блгарија, I - X. Изд. на БАН. Софија.
- Јосифовић, М. - ед. (1970 - 1977): Флора СР Србије, I-IX. САНУ. Београд.
- Кнежевић, М. (1995): Туристички ресурси и потенцијали Проклетија, Монографска студија. "Тригорије Божовић", Приштина.
- Лакушић, Р. (1968): Планинска вегетација југоисточних Динарида. Гласник Републ. завода за заштиту природе, 1 : 9-77. Титоград.
- Сарић, М. - ед. (1986): Флора СР Србије, II. САНУ. Београд.
- Сарић, М. - ед. (1992): Флора Србије I. САНУ. Београд.
- Стевановић, В. (1992): Флористичка подела територије Србије са прегледом виших хориона и одговарајућих флорних елемената. In Flora Србије I (Сарић, М. - ед.): 37-49. САНУ. Београд.
- Tutin, T.G., Heywood, V.H., Burges, N.A., Moore, D.M., Valentine, D.H., Walters, S.M. et Web, D.A. - eds. (1964 - 1980): Flora Europaea, I - V. Cambridge Univ. Press. London.

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REZIME

VISOKOPLANINSKA FLORA NEDŽINATA I ŽUTOG KAMENA (PROKLETIJE)

Lidija AMIDŽIĆ¹, Zoran KRIVOŠEJ²

¹Zavod za zaštitu prirode Srbije, Odsek za biologiju PMF-a Univerziteta u Prištini

²Odsek za biologiju PMF-a Univerziteta u Prištini

U ovom radu su prikazani rezultati terenskih istraživanja visokoplaninske flore Nedžinata (2441 m n.v.) i Žutog kamena (2522 m n.v.), severozapadnog grebena i najvišeg vrha Lumbardske planine.

Nedžinatsko-lumbardska oromorfološka celina zajedno sa Streočko-zavojskom i Čakorsko-veličkom čini srednju grupu jugoslovenskog, odnosno, severozapadnog dela planinskog sistema Prokletije. Na krečnjačko-dolomitskoj podlozi u uslovima surove periglacialne klime visokoplaninske zone ovog dela

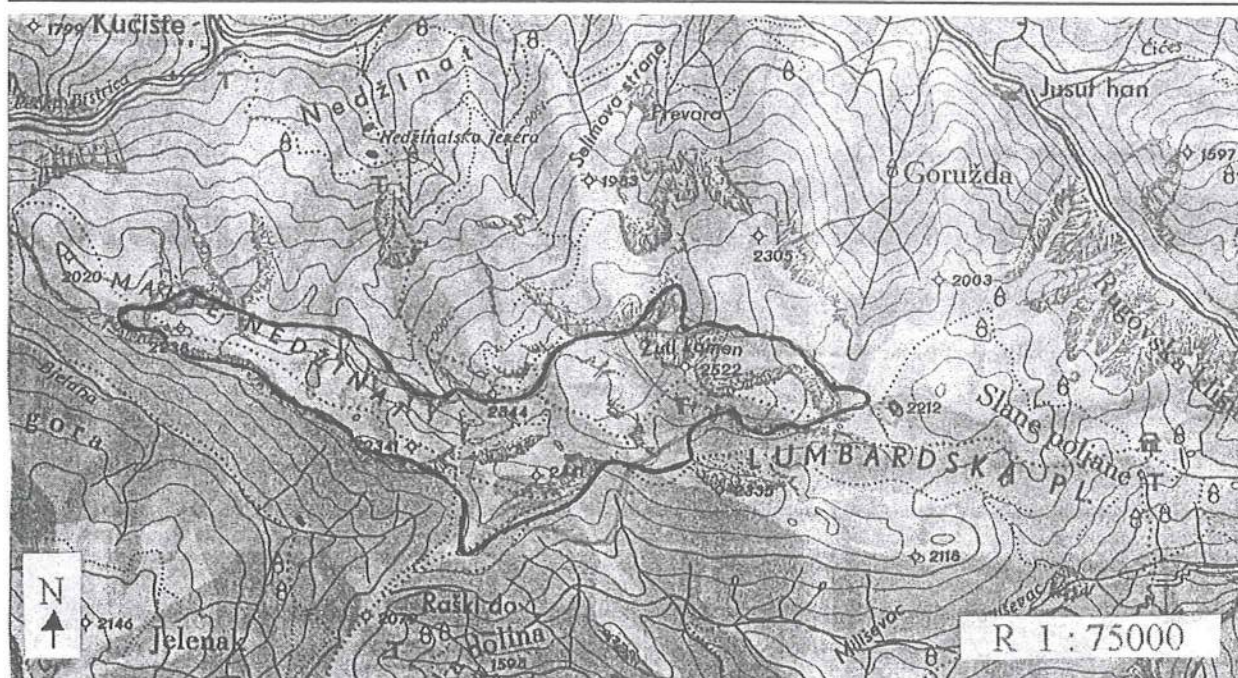


Figure 1. Part of Nedžinat and Zuti Kamen, from which, the plant material was collected

Prokletija, egzistira vegetacija rudina, kamenjara, u pukotinama stena i oko snežanika. Gradi je 176 registrovanih biljnih vrsta raspodeljenih u 4 odeljka. Od ovog ukupnog broja odeljku Lichenophyta pripada 1 familija, odeljcima Pteridophyta i Gymnospermae po 2 familije, a odeljku Angiospermae 36 familija. U okviru odeljka Angiospermae 31 familija je svrstana u klasu Dicotyledones a 5 familija u klasu Monocotyledones. Najzastupljenije po broju rodova su familije Asteraceae (16), Poaceae (9), Caryophyllaceae (6), Brassicaceae i Rosaceae (5). Najveći broj vrsta je obuhvaćen rodovima Saxifraga (7), Gentiana, Poa (5), Silene, Geum, Potentilla i Hieracium (4).

Areal spektar determinisane flore ovog dela Prokletija ukazuje da dominiraju planinski elementi. U okviru njih možemo izdvojiti srednje južnoevropsko planinske (SJEP - 25,00 %), srednjeevropske planinske (SEP - 22,15 %) i južnoevropske planinske (JEP - 17,05 %). Veliki broj vrsta, posebno onih koje pripadaju istočnim elementima (E) ovih planinskih grupa, predstavlja endemite. Najveći broj endemita se javlja u okviru istočnih južnoevropsko-planinskih elemenata (JEP / E), ali ih ima i među istočnim srednjeevropskim-planinskim (E/SEP) i istočnim srednjejužnoevropskim-planinskim (SJEP / E) elementima. Prvenstveno predstavljajući kontinuitet drevne tercijarne flore, ovi se elementi javljaju kao kombinacije dinarskih (din), mezijjskih (mes), skardo-pindskih (scpind) ili balkanskih (balk) endemita zapadnog (w), istočnog (e) ili centralnog (C) zračenja. Od 176 determinisanih vrsta

, 33, odnosno, 18,75 % su endemiti užeg rasprostranjenja koji zajedno sa subendemičnim vrstama prisutnim na delovima planinskih regiona alpsko-karpatobalkansko-apaninske celine, čine 35,23 % endemične flore. Posebnu specifičnost predstavljaju lokalni endemiti Prokletija, *Wulfenia blecicii* i *Silene macrantha* kao i endemiti dinarida *Ranunculus oreophilus*, *Aquilegia blecicii*, *Minuartia bosniaca*, *Pedicularis brachyodonta* i *Edraianthus montenegrinus*.

Pored planinskih elemenata južne i srednje evrope različitog porekla i starosti, na ovom delu Prokletija se javlja i veliki broj glacialnih vrsta arktičko-alpijskog rasprostranjenja (ARKT-ALP - 9,96 %) kojima se pridružuju cirkumborealne vrste (CIRCBOR - 6,81 %). Ovo ukazuje da je pleistocenska glacijacija snažno uticala na floru Prokletija ne samo u smislu njenog siromašenja u oromediteranskim tercijarnim taksonima, nego i u smislu istovremenog bogaćenja glacialnim pridošlicama sa arktika ili severnih delova evropske tajge.

Florogenetsku strukturu visokoplaninske oblasti Nedžinata i Žutog kamena još više usložnjava prisustvo cirkumholarktičkih elemenata (CIRCHOL-2,24 %), kao i veoma heterogene grupe srednjeevropskih (SE - 7,95 %) i evroazijskih (EVR - 5,11 %) areal tipova različite florogeneze i pravaca zračenja.

