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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 atittude 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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ORIGINAL SCIENTIFIC PAPER

An Encryption Method by Duble Key (DK)

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ABSTRACT

Described in this paper is a method for encryption and decryption of secret messages on the basis of [2].

Keywords: cryptosystem, encryption, decryption

1. Introduction

In [3], on the basis of the Euler's theorem for system of reminders, the RSA cryptosystem for encryption and decryption of secret messages is defined. Let N = pq, where p and q are primes. Then $\varphi(N) = (p-1)(q-1)$ ($\varphi(n)$ is the Euler's function, i.e., $\varphi(n)$ is the number of natural numbers not greater than n, and are primes to each other with n). Let us assume that, for some natural number k, $k(p-1)(q-1)+1=nm$, where m and n are natural numbers. Then it is, for natural number a which is prime with N.,

$$a^{mn} \equiv a \pmod{N}.$$

The RSA cryptosystem is based upon the stated fact. To make the cryptosystem reliable, it is required to initially determine the primes p and q, so that each of them has at least 200 binary digits.

It will be shown in this paper that in the case of the DK cryptosystem this condition does not necessarily apply, i.e., the modulo of enciphering is not the product of two primes. An example of encryption modulo of 10^n will be presented.

2. Period of repeating

The following definitions and theorems are given in [1] and [5]

Definition 1 $\varphi(n)$ is the function whose value is a number of natural numbers not greater than n, and are primes to n.

Euler proved the following theorem:

Theorem 1 If a and m are primes to each other, then

$$a^{\varphi(m)} \equiv 1 \pmod{m}.$$

In [4] it is given the theorem which is a generalization of this Euler's theorem:

Theorem 2 If $\gcd(a^{n+1}, m) = \gcd(a^n, m)$, then

$$a^{\varphi(m)+n} \equiv a^n \pmod{m}.$$

In [2] the following theorem is given:

Theorem 3 For any a, j, n N, i i =0,1,2 applies:

a) $a^{n+i} \equiv a^{n+i+j*4*5^{n-1}} \pmod{10^n}$ for $a \equiv 2*s \pmod{10}$, s=0,1,2,3,4

b) $a^i \equiv a^{i+j*4*10^{n-1}} \pmod{10^n}$ for $a \equiv 2*s+1 \pmod{10}$, s=0,1,3,4

c) $a^{n+i} \equiv a^{n+i+j*4*10^{n-1}} \pmod{10^n}$ for $a \equiv 5 \pmod{10}$.

This theorem can be proved in two ways. In the first proof, Euler's theorem and the generalization of Euler's theorem is applied. The second proof (it is not presented hereinafter) is based on multifold mathematical induction, without the application of the mentioned theorems.

Proof

a) For s = 0, the proof of the theorem is obvious. Let $s \neq 0$. Then

(1) $\quad scd(2*s, 5^n)=1.$

Based on the proved characteristics of function φ(n) in [2]

(2) $\quad \varphi(p^n)=p^n \varphi(p)$

it can be seen that

(3) $\quad \varphi(5^n)=4*5^{n-1}$

As equations (1) and (3) apply based on theorem 1 we have

$$(2*s)^{4*5} \equiv 1 \pmod{5^n}$$

$$\Rightarrow 5^n \mid (2*s)^{4*5^{n-1}} - 1$$

$$\Rightarrow 10^n \mid 2^n *((2*s)^{4*5^{n-1}} - 1)$$

$$\Rightarrow 10^n \mid 2^n *s^n *((2*s)^{4*5^{n-1}} - 1)$$

$$\Rightarrow (2s)^n \equiv (2*s)^{n+4*5^{n-1}} \pmod{10^n}.$$

(4) $\quad \Rightarrow a^n \equiv a^{n+4*5^{n-1}} \pmod{10^n}.$

The proof of theorem 3 under a) can be given by induction by j. For j=1 induction by i should be applied, using proof (4).

b) The proof of the statement can be given by induction by j. Here, only the first induction step will be given, i.e., j = 1, since the proof of the third step based on induction hypothesis is trivial. It applies that $gcd(a^{i+1}, 10^n) = gcd(a^i, 10^n)$, for a=2*s+1 and s=0,1,3,4, therefore theorem 2 can be applied:

(5) $\quad a^i \equiv a^{\varphi(10^n)+i} \pmod{10^n}$

Based on statement (2) we can write

(6) $\quad \varphi(10^n)=\varphi(10)*10^{n-1}=4*10^{n-1}$

Based on equation (6) statement (5) is equivalent to

$$a^i \equiv a^{i+10^n} \pmod{10^n},$$

which had to be proved.

c) Let us note that $\gcd(5^{i+1}, 10^n) \neq \gcd(5^i, 10^n)$, i.e.

(7) $$\gcd(5^{n+i+1}, 10^n) = \gcd(5^{n+i}, 10^n).$$

Since equation (7) is satisfied, theorem 2 can be applied. Based on the above mentioned, by a procedure analogue to that one in the proof of statement b), the statement under c) can be proved.