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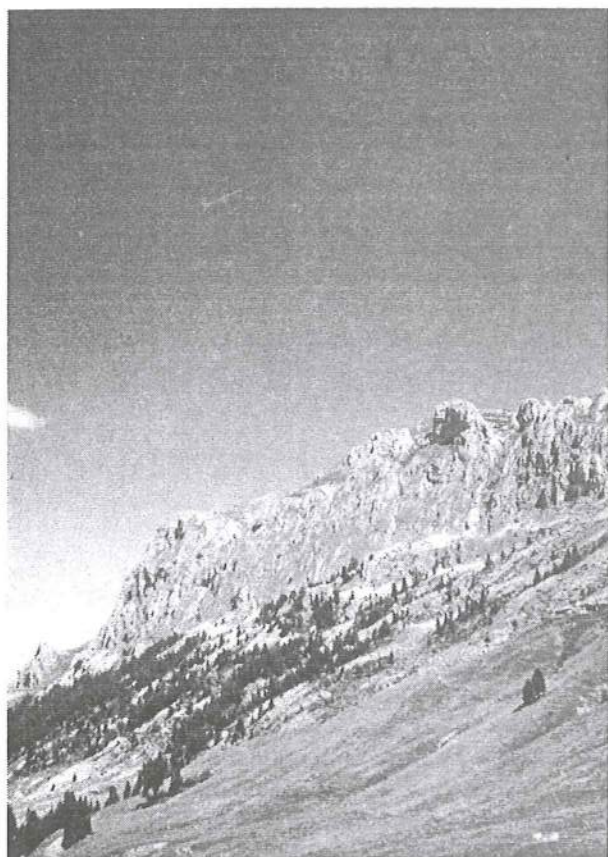


Figure 2. The Nedzinat Range

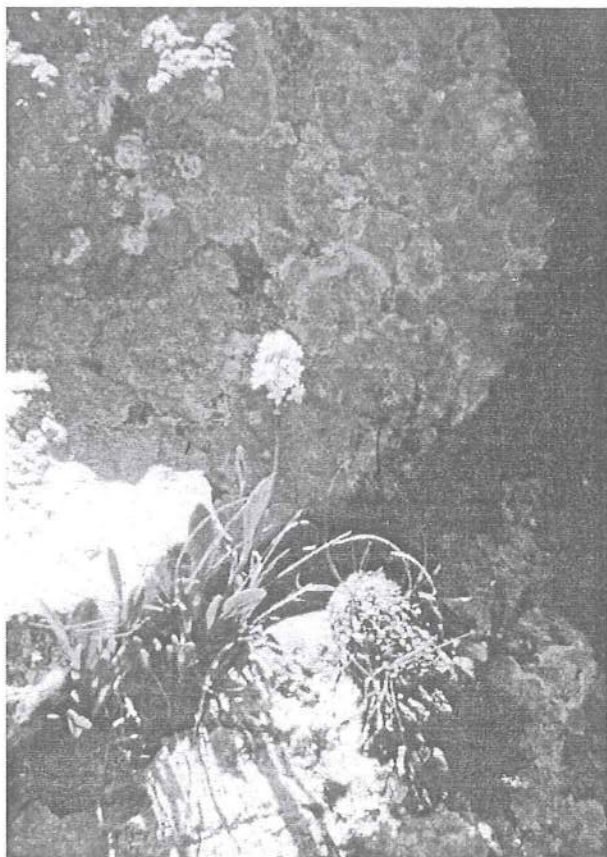


Figure 4. *Valeriana pančičii* Hal. et Bald.

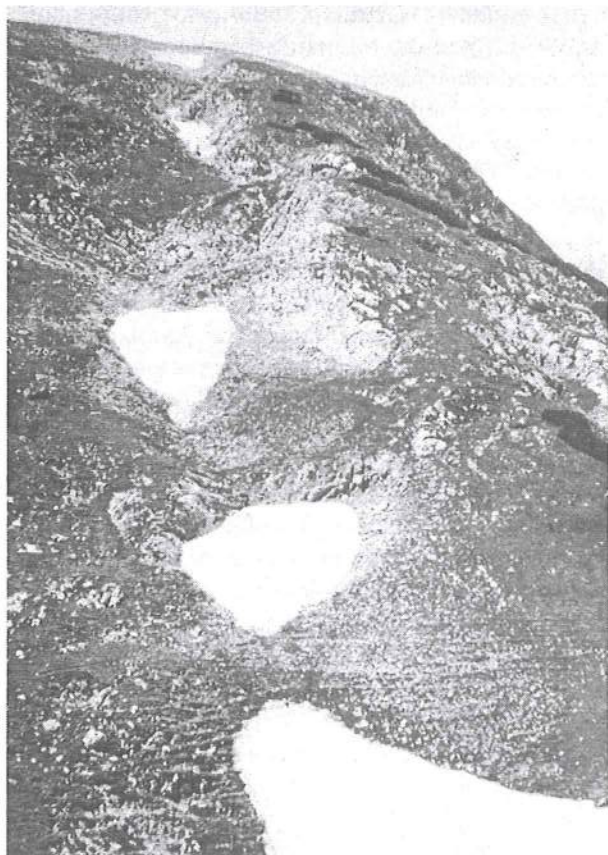


Figure 3. The Zuti Kamen Firm Snow



Figure 5. *Viola zoyssii* Wulf.

The Influence of an Increased Concentration of Zinc-chloride on *Drosophila melanogaster* Longevity

Svetlana BASANOVIC

The Pristina Museum, The King Milutin Square No. 13, Pristina, Yugoslavia

Abstract

The effect of zinc-chloride (10% and 20%) and of optimal living conditions on the longevity variability of *Drosophila melanogaster*, coming from Kosovska Mitrovica and Mojave Desert - California, were examined. The offspring, brought into homozygous and heterozygous state by the techniques of crossbreeding, for the

second and third chromosome, was also studied. Significant genetic load was found regarding the longevity within all breeding conditions. The results were discussed concerning the maintenance of genetic variability in natural populations through inter-genes interactions and the genes and environment interactions too.

Key words: *Drosophila melanogaster*; longevity, zinc-chloride, genetic load, genetic variability.

INTRODUCTION

The longevity is considered to be an important component of adaptive value, especially in organisms that are fertile during whole life, as is the case with the species of *Drosophila* genus. Numerous papers have indicated that longevity represented a metric characteristic with polygenic inheritance manner. Certain results suggest the longevity could be controlled by the polygenes with epistatic interactions (Clarke and Maynard Smith 1955, Lints 1980, Boirgois and Lints 1982). According to Luckinbill et al. 1985, the longevity is under polygenic control with the participation of all chromosomes. The respective should suppose that there have to be genes controlling the process of aging. However, as natural selection did not succeeded in eliminating "the genes of aging", thus the evolution theory of aging is explained in two ways (Abrams and Ludwig 1995), as follows: by the mutation-accumulation theory and the pleiotropic theory respectively. The first one is non-adaptive theory based on the selection weakness against the modifier genes, delaying the time of harmful gene action. The second one is the adaptive theory providing the aging is the result of the selection of pleiotropic genes for the useful effect characteristics in the first stage of life, while with harmful ones, in the later period of life.

Experiment results, contributing to the pleiotropic theory (Rose and Charlesworth 1980, 1981 a,b., Tucic et al. 1988, Service 1993, Hughes and Charlesworth 1994), are more numerous, thus, it may be stated that pleiotropic genes are mainly responsible for the organism process of aging. The correlation between the fitness components, found by the pleiotropic theory representatives, suggested the genetic changes, that lead toward the aging of an organism, are a part of the overall ontogenesis.

The experiment objective, here, is to confirm the thesis, through the research of longevity of homozy-

gotes and heterozygotes of various population of *D. melanogaster* in various living conditions, that genetic recessive changes are the result and consequence of aging, i.e., these mostly resulted from programmed processes.

MATERIAL AND METHODS

The research was made on the samples of *D. melanogaster* coming from Kosovska Mitrovica and Mojave Desert - California. The gnats were first brought into homozygous state for the second and the third chromosome pair. The experimental procedure of separating certain chromosomes into homozygous state was described by Marinkovic and Kunic (1967). It should be mentioned that, in this experiment, as a difference to previous ones, females were used instead of males, as the initial carriers of wild type of chromosomes from the natural populations. The respective created the conditions that "wild" chromosomes were combined and expressed in their own "wild" cytoplasm. Simmons et al. (1980) shown the importance of cytoplasm for the expression of fitness characteristics in homozygote and heterozygote chromosomes of *D. melanogaster*.

The procedure consisted of the following: a female from the wild population $+^1/+^2 +^{m1}/+^{m2}$ was crossed with several males of standard marker line with balanced second and third chromosome Cy/Pm Sb/Ubx. Marker lines had mutant dominant genes creating visible morphologic changes. Each of these chromosomes had homozygote lethal recessive mutations, as well as, other inversions preventing the crossing over. From the P1 generation offspring, only one female was selected $+^1/Cy +^{m1}/Ubx$, or $+^2/Pm +^{m2}/Sb$ that was again crossed with the marker line males. In

Table 1. The Review of Dead Homozygote and Heterozygote Population Individuals of *D. melanogaster* coming from Kosovska Mitrovica

Ngevity	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20		Days
Homozygote 20% ZnCl2 N=158	6	23	58	39	18	4	3	1	3	2				1							
Heterozygote 20%ZnCl2 N=149	1	16	53	25	26	21	2	3	1						1						
Homozygote 10% ZnCl2 N=199		6	22	50	37	29	12	5	4	3	1	5	5	2	1	2	1	2	7		
Heterozygote 10%ZnCl2 N=208		13	33	40	20	21	11	13	11	3	6	4	7	2	2	1	7	2	2		
Longevity	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	
Homozygote K N=195	1		1	3	5	26	43	24	37	7	11	3	6	10	4	2	2	1	2	2	
Heterozygote K N=208		1	1	10	9	35	48	54	27	29	9	15	40	34	23	9	8	5			

Table 2. The Review of Dead Homozygote and Heterozygote Population Individuals of *D. melanogaster* coming from Mojave Desert - California

Longevity	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20		Days
Homozygote 20% ZnCl2 N=154	3	18	32	25	24	15	1	13	3	5	2	4	4	2	1			1			
Heterozygote 20%ZnCl2 N=204		11	53	57	34	10	6	3	4	1		1	3	2	3	5	1		3		
Homozygote 10% ZnCl2 N=103		12	7	13	23	6	6	4	3	3	5	1	5			3		1			
Heterozygote 10%ZnCl2 N=200	1		11	20	24	25	13	6	1	11	10	4	7	5	4	8	11	5	6		
Longevity	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40	42
Homozygote K N=147			2	4	3	18	11	15	24	24	4	7	5	3	4	4	4	8	3	3	
Heterozygote K N=151	2			1		3	19	13	3	4	5	6	24	21	17	11	3	3	5	1	

the next F2 generation, in addition to other combinations, the following were also obtained: +"/Cy +"/Ubx, +"/Pm +"/Ubx, +"/Cy +"/Sb, +"/Pm +"/Sb, that consisted of the same "second" and "third" chromosome coming from the natural population. By inter-crossing the males and females, carrying one of these combinations, the homozygotes for "second" and "third" pair of chromosomes were obtained in F3 generation. The homozygous lines for the second and third chromosome, from both samples of *D. melanogaster* were selected in such a manner. The heterozygotes for the second and third pair of "wild" chromosome was obtained by crossing the individuals of various homozygous chromosome (lines) of a population, just before the beginning of the experiment. The genotypes, experiencing the elimination of recessive genes (mutation), that decrease the fertility completely or severely, were received by separating the homozygous lines.

Through the research series of toxic effect of various concentrations of zinc-chloride on the adaptive component values, over the *Drosophila melanogaster* sample from the natural population, a semi-lethal dose of zinc-chloride (20% ZnCl2) was determined and a decision was made to examine the

effects of 10% and 20% ZnCl2 against the longevity of adult homozygous and heterozygous lines of Mitrovica and Californian population of *D. melanogaster*. The longevity was defined as the adult gnat life duration from the eclosion till the death. The gnats were kept in 70-ml vials with Kalmus substrate covered with two drops of zinc-chloride certain concentration. The gnats of homozygous or heterozygous lines of one population were collected and distributed as 50 individuals in each vial. Each "treatment", as well as, the control had at least three replicas. Dead gnats were calculated each day, and each fifth day, were transferred to a new substrate. An average longevity was determined and the statistic significance of comparing results was established by the t-test.

RESULTS

Based on the review of the gnats died, given in Tables 1 and 2, an average longevity of homozygous and heterozygous lines of both examined populations was calculated (Table 3). The results indicated that the heterozygotes lived longer compared to homozygotes, within all breeding conditions. The fact, the differences

Table 3 Average Values of Longevity in Days, for the Homozygote and Heterozygote Lines for the 2nd and 3rd Chromosome, Natural Population of *D. melanogaster*, coming from Kosovska Mitrovica and Mojave Desert - California, in Various Breeding Conditions.

Lines	10% ZnCl ₂			20% ZnCl ₂			Control		
	- X	+ -	SE	- X	+ -	SE	- X	+ -	SE
Hetero. KM	8.51	±	0.56	5.02	±	0.12	19.98	±	0.4
Homo. KM	8.17	±	0.32	4.64	±	0.14	17.32	±	0.42
Hetero. MD	12.68	±	0.69	5.51	±	0.2	23.25	±	0.62
Homo. MD	8.98	±	0.55	6.25	±	0.25	18.55	±	0.53

Table 4 T-test results Obtained for the Difference of Longevity Between Homozygote and/or Heterozygote Lines, for the 2nd and 3rd Chromosome of the Population of *D. melanogaster*, Coming from K. Mitrovica and M. Desert.

Lines	10% ZnCl ₂	20% ZnCl ₂	Control
Homo. KM	0.83	2.11*	4.59***
Hetero. KM	df=405	df=305	df=546
Homo. MD	4.2***	2.31*	5.4***
Hetero. MD	df=301	df=356	df=298
Homo. KM	1.27	5.55***	1.81
Homo. MD	df=300	df=310	df=340
Hetero. KM	5.64***	2.1*	4.42***
Hetero. MD	df=406	df=351	df=504

** p<0.01
 * p<0.05 *** p<0.001

are mainly statistically significant, is confirmed by the t-test results, given in Table 4, indicating a significant share of genetic constitution toward the survival of adult individuals, which also had an impact on the daily variability of the gnats died (Table 1 and 2). If the results of the populations are compared, one can observe, the Mojave Desert gnats live longer (Table 3). Those differences are statistically significant among heterozygote lines in all breeding conditions, while among homozygote, only on the substrate with 20% zinc-chloride (Table 4). The significance of genetic constitution regarding the longevity is also indicated on the graphic presentation of survival of various populations. (Figure 1), with the genetic differences being especially emphasized in optimum environmental conditions.

The longevity is in correlation with the degree of the substrate contamination. Thus, gnats bred on 20% zinc-chloride live the shortest life, and on the control sample, the longest one. The environmental factor indicated to be significant in the daily variability of the gnats died, and was often above the genetic influence (Table 1 and 2). The largest number of deaths per day was in case of contaminated substrate, in both, the homozygote, or heterozygote individuals of various samples. Thus, in case of substrate with 20% zinc-chloride, the top was achieved at fourth day of life already, while, in case of substrate with 10% zinc-chloride, the most critical were fifth and sixth day of life. In case of the control group, there were no sharp shifts; an increased mortality began with 12th day.

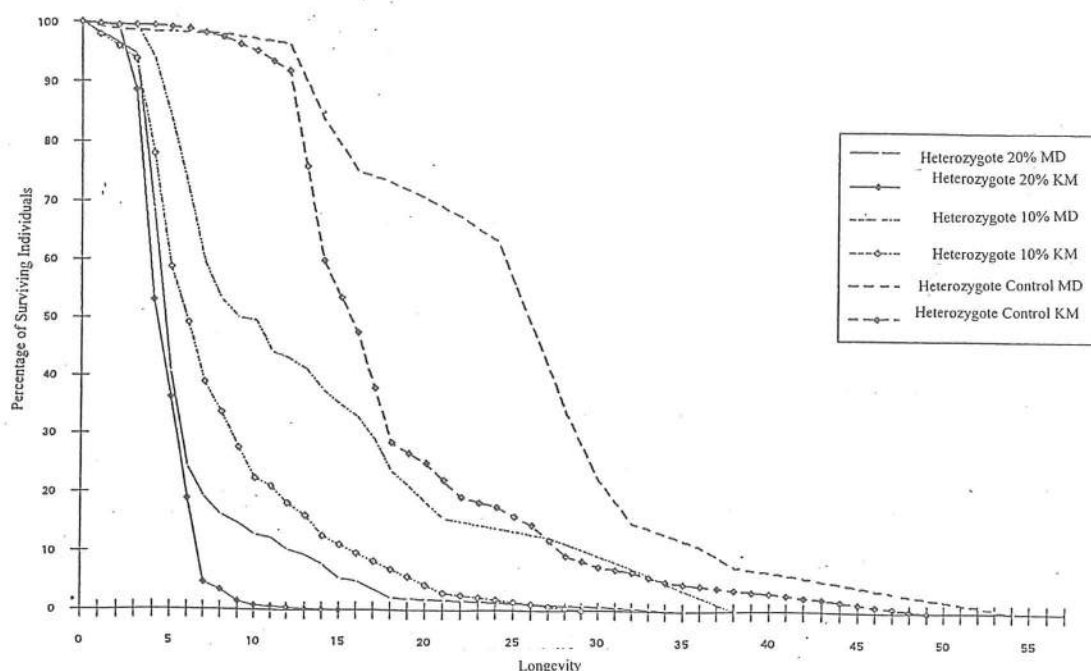


Figure 1. The Longevity of Heterozygote Genotypes of Mitrovica and Californian Population of *D. melanogaster*, with Various Environmental Conditions

DISCUSSION

Numerous researches discovered the existence of significant loads on the longevity of the species of *Drosophila* genus. Marinkovic (1975), Andjelkovic et al. (1979), Marinkovic and Tucic (1982), Marinkovic and Bajraktari (1982) have shown that the genetic, recessive changes were the result of and caused by aging, and the respective usually had harmful effect in homozygote state, regarding relative survival and longevity. The respective assumed, the genetic load is hereditary regarding the longevity (Andjelkovic et al. 1979), and the increase of load is probably due to the accumulation of recessive mutations.

However, some results do not indicate significant difference in longevity between homozygotes and heterozygotes (Marinkovic and Wattiaux 1967). In determining the adaptive values of the component, the authors explain the absence of difference because of unequal role of genetic factors placed in various chromosomes. Their results, however, indicate that, even apart from the absence of difference between homozygotes and heterozygotes, there is a significant phenotype variability of longevity that speaks of an independent action of these parameters.

The impossibility of the selection to increase the longevity suggests that, great phenotype variability in longevity of *D. melanogaster* does not depend of the precise set of genes, or polygenes with additive action (Lints et al. 1979). Parsons (1977) determined high level of environmental variability. It has been almost impossible to make a clear distinction between the

genetic and environmental factor in the determination of longevity. Clare and Luckinbill (1985) indicated the longevity of *D. melanogaster* varies as a result of gene - environment interaction and is strictly determined by the environmental conditions during its pre-adult development. Impossibility of earlier studies in selecting the gene of longevity Luckinbill and Clare (1985) explained by significant gene - environment interactions.

The existence of significant genetic loads, in our paper on, longevity is in contradiction with the results obtained for fecundity and pre-adult survival of the same genotypes (Basanovic 1994). This could be the consequence of pleiotropic gene action, as these were the genotypes with the selection made regarding the harmful genes in the first stages of life. Negative correlation also indicates, the same gene complexes do not have to participate in the determination of fitness components from early and late period of life. Marinkovic (1985) supposed these were the processes covering the whole genome. Rose and Charlesworth (1980), Tucic et al. (1987), Parsons (1977) indicated that the genetic component is an important one in the overall variability of longevity in various populations. The differences discovered in the paper between the homozygote and heterozygote within the population, as well as, among the populations (Table 4) confirm that, various genic arrangements in these chromosomes result in significant phenotype variability of longevity. A significant genetic variability is also present in case of zinc-chloride treatment (Table 4), although its toxic

characteristic is strong. A discovered genetic variability assumes that changes leading to the organism aging are programmed (Tucic et al. 1980, Marinkovic and Tucic 1982, Marinkovic 1985).