3. Preparation of the text for encryption

There will be given one of the possible ways of text preparation for enciphering. We divide the text to be enciphered into a certain number of blocks. The block is presented by

$$B^k_{t,r}$$

where indices k, t and r are:

t - ordinal numeral of block

k - length of block, and

r - number of characters, blanks and punctuation marks of an important secrecy

The remaining part of the block, i.e., k-r marks are arbitrary.

Example $B^{40}_{3,\,27}$ denotes the third block, which has totally 40 characters, out of which the last 13 should be transmitted secretly, 40 -13 = 27 first characters are arbitrary and of no importance regarding secrecy.

ADFSG VDNDBV AS THIS IS IN FACT THE MESSAGE

After dividing the text into blocks, each block is translated into number value by the function h: S→N, where S is a set of text characters and marks. Function h should have a maximum in the final set. (One possibility is to represent the characters and marks as ASCII characters)Let:

(8) $$\max h(B^k_{t,r}) = m.$$

4. Enciphering and Deciphering

Let α be the message to be enciphered. We divide message α into blocks $B^k_{t,r}$. Number r is constant, and in a general case it can be the same for all the blocks. Let us mark the first block $a = B^k_{t,r}$. Let us see the procedure of enciphering and deciphering of the first block.

The statement of theorem 3 under b) imposes the first condition that must be fulfilled before the enciphering itself: the message must be an odd natural number, whose last digit is different from number 5. Let:

(9) $$b=g(a),$$

where g:N→N is a function having inverse function and meets the mentioned condition. To enable enciphering the message, it should be applicable:

(10) $$g(m)<10^n.$$

For example, for the g function, the linear function can be taken as follows:

$$b=10*a+1.$$

Then in selecting the enciphering modulo n, based on (10), it should apply

$$10m+1<10^n.$$

After selection of the enciphering modulo, the enciphering exponent x is selected, provided;

(11) $$\gcd(x, 4*10^{n-1})=1.$$

Based on the Diaphant equation:

(12) $$k*x=1+j*4*10^{n-1}$$

the deciphering exponent k is selected.

As n and x are known and (11) applies, equation (12) can be solved for k in the set of natural numbers.

Enciphering: $c \equiv b^x \pmod{10^n}$,

where c is the enciphered message.

Based on theorem 3, deciphering is performed in the following way:

$$c^k \pmod{10^n} \equiv (b^x)^k \pmod{10^n}$$

$$\equiv b^{x*k} \pmod{10^n}$$

$$\equiv b^{1+j*4*10^{n-1}} \pmod{10^n}$$

$$\equiv b \pmod{10^n}.$$

In order to obtain the original message a, the inverse function, of function g should be applied to message b, i.e.,

$$a=g^{-1}(b).$$

The selection of function g is in fact the second key in the considered enciphering method. The enciphering modulo n, enciphering exponent x and deciphering exponent k are secret.

5. Illustration example

let us take a = 2, g(a)=10a+1 and n=2, condition (11) is fulfilled. Presented are three different examples of such selected a, g(a) and n.

a) x=3 ((12) applies).

Then from 3k=1+4j10 for j=2 we have k = 27.

Enciphering

$$b=10\cdot 2+1=21$$

$$c \equiv 21^3 \pmod{10^2}$$

$$c \equiv 9261 \pmod{10^2}$$

$$c \equiv 61 \pmod{10^2}$$

Enciphered message is c=61.

Deciphering

$$c^{27}=61^{27}\equiv 21 \pmod{10^2}.$$

$$b=21 \Rightarrow a=2.$$

b) x=7 ((12) applies)

Then from 7k=1+4j10 for j=7, we have k=23.

Enciphering

$$b=10\cdot 2+1=21$$

$$c\equiv 21^{7} \pmod{10^2}$$

$$c\equiv 41 \pmod{10^2}$$

Enciphered message is c=41

Deciphering:

$$c^{23}=41^{23}\equiv 21 \pmod{10^2}.$$

$$b=21 \Rightarrow a=2.$$

c) x=9 ((12) applies)

Then from 9k=1+4j10 for j=2, we have k=9.

Enciphering

$$b=10\cdot 2+1=21$$

$$c\equiv 21^{9} \pmod{10^2}$$

$$c\equiv 81 \pmod{10^2}$$

Enciphered message is c=81

Deciphering:

$$c^{9}=81^{9}\equiv 21 \pmod{10^2}.$$

$$b=21 \Rightarrow a=2.$$

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Rezime

METOD ŠIFROVANJA DVOSTRUKIM KLJUČEM (DK)

PETOJEVIĆ Aleksandar

Na osnovu teoreme dokazane u [2] dat je primer kriptosistema kod koga se šifrovanje i dešifrovanje poruka izvršava po modulu koji nije proizvod dva prosta broja.