CONCLUSION

Significant genetic loads of longevity were discovered, even in the conditions of strong toxic action of zinc-chloride, that leads to the conclusion, the genetic variability is an important component and is probably the result of a programmed process in the overall variability of longevity.

The genetic load of longevity is in negative correlation with the results obtained for fecundity and pre-adult survival. This assumes that, genes with pleiotropic action participate in the determination of fitness components with a useful effect in the first stage of life, and harmful one in the later period of life, respectively.

High level of environmental factor in daily variability of dead individuals was determined, suggesting that, genetic variability maintenance be done, not only, through the inter-genes interactions, but also through the interaction of genes and environment

REFERENCES

- Abrams A. P. and D. Ludwig 1995: Optimality theory, Gompertz, low and the disposable soma theory of senescence. *Evolution* 49 (6) pp. 1055 - 1066.
- Anđelković, M. et al. 1979: Age affected changes in viability and longevity loads of *Drosophila melanogaster*, *Am.Nat.* 114, 915.
- Bašanović, S. 1994: Uticaj povećane koncentracije cink - hlorida na komponente adaptivne vrednosti različitih genotipova *Drosophila melanogaster*, (Meigen, 1831.). Magistarski rad, Beograd.
- Boirgois, N. and F.A. Lints 1982: Evolutionary divergence of growth components and life span in subpopulations of *D.melanogaster* raised in different environment. *Advanced in Genetics Development and evolution of Drosophila*, 211 - 226.
- Clarcke and Maynard Smith, J. 1955: Genetics and cytology of *D.subobscura*. XI. Hybrid vigour and longevity. *Gen.Res.(Camo)* 26: 1 - 10.
- Clare, J. M. and Luckinbill, S. L. 1985: The effects of gene-environment interaction on the expression of longevity. *Heredity* 55 19 - 29.
- Hughes, K. A. and B. Charlesworth, 1994 : A genetic analysis of senescence in *Drosophila*. *Nature* 367: 64 - 66.
- Lints, F. A. 1980: *Drosophila* and the future research in the genetic of ageing. *Acta Biol. Yugoslavia (Genetika)*: 12: 187 - 200.
- Lints, F. A., J. Stoll, G. Grouez, and C.V. Lints 1979: An attempt to select for increased longevity in *D.melanogaster*. *Gerontology* 25: 192 - 204.
- Luckinbill, L., Arking, R. Clare, J.M. Cirocco, C.M. and Buck, A.S. 1984: Selection for delayed senescence in *D.melanogaster*. *Evolution* 38: 996 - 1003.
- Luckinbill, L. and Michael, J.C. 1985: Selection for life span in *D.melanogaster*. *Heredity* 55: 9 - 18.
- Marinković, D. 1975: Balancing selection and the maintenance of genetic polymorphisms, *Genetika* 7: 95 - 107..
- Marinković, D. 1985: Contribution to the evolutionary theory of ageing. V. Age - affected changes in the viability genetic loads of second and third chromosomal homozygotes of *D. melanogaster*. *Genetika* 17: 1 - 11.
- Marinković, D. and Bajraktari, I. 1988: Parental age dependent changes as sources of genetic variation in *D.melanogaster*. *Genetika* 77: 113.121.
- Marinković, D. and Krunic, M. 1969: Genetička opterećenja u prirodnoj populaciji *D.melanogaster* sa Fruške Gore. *Arhiv biol. nauka* 19, 37.
- Marinković, D. and Watiaux, M. J. 1967: Genetic load affecting longevity in natural population of *D.pseudoobscura*. *Nature* 216: 170 - 171.
- Marinković, D. and Tucić, N. 1982: *Advanced in: Genetics, development and evolution of Drosophila*. Ed by Seppo Lakova Plenum Press. New York and London.
- Parsons, P.A. 1977: Genotype-temperature interactions for longevity in *D.simulans*. *Exp.Gerontol.* 12: 241 - 244.
- Rose, M. and Charlesworth, B. 1980: A test of evolutionary theories of senescence. *Nature* 287: 141.
- Rose, M. and Charlesworth, B. 1981a: Genetics of life history in *D.melanogaster*. I. Sib analysis of adult females, *Genetics* 97: 173 - 186.
- Rose, M. and Charlesworth, B. 1981b: Genetics of life history in *D.melanogaster*. II. Exploratory selection experiments. *Genetics* 97: 187 - 196.
- Simmons, M., Preston, Ch. and Engels, W. 1980: Pleiotropic effects on fitness of mutations affecting viability in *D. melanogaster* *Genetics* 94: 467 - 475.
- Tucić, N., Cvetković, D., Milovanović, D., and M.Lazić (1987): Genetic variation in fitness components and recombination rates in *D.melanogaster* females. *Genetika*, 19: 13 - 25.
- Tucić, N., Cvetković, D., Milovanović, D., and M.Lazić (1988): The genetic variation and covariation among fitness components in *D.melanogaster* *Heredity* 60: 55 - 60.
- Service, P.M. 1993. Laboratory evolution of longevity and reproductive fitness components in male fruit flies mating ability. *Evolution* 97: 387 - 399.

REZIME

UTICAJ POVEĆANE KONCENTRACIJE CINK-HLORIDA NA DUŽINU ŽIVOTA KOD DROSOPHILA MELANOGASTER

BAŠANOVIĆ Svetlana

Muzej u Prištini, Trg Kralja Milutina 134, Priština, Jugoslavija

U radu je ispitivan efekat cink - hlorida (10 i 20%) na varijabilnost dužine života u *Drosophila melanogaster*, poreklom iz Kosovske Mitrovice I iz Mojave Desert - Kalifornija. Studirano je potomstvo koje je specijalnim tehnikama ukrštanja dovedeno u homozigotno i heterozigotno stanje za drugi i treći hromozom, što čini oko 80% od ukupnog genoma vinske mušice. Vinske mušice su držane u teglama od 70ml na Kalmusovom supstratu, premazanom sa po dve kapi određene koncentracije cink - hlorida.

Rezultati su pokazali da u svim uslovima gajenja heterozigoti duže žive od homozigota, što govori o značajnim genetičkim opterećenjima, čak i u uslovima

jakog toksičnog dejstva cink - hlorida (Tabele 3 i 4). Rezultati su u negativnoj korelaciji sa onima koje smo dobili za fekunditet i preadultno preživljavanje. Pošto smo radili sa genotipovima kod kojih su u prvim stadijumima života eliminisani štetni geni, to pretpostavlja da u determinaciji ove fitnes komponente učestvuju geni sa plejotropnim dejstvom, tj. sa korisnim efektom u prvim stadijumima života a štetnim u kasnijem periodu života.

Sredinski faktor se pokazao značajnim u dnevnoj varijabilnosti uginulih mušica, pa je često nadmašivao genetički uticaj (Tabele 1 i 2). Tako je na kontaminiranom supstratu najveći broj uginulih mušica nađen u toku istog dana, kako kod homozigota tako i kod heterozigota. To sugeriše da se održavanje genetičke varijabilnosti obavlja ne samo preko intergenskih interakcija već i preko interakcije gena i sredine.

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Mathematical indicators of the spiral growth of Ammonite with its mechanical and biological interpretation

Ranko BABIC

Faculty of Electrical Engineering, University of Pristina, 38000 Pristina, Yugoslavia, babic@prishtina.com

Predrag JAKSIC

Faculty of Natural Sciences and Mathematics, Dept. of Biology, University of Pristina, Pristina

Aleksandar LJAMIC

Faculty of Electrical Engineering, University of Pristina, Pristina, ljama@sezampro.yu

ABSTRACT

Starting from the Ammonite shell, that contains the whole trace of its growth, which form follows the logarithmic spiral, we seek for such mathematical indicators of the spiral that would describe the process of the organism growth in the most appropriate way.

In that sense, besides common parameters that characterize the change in the spiral, several other ones, continuous and discrete as well, are proposed and are related to 2D or 3D aspects of the growth. The later case assumes circular cross section of the spiral tube in corresponding snail

shell. Discrete parameters stem from circumscribed and respective inscribed rectangular spirals, defined as the succession of mutually orthogonal tangents.

On that base it is also given mathematical interpretation of the growth law as a consequence of the invariant relative rate of change that stands behind the exponential increase, mechanical explanation of the snail form of the shell, related to the motion of Ammonite and accompanying drag moments in fluids.

Key words: growth, Ammonite, logarithmic spiral, growth parameters

INTRODUCTION

The study of the growth of organisms [1,2] and determination of related laws, with its indisputable biological and ecological significance, generally encounters many difficulties among which, from the methodological point of view, we can distinguish two different categories.

The growth of living organisms should be traced during a long period of time. The complexity of measurements highly depends on the approach, or which quantities are to be measured. In the tracking of the global growth general parameters of the size are periodically measured. But during the track of so-called compositional growth it is necessary to follow the volume or mass increase of all particular organs and systems, that appears to be a really difficult task. Then, from the measurement results the existing relationships are extracted and eventually expressed mathematically. On the other hand, a trade-off between the long term tracking of a single organism and simultaneous measurements of many taxons of different age is quite possible, with inevitable introduction of factors for dispersion corrections.

Extinct species and organisms impose additional obstacles to the endeavor of growth law extraction, since the whole growing process is represented through its just one state - in the moment of the death, either natural or sudden (decease, accident), which

makes the estimation of the organism age very unreliable. Besides, the only remnants which the estimation relies on, are restricted to the bones or skeletons and fossils, i.e. without soft tissue. In such cases correction and inter/extrapolation methods (algorithms) are of particular valuability.

On the other hand, there are species that leave complete traces of their, although global, growing process, which can be investigated in detail after hundreds of millions of years by their fossils. Maybe the best such an example are Ammonite (*Ammonoidea*, a subclass of *Cephalopoda*) or their still living successor Nautilus (*Nautilus pompilius*). They generally have planispirally, tightly coiled, septate shells, that apparently resemble the logarithmic spiral.

PARAMETERS THAT DESCRIBE THE CHANGE IN LOGARITHMIC SPIRAL

Continuous parameters

Considering the logarithmic spiral as a mathematical equivalent of Ammonite shell form (Fig.1 [3]), besides common parameters [4,5] that describe the change, several others will be introduced and defined, with the intention to represent the growth of Ammonite in the most proper way.

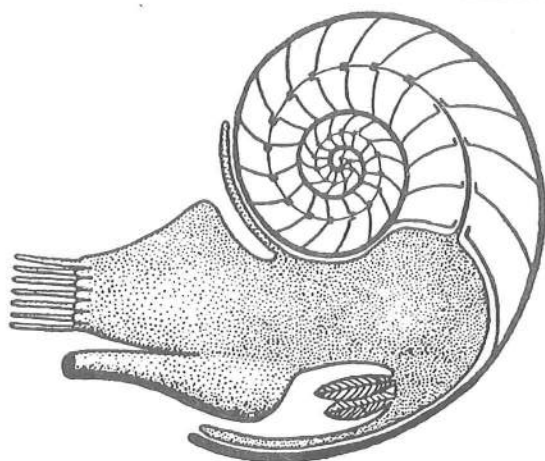


Fig.1 Planar cross-section of Nautilus showing internal coiled and septated shell that follows logarithmical spiral.

Sl.1 Planarni presek Nautilusa pokazuje zakon logaritamske spirale.

Seemingly plain (the term "plain" is pretty relative in polar coordinates as e.g. $\rho = a$ describes a circle) expression of logarithmic spiral in polar coordinates

$$\rho = f(\varphi) = a^{\varphi}, \quad a > 0 \quad (1)$$

or in an alternative form

$$\rho = b e^{c\varphi}, \quad b, c > 0 \quad (1')$$

comprises many invariants and interesting relationships, rarely or never found in other transcendental curves.

The polar derivation of Eq. (1), i.e. the angle μ between the positive direction of a radius-vector and corresponding tangent (Fig.2)

$$\operatorname{tg} \mu = \frac{\rho d\varphi}{d\rho} = \frac{\rho}{\rho'} \quad \left(= \frac{1}{\ln a} \quad \text{za } (1) \right) \quad (2)$$

is always constant which else stands only for the circle. The value of a that gives the necessary angle μ_1 is simply

$$\operatorname{tg} \mu_1 = \frac{1}{\ln a} \Rightarrow a = e^{\operatorname{ctg} \mu_1} \quad (3)$$

and we get $\rho = e^{\varphi}$ for $\mu = 45^\circ$.

The radius of curvature of logarithmic spiral in arbitrary point is given by (for Eq. (1))

$$R = \frac{[\rho^2 + (\rho')^2]^{\frac{3}{2}}}{\rho^2 + 2(\rho')^2 - \rho\rho''} = \rho\sqrt{1 + \ln^2 a} \quad (4)$$

and it is always proportional to the radius-vector of the point. The arc length between the points (r_1, φ_1) and (ρ_2, φ_2) will be (for Eq. (1))

$$L = \int_{\varphi_1}^{\varphi_2} \sqrt{\rho^2 + (\rho')^2} d\varphi = \frac{\sqrt{1 + \ln^2 a}}{\ln a} (\rho_2 - \rho_1) \quad (5)$$

As an especially convenient change indicator of logarithmic spiral could be taken as the area confined by two rays, with the angle $\Delta\varphi$ between, and belonging arcs of two successive coils (Fig.2)

$$S_I = \frac{1}{2} \int_{\varphi_1}^{\varphi_2} \rho^2 d\varphi - \frac{1}{2} \int_{\varphi_1 - 2\pi}^{\varphi_2 - 2\pi} \rho^2 d\varphi = \frac{a^{2\varphi_2} - a^{2\varphi_1}}{4 \ln a} \quad (6)$$

$$S_I = \frac{a^{2\varphi_1}}{4 \ln a} (a^{2\Delta\varphi} - 1), \quad \varphi_2 - \varphi_1 = \Delta\varphi$$

The ratio of such two areas (Fig.2), separated by an angle β will be

$$K_S = \frac{S_I}{S_{I-\beta}} = a^{2\beta} \quad (7)$$

Assuming that the spiral is a planar cross-section of a coiled tube in the Oxj plane with circular cross-section, which diameter varies along the tube axis as $2R = \rho(\varphi + 2\pi) - \rho(\varphi)$, we can define a very suitable quantity - elementary volume, as a part of the tube confined between two planes orthogonal to $Ox\varphi$ and containing origin of coordinates. Obviously, it is consisted of infinitesimal slices, which volume can be written as (Fig.3)

$$dV = R^2 \pi \rho(\varphi) d\varphi + \frac{1}{2} R^2 \pi 2R d\varphi \Rightarrow dV = \frac{1}{8} \pi (1 + a^{2\pi}) (1 - a^{2\pi})^2 a^{3\varphi} d\varphi \quad (8)$$

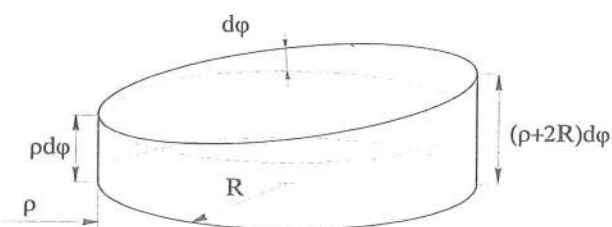


Fig.3 Infinitesimal element of tube section with labels which simplify calculation of its volume.

Sl.3 Izgled diferencijala zapremine sektora cevi kojim se olak{ava ra~unanje zapremine.

The calculation of a section is readily done over the formula

$$V_I = \int_{\varphi_1}^{\varphi_2} dV \quad (9)$$

so, formally we are able to define a parameter that would describe the growth of Ammonite in the best way, i.e.

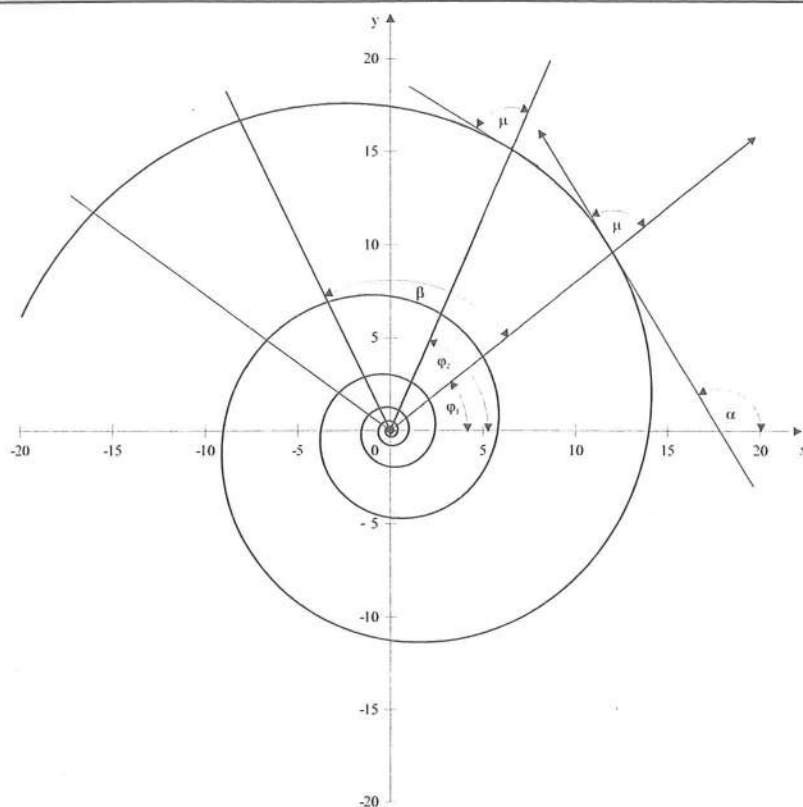


Fig.2 Geometrical relations in logarithmic spiral that define certain growth parameters.
 Sl.2 Geometrijski odnosi u logaritamskoj spirali na osnovu kojih se definišu neki parametri promene.

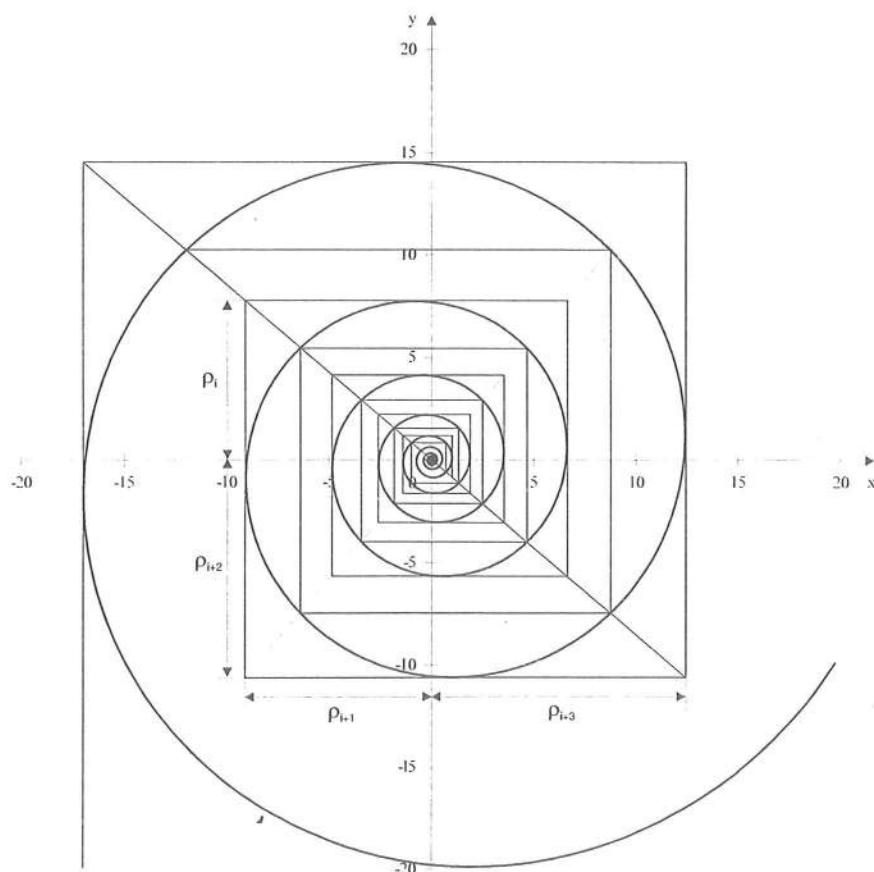


Fig.4 Circumscribed and inscribed rectangular spirals describe discrete increase of a logarithmic spiral and create progressive sequences.

Sl. 4 Opisana i upisana rektangularna spirala opisuju diskretnu promenu gabarita logaritamske spirale i definišu rastuće numeričke nizove.

$$K_V = \frac{V_I}{V_{I-\beta}} = a^{3\varphi} \quad (10)$$

Discrete parameters

Along with continuous parameters, simply by taking discrete values of the argument j , logarithmic spiral comprises some interesting numerical relationships.

Hence, for values of the independent variable j that form an arithmetical progression

$$\varphi: 0, \varphi_1, 2\varphi_1, 3\varphi_1, \dots$$

corresponding values of radius-vector create a geometrical progression

$$\rho: 1, \rho_1, \rho_1^2, \rho_1^3, \dots$$

Besides this classic sequence, there is another one which reveals some properties of the spiral. It stems directly from circumscribed rectangular spiral, comprising segments tangential to particular points (Fig.4).

Substituting into the relation $\alpha = \varphi + \mu$ (see Fig.2) the condition $\alpha = n(\pi/2)$ (Fig.4), where n is an integer we get the values of variable φ indicating points with perpendicular tangents respective to the axes Ox and Oy :

$$\varphi_n = n\frac{\pi}{2} - \arctg \mu = n\frac{\pi}{2} - \arctg \frac{1}{\ln a} \quad (11)$$

and corresponding radius-vectors (rays) are

$$\rho_n = a^{\varphi_n} = a^{n\frac{\pi}{2} - \arctg \frac{1}{\ln a}} \quad (12)$$

The length of a segment (Fig.4) include projections of a pair of opposite rays, i.e.

$$\rho_n^{(p)} = \rho_n \cos \varphi_0 = \rho_n \cos \left(\arctg \frac{1}{\ln a} \right) \quad (13)$$

Now it is easy to create a sequence of numbers, but for our purpose it is much more convenient to examine ratios of the form

$$\frac{\rho_{i+3} + \rho_{i+1}}{\rho_{i+2} + \rho_i} \quad (14)$$

where i is an integer. Simple analysis proves that the ratio is always invariant, with, obviously, different values for particular spirals.

Exactly the same holds for an inscribed rectangular spiral because of similarity of related triangles (Fig.4).

INTERPRETATION OF THE SPIRAL FORM OF AMMONITE

Mathematical interpretation

It is evident that the logarithmic spiral hides many striking invariants which are all simple. Does not surprise J. Bernoulli's mystical fascination by its properties.

What essentially stands behind such relationships, that seems to be one and the same? To set the things explicitly, just the increase of the spiral, i.e. the distance $\Delta p = \rho(\varphi + 2\pi) - \rho(\varphi)$, could be equivalently presented in the coordinate system Oxy instead of $O\rho\varphi$. The spiral shows a pure exponential increase, and that fact is also obvious from its "kinematics": the trajectory of logarithmic spiral is a combination of a uniform circular and exponentially accelerated (as $s = at^2$) linear motions.

Also, it is important to stress the invariance of exponential function derivatives

$$e^x = \frac{d}{dx} e^x = \frac{d^n}{dx^n} e^x \quad (15)$$

Behind all these properties and exponential change stands specific relative (local) law of variation including constant rate of change, either positive or negative.

The essence of such a change will be illustrated through Ammonite growth, where its whole mass is considered as the changing quantity. If the mass of an organism in a certain moment t_1 (when we start observation) amounts $m_p = m(t_1)$ and it grows for Δm during a period of ΔT , then its mass at the end of the period ΔT will be

$$m(t_1 + \Delta T) = m_{(\Delta T)} = m_p (1 + k) \quad (16)$$

where

$$k = \frac{\Delta m}{m_p} \quad (17)$$

is the rate of growth. After the period of $2\Delta T$ we get

$$m_{(2\Delta T)} = m_{(\Delta T)} (1 + k) = m_p (1 + k)^2 \quad (18)$$

and, finally, after n periods the whole mass would be

$$m_{(n\Delta T)} = m_p (1 + k)^n \quad (19)$$

For a reduced interval of observation $\Delta t = \Delta T/p$ the increase of the mass will be p times smaller, and after the single Δt we have $m_p(1 + k/p)$, and after n intervals Δt

$$m_p \left(1 + \frac{k}{p}\right)^{np} \quad (20)$$

Let the $p \rightarrow \infty$ and the final result will be

$$\lim m_p \left(1 + \frac{k}{p}\right)^{np} = m_p e^{km} \quad (21)$$

That means the growth rate is infinitesimal but only if the time interval, within which the increase is observed, is also infinitesimal. In other words, the relative rate is always the same. Such an invariant transfers itself in all parameters of the logarithmic spiral, which express its change on one way or another, making them to be invariant too. Judging by untermiated spiral form of Ammonite shell it seem its growth continues during the whole life.

Mechanical interpretation

Despite the understanding of exponential increase of tube aperture during the growth of Ammonite there remains the question of tube spiral form, instead of its e.g. funnel-shaped form. In our opinion, there are several reasons explaining why namely the spiral form, where each next coil relies on internal one, represents the ultimate reach of shell shape in Ammonite evolution.

One of the reasons is, obviously, significantly smaller global size of the shell, that could be described by a parameter indicating the ratio of volumes of a parallelepiped encompassing spiral tube and another one circumscribing respective, but outstretched tube. Taking the angle of Ammonite shell's aperture plane to be $j_{\max} = j_0$, so that $r(j_0) = r_0$, the ratio of volumes will be

$$\frac{V_S}{V_L} = \frac{(\rho_0 + \rho_{0-\pi})(\rho_{0-\pi/2} + \rho_{0-3\pi/2})(\rho_0 - \rho_{0-2\pi})}{(\sqrt{1 + \ln^2 a} / \ln a) \rho_0 (\rho_0 - \rho_{0-2\pi})} = \frac{(a^\pi + 1)^2 \ln a}{a^{\pi/2} \sqrt{1 + \ln^2 a} (a^{2\pi} - 1)} \quad (20)$$

Spiral form makes the snail-shell to be more rigid and robust since its coils firmly rest upon each other. Additionally, the curved shape of the tube wall, in both orthogonal directions, enhances its rigidity, so the shell is more resistant to impacts, and the soft tissue better protected from injuries. It should be stressed that the planar spiral coiling in Ammonite shell evolutionary precedes conical coiling, found in today's snails, which is, no doubt, mechanically much more effective.

The motion of Ammonite, especially maneuvers, are facilitated by compactness and globally rounded form of the shell, thus reducing its moment of inertia and drag moments of the fluid, which would be intolerable for linear funnel-shaped tube and cause, especially during turns, the body to drift away. It is known that the sphere rotating around its center experiences the least drag, just from fluid viscosity, that originates only within the bordering layer of fluid next to the ball surface. All other shapes, including the sphere itself, but which rotates around any axes off its center, encounter additional drag as eccentric parts of the body must "push" away the fluid.

CONCLUSION

The introduced parameters defining the change in logarithmic spiral with an intention to be used as growth indicators of Ammonite, and snails as well, could be treated as very convenient quantities for such a purpose. Therefore, in addition to their discrete counterparts, they represent a general set of attributes for characterization of a particular shell type. Very plain and mathematically elegant expressions of proposed parameters are explained by very simple basic mechanism of growth, given through constant growth rate. In considerable detail it is given the interpretation of mechanical causes and factors that shaped the Ammonite shell during the evolution.

LITERATURE

1. Browder L.W. Developmental Biology, 2nd ed. Philadelphia, Saunders, 1984.
2. Walbot V, Holder N. Developmental Biology, New York, Random House, 1987.
3. Kin, Alfred Osnovi opšte zoologije, Sarajevo, Veselin Masleša, 1960. (prev. s nem.)
4. Savelov, A.A. Ravninske krivulje, Školska knjiga, Zagreb 1979., (prev. s ruskog)
5. Smirnov, V. I. Kurs vžšaei matematiki, tom I, Moskva 1957.

REZIME

MATEMATIČKI INDIKATORI SPIRALNOG RASTA AMONITA I NJIHOVA MEHANIČKA I BIOLOŠKA INTERPRETACIJA

Ranko BABIĆ

Faculty of Electrical Engineering, University of Pristina, 38000 Pristina, Yugoslavia, babic@prishtina.com

Predrag JAKŠIĆ

Faculty of Natural Sciences and Mathematics, Dept. of Biology, University of Pristina, Pristina

Aleksandar LJAMIĆ

Faculty of Electrical Engineering, University of Pristina, Pristina, ljama@sezampro.yu

Opšti problem proučavanja rasta organizama, koji je postavljen kroz detaljno razmatranje metodologije praćenja rasta kod recentnih i izumrlih vrsta, partikularizovan je na primeru ljuštura amonita

(Ammonoidea) koje, u ovom smislu, predstavljaju kompletan trag procesa rasta. Polazeći od činjenice da oblik planarne ljuštore sledi logaritamsku spiralu, uz njene poznate parametre, predloženi su i definisani posebni parametri tako da budu što podesniji za opisivanje rasta amonite. Njihovom primenom na bilo koju vrstu, posle odgovarajućih merenja ljuštore, može se na vrlo obuhvatan način okarakterisati rast, što može poslužiti kako za određenu rekonstrukciju života organizma, tako i za dopunsku determinaciju vrste.

Posebna pažnja je posvećena tumačenju uzroka i faktora koji su uticali i mogli uticati da ljuštura dobije upravo takav oblik. Iza analitičke jednostavnosti logaritamske spirale, a posebno predloženih parametara, stoji vrlo prost mehanizam rasta određen relativnom konstantnom stopom rasta.

Razmotrena je povezanost oblika ljuštore i mehaničkih faktora što objašnjava spiralnost oblika.

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BOOK REVIEWS - PRIKAZI

DRAGIĆ, S.

NEUROMUSKULARNA SINAPSA. Izdavač: "Novi svet", Priština, 1997.

Ova je monografija proistekla iz doktorske disertacije autora, pa je kao takva pretrpela skraćivanje teksta, što joj nije umanjilo kvalitet. Obim monografije iznosi 68 strana teksta. Sadržaj je podeljen na sledeća poglavlja: Uvod, Istorijski podaci, Neuromuskularna sinapsa, Literatura i Sadržaj. Centralni deo monografije - Neuromuskularna sinapsa - sadrži dva logična poglavlja: Presinaptički deo neuromuskularne sinapse (str. 10 - 31) i Postsinaptički deo neuromuskularne sinapse (str. 32 - 52).

Naizgled malog obima ova monografija sadrži iscrpne i detaljne podatke o morfologiji, fiziologiji, patofiziologiji i drugim biomedicinskim aspektima ove citološko-histološke strukture. Dati su detaljni opisi izgleda sinapse pod svetlosnim mikroskopom, kao i pod elektronskim mikroskopom. Uz opise je dat i istorijat otkrića, kao i vrlo kvalitetni crteži. Objasnjeno je mehanizam biosinteze neurotransmitera: mesto, način transporta i način izlučivanja. Ostalo je nedorečeno mesto sinteze acetilholina (u somi neurona

- gde?). Detaljno je objašnjena uloga jona Ca^{++} u neuromuskularnoj transmisiji. Dati su primeri uticaja brojnih supstanci na normalnu fiziološku aktivnost neurotransmitera, kako u presinaptičkom tako i u postsinaptičkom prostoru.

Korišćena je literatura od 150 referativnih jedinica, koja ukazuje na ozbiljnost autorovog pristupa i agilnost da se dodje kako do klasičnih tako i do najnovijih podataka.

Budući da je monografija proistekla iz doktorske disertacije ostaje jedna principijelna zamerka. Autor nije istakao (ili makar ne dovoljno jasno) koji je naučni problem bio predmet njegovog istraživanja, koje su metode upotrebljene u radu, koji su glavni postignuti rezultati i koji je autorov originalni doprinos nauci. Ovakvim stilom napisana monografija deluje kao izuzetno kvalitetna kompilacija. Naravno, i u takvoj formi njena upotrebna vrednost je velika, kako u biomedicinskim fundamentalnim i primenjenim istraživanjima tako i kao edukativnog štiva.

Izdavačkoj kući "Novi svet" možemo čestitati na profesionalno kvalitetno urađenom poslu ali i uputiti zamerku što nije uradila CIP-katalogizaciju monografije.

P. Jakšić

LAČKOVIĆ Vesna,

HISTOLOGIJA. EPITELNA TKIVA. "Nauka", Beograd, 1997.

611.018.7 (075.8)
ID = 52780812

Ovaj udžbenik predstavlja deo budućeg integralnog teksta u kome će biti obradjena kompletna medicinska histologija. Takodje, ovaj udžbenik ne sadrži poglavlje o histološkim tehnikama i mikroskopiji jer je taj tekst dat kao zaseban u praktikumu "Histološki atlas", koji je (u koautorstvu) publikovan 1995. godine.

Udžbenik sadrži dva dela: Opšte odlike epitela i Klasifikacija epitela. U prvom delu su detaljno opisane polarizovane strane epitelske ćelije i analizirane tvorevine na njima. Objasnjena je i uloga jona enzima čiji se metabolizam realizuje sa dve strane plazmatične membrane. Metabolički i drugi procesi razmene materija kroz plazmatičnu membranu nisu sistematizovani u potpunosti i nisu objašnjeni dovoljno. To i nije nedostatak jer ta materija spada u domen molekularne biologije, biohemije i fiziologije. Od unutarćelijskih organela obradjeni su mikrotubuli i mikrofilamenti, kao i citoskelet.

Poznato je da je epitelna tkiva moguće podeliti po više osnova: prema poreklu, genezi, gradnji, funkciji i dr. i da zbog toga jedinstveno prihvaćena podela epitela ne postoji. U drugom delu autor vrši podelu epitela na četiri grupe: zastorni, žlezdani, mioepitel i neuroepitel. Unutar svakog od ovih tipova razradjena je dalja podpodela, prema pojedinim morfološko-fiziološkim odlikama. Ističemo ovde posebno autorovo gledište o svrstavanju receptorskih ćelija u epitelske - neuroepitelske ćelije. Autor to čini na bazi činjenica da neuroepitelske ćelije imaju klasične, za epitelske ćelije specifične tvorevine na apikalnoj površini: treplje i cilije, okludentne i adherentne spojeve na lateralnim površinama, kao i sinapse na bazalnoj membrani preko kojih se komunicira sa neuronima. Ističemo ovo jer je upravo beogradska škola (pa čak i Guythou) dugo istrajavala na stavu da su pojedine receptorske ćelije nervne a ne epitelske.

Udžbenik je ilustrovan sa brojnim mikrografijama i crtežima, čime se znatno olakšava praćenje i razumevanje teksta.

Ovaj udžbenik će biti od koristi ne samo studentima medicine već ga mogu koristiti i studenti biologije, veterine i dr. fakulteta gde je zastupljena zoologija u gradivu.

P. Jakšić

KARSHOLT O. & RAZOWSKI J.,

The Lepidoptera of Europe. A Distributional Checklist.

"Apolo Books", Stenstrup, 1996.

ISBN 87-88757-01-3

U prethodnom broju ovog časopisa (Vol. 4, No 2) dali smo prikaz knjige Leraut-a (1997) u kojoj je data kompletna lista od 5.015 vrsta Lepidoptera Francuske, Belgije i Korzike. U prilici smo da ovde prezentiramo po sadržaju slično delo Karsholt-a i Razowskog, sa malim zakašnjenjem uzrokovanim činjenicom da je ono štampano samo u hiljadu primeraka i da je do njega bilo teško doći.

Dakle, prvi put je na jednom mestu dat integralni tekst u kome je navedeno 8.470 vrsta Lepidoptera Evrope, svrstanih u 1680 rodova, 85 familija i 31 superfamiliju. Iz popisa literature na kraju knjige se vidi da su ovde objedinjeni podaci iz svih važnijih kataloga i nacionalnih fauna. Praktično je sumiran rezultat rada lepidopterologa koji traje dva veka.

Nas, naravno, interesuje prvenstveno faunistički spisak Lepidoptera Jugoslavije. Najpre možemo da se podsetimo da je Zečević (1996) dao preliminarni spisak na kome je navedeno 1334 vrste "Macrolepidoptera". Sada, u ovome delu imamo listu od 3.454 vrsta Lepidoptera. Ali, i ova lista nije još definitivna iz dva razloga. Najpre, autori nisu razdvajali sadašnje odcepljene delove prethodne Jugoslavije. To znači da unutar te cifre od 3.454 vrste treba izvršiti deobu (da primetimo rezignirano: uz deobu imovine federacije treba izvršiti i deobu nacionalne faune!). Sa druge strane, ova cifra predstavlja samo napredak u odnosu na Zečevićevu listu, ali svakako predstavlja ne više od 80% fonda vrsta u sadašnjoj Jugoslaviji. Dakle, zadatak je budućih lepidopterologa da revidiraju i dopune ovu listu.

BUSZKO, J.,

Atlas rozmieszczenia motyli dziennych w Polsce 1986 - 1995 /

A distribution atlas of butterflies in Poland 1986 - 1995.

"Oficina wydawnicza Turpress, Turuń, 1997.

ISBN 83-86781-40-8

Već više od 20 godina deluje Odbor za kartiranje beskičmenjaka Evrope (European Invertebrate Survey). Primarni je njegov zadatak da inicira evidentiranje i kartiranje pojedinih grupa beskičmenjaka unutar nacionalnih fauna. Dnevni leptiri kao dobro proučena grupa organizama su najčešće prva grupa

Upoređivanjem Leraut-ovog (1997) taksonomskog sistema sa ovde primenjenim sistemom vidimo značajne razlike i u broju familija i superfamilija i u njihovom redosledu. To je odraz činjenice da jedinstveni filogenetski sistem još nije urađen i da je to jedan od najkrupnijih zadataka koji čeka lepidopterologe. U ovom delu autori su nužno morali da izvrše i čitav niz taksonomskih i nomenklaturnih izmena. Kada su u pitanju dnevni leptiri Jugoslavije najkrupnija je izmena brisanje familija Satyridae i Libytheidae. One su sada samo podfamilije u okviru familije Nymphalidae. Kada su u pitanju vrste naših dnevnih leptira najkrupnija je izmena preimenovanje *Colias balcanica* Rebel u *C. caucasica* Staudinger. Kao manji propust možemo smatrati to što autori pojedine vrste dnevnih leptira nisu uvrstili u sastav naše faune (*Erebia orientalis* Elwes, *E. alberganus* Prunner, *Danaus chrysippus* L.). To je i razumljivo jer je njihovo prisustvo u našoj fauni tek nedavno dokazano.

Lista vrsta je data tako da se za svaku vrstu odmah može lako videti i u kojoj evropskoj zemlji je ona zastupljena. Zahvaljujući tome se mogu studirati i nacionalne faune pojedinih zemalja. Upotreba vrednost ove monografije je izuzetno velika. Poput rečnika ova će knjiga morati da bude stalno nadohvat ruke. Na osnovu nje će generacije entomologa moći da sprovedu uniformnu taksonomiju i nomenklaturu. Ona će biti podstrek za faunistička istraživanja jer se prostim uvidom u faune susednih zemalja može prognozirati i prisustvo date vrste u fauni jedne zemlje. Za nas to konkretno znači da možemo očekivati makar dobrih 3.000 vrsta Lepidoptera više!

Knjiga je odštampana na kvalitetnom papiru formata A4, sadrži 380 stranica a ukoričena je tvrdim plastificiranim povezom. Uz knjigu dolazi i CD što omogućava kompjutersko pretraživanje različitih baza podataka.

P. Jakšić

kartiranih organizama. Tako su već završena kartiranja za Francusku (Willien, 1979), Englesku (Heath & all., 1984), Švajcarsku (Gonseth, 1987), Jugoslaviju (Jakšić, 1988), Holandiju (Tax, 1989), Češku (Kudrna, 1994) i sada za Poljsku.

U ovoj monografiji su predstavljeni rezultati rada 126 poljskih lepidopterologa, amatera i profesionalaca. Oni su tokom desetogodišnjeg perioda sakupljali podatke na celoj teritoriji Poljske. Mrežni UTM sistem Poljske sadrži 1.225 polja dimenzija 10 x 10 km. Iz ovoga se vidi da je svaki učesnik u projektu imao prosečno zaduženje da registruje vrste na 10 UTM polja, što znači da je kvalitet karata distribucije izuzetno visok.

Rezultat ovakvih koordinisanih napora i timskog rada jesu karte na kojima je predstavljeno 149 vrsta dnevnih leptira Poljske. Ovi rezultati pokazuju da deset vrsta dnevnih leptira, ranije poznatih u fauni Poljske, nije istraživanjima potvrđeno. Za jednu vrstu (*Pyronia tithonus* L.) je dokazano da je zauvek iščezla sa jedinog poznatog lokaliteta u Poljskoj. Sa druge strane, jedna nova vrsta je zabeležena, to je stepska vrsta *Colias erate* (Esp.). Ova je vrsta u svom nastupanju na zapad nadjena i u Madjarskoj, Jugoslaviji, Hrvatskoj i dr. evropskim zemljama.

Osim što daje vrlo iscrpne podatke o nacionalnoj fauni dnevnih leptira Poljske ovaj atlas predstavlja i perfektnu polaznu osnovu za radna zaštiti nacionalne faune. Tako, na pr., on pruža podatke o vrlo uskom rasprostranjenju čitavog niza vrsta, iz čega proizilazi i potreba njihove zaštite. Primera radi, vrste *Cupido alcetas* (Hoffmansegg), *Argynnis pandora* (D. und S.), *Melitaea phoebe* (D. und S.), *M. aurelia* Nickerl, *Erebia*

pronoe (Esper), *Coenonympha oedippus* (F.), *Pyrgus armoricanus* (Oberthur) i *Spialia sertorius* (Hoffmansegg) su nadjene samo na po jednom lokalitetu u Poljskoj. Jasno je da ukoliko se ta staništa ne zaštite da pri sledećem popisu one neće više biti evidentirane.

Naredni zadatak poljskih entomologa, kako sami ovde ističu, je da sprovedu biomonitoring evidentiranih vrsta i da rezultate publikuju 2.005 godine. Biće to izuzetno dragoceno svedočanstvo o stepenu i nivou čovekove destrukcije prirode, tj. o njegovim mogućnostima da stvarno zaštiti prirodu. Ova izuzetno vredna monografija je i perfektno odštampana pa autoru zaista možemo uputiti čestitke na kompletnom uspehu.

P. Jakšić

STANKOVIĆ, M.S.,

Planinska jezera Crne Gore - limnološka monografija.

Srpsko geografsko društvo, Beograd.

914.971.6(285.2)
ID = 59253516

Opredjelivši se za proučavanje planinskih jezera Crne Gore dr Stevan M. Stanković je početkom sedamdesetih godina uspešno popunio dotadašnju prazninu, kako u široj javnosti, tako i u naučnoj i stručnoj literaturi, o ovim interesantnim hidrografskim objektima. Prvo izdanje "Planinska jezera Crne Gore" objavilo je Društvo za nauku i umjetnost Crne Gore 1975. godine. Pokazavši se višestruko korisnim cijeli tiraž ove knjige ubrzo je bio rasprodat. Zato se pokazala potreba za ponovnim publikovanjem. Zahvaljujući autoru i Srpskom geografskom društvu čitaoci su dobili interesantnu knjigu o "gorskim očima" - koja uvijek priredjuju neponovljive doživljaje i slike.

Knjiga ima 228 strana teksta i izuzetno je dokumentovana. Mnoštvo fotografija, skica i tabela sa podacima obogaćuju štivo, koje se sastoji od 11 odjeljaka.

Poslije predgovora i uvoda, prikaz obradjenih planinskih jezera dat je po planinama na kojima se nalaze. Najprije su date fizičko-geografske karakteristike planina a zatim njihovih jezera, i to: na Durmitoru (10 jezera), na Bjelasici (6 jezera), na Prokletijama i Visitoru (5 jezera), na Volujku (2 jezera), na Sinjavini (2 jezera) i na Lukavici (2 jezera).

Za svako od 28 planinskih jezera Crne Gore, pored odabranih fotografija, dat je položaj i pristupačnost, izobatske karte sa krivim površinama, tačkama najvećih dubina i poprečnih profila jezera,

postanak jezerskog basena, režim nivoa vode i fizičke i hemijske osobine vode, kao i značaj vode za okolinu, naročito na propustljivim terenima, gdje je ona dragocjena.

Dr Stevan M. Stanković, naš najbolji poznavalac jezera u odjeljku o genetskoj i hidrološkoj klasifikaciji proučavanih jezera izdvaja 5 grupa jezera prema načinu postanka basena i 7 grupa prema njihovim hidrološkim svojstvima. Takođe, kod hidrološke klasifikacije prema načinu hranjenja i gubljenja vode jezera, utvrđuje njihove znatne razlike i sličnosti. U odjeljku o Problemima zaštite i valorizacije proučavanih jezera, autor zapaža da prostor na kome se nalaze jezera: "još nije zahvaćen tako intenzivnim turističkim kretanjima kakva će, vjerovatno, biti u budućnosti. Zbog toga je neophodno u pravo vreme pronaći najbolje načine zaštite jezera koja se tu nalaze i koja će uvek biti privlačna za posetioce. Ovo je utoliko značajnije što su za zaštitu, sanaciju i valorizaciju hidrografskih objekata neophodna obimna istraživanja prirodnih zakonitosti koja, kada su u pitanju voda i kraški tereni, često mogu da iznenade sva očekivanja. Zaštita prirodne sredine, pa prema tome i jezera, ne znači konzervaciju određenih područja i sprečavanje bilo kakve ljudske aktivnosti u njima. Naprotiv, zaštita jezera mora značiti iznalaženje najboljih načina njihove valorizacije sa što je moguće manjim štetnim posledicama za njihovu evoluciju i opstanak". Ovaj problem za sada posebno je složen i aktuelan na primjeru Crnog jezera, Biogradskog jezera i Plavskog jezera.

Za našeg čitaoca značaj knjige "Planinska jezera Crne Gore" je višestran. Ona je svojevrsna čitanka ovog prostora, koja svojom temeljitošću i pouzdanošću, čini najvredniji rad iz ove geografske oblasti.

D. M. Kićović



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EDITOR

Predrag Jakšić, Ph. D.
Faculty of Science
Vidovdanska b.b.
38000 Pristina
Yugoslavia