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ORIGINAL SCIENTIFIC PAPER

On $\{d_n\}$ Sequence

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ABSTRACT

Presented in this paper is the generalized Kurepa's hypothesis trought $\{d_n\}$ sequence. It is defined the $\{a_n\}$ sequence and associated with the $\{d_n\}$ sequence. Throught sequence $\{s_n\}$ and $\{b_n\}$ one more equivalent of the Kurepa's hypothesis is given.

Keywords: Kurepa's hypothesis is given

1 Introduction

In [1], it is defined left factorial !n with $!n=0!+1!+2!+...+(n-2)!+(n-1)!$. Also, the hypothesis, which is called latter *Kurepa's hypothesis for left factorial (KH)*:

(1) $$(!n,n!)=2,\ n\in N,\ n>1,$$

where (!n,n!) is the greatest common divisor for !n and n!.

In [1], it is proved that the equivalent assertion for (1) is the assertion that for any prime numbers p, p>2 it applies:

(2) $$!p\not\equiv 0 \pmod p.$$

The stated problem is considered in [2],[3],[4],[5] and [6].

In [7] the following Theorem is proved:

Theorem The required and sufficient condition for number n>1 to be a prime number for every $m\in N$, it applies:

$$(m-1)!\,(n-m)!+(-1)^{m-1}\equiv 0 \pmod n.$$

When proving the assertion in this paper diferent variants of the Theorem are used.

2 $\{d_n\}$ sequence and KH for left factorial

In [6], the following definitions and assertions with proofs are given:

Definition 1 The sequence of integer $\{d_n\}$ is defined by the following recurrent formula:

$$d_1=-1,$$
$$d_n=-(n+1)d_{n-1}-1,$$

for every natural number n.

The terms of sequence $\{d_n\}$ are $d_1=-1$, $d_2=2$, $d_3=-9$, $d_4=44$, $d_5=-265$,...Sequence $\{d_n\}$ is the union of two disjuctive sub-sequences, a sub-sequences whose terms are negative numbers $\{d^-_n\}$ and a sub-sequences whose terms are positive numbers $\{d^+_n\}$.

Definition 2 $d_j\in\{d^-_n\}\Leftrightarrow(\ d_j\in\{d_n\}\wedge d_j<0\ ).$

Definition 3 $d_j\in\{d^+_n\}\Leftrightarrow(\ d_j\in\{d_n\}\wedge d_j>0\ ).$

Consequence 1 Sequence $\{d^-_n\}$ is given by the following recurrent formula:

$$d^-_1=-1,$$
$$d^-_n=(2n-1)(2n\, d^-_{n-1}+1),$$

for every natural numbers n.

Consequence 2 Sequence $\{d^+_n\}$ is given by the following recurrent formula:

$$d^+_1=2,$$
$$d^+_n=2n((2n+1)\, d^+_{n-1}+1),$$

for every natural numbers n.

Theorem 1 For every term of sequence $\{d_n\}$, the following holds:

a) $d_n+1 \equiv 0 \pmod{n-1}$

b) $d_n \equiv 0 \pmod{n}$

c) $d_n+1 \equiv 0 \pmod{n+1}$

Theorem 2 For every term of sequence $\{d_n\}$, the following holds:

a) $d_i>0 \Rightarrow d_{i+2} \,/\, (\,|\,d_i\,|+|\,d_{i+1}\,|\,)= i+2$

b) $d_i<0 \Rightarrow d_{i+2} \,/\, (\,|\,d_i\,|+|\,d_{i+1}\,|\,)= -(i+2)$

Consequence 3 For every term of sequence $\{d_n\}$, the following holds:

$$d_{i+2} \equiv 0 \pmod{|\,d_i\,|+|\,d_{i+1}\,|}.$$

Theorem 3 Let p be a prime number. Then:

$$!p \equiv 0 \pmod{p} \Leftrightarrow d_{p-2} \equiv 0 \pmod{p}$$

where $d_{p-2} \in \{d_n\}$.

Based on (2), Theorem 3 is an equivalent KH for left factorial.

3 Generalization

Theorem 4 Let p prime number. Then:

$$!p \equiv -d_{p-2} \pmod{p},$$

where $d_{p-2} \in \{d_n\}$.

Proof

$(p-1)!+(p-2)!+(p-3)!+...+2!+1!+0! \equiv !p \pmod{p}$

$\Leftrightarrow (p-3)!+(p-4)!+...+2!+1!+0! \equiv !p \pmod{p} \,/\, (p-2) \equiv -2$

$\Leftrightarrow (p-2)!+(p-2)(p-4)!+...+(p-2)1!+(p-2)0! \equiv !p(-2!) \pmod{p}$

$\Leftrightarrow (p-2)(p-4)!+...+(p-2)1!+(p-2)0! \equiv -1+!p(-2!) \pmod{p} \,/\, (p-3) \equiv -3$

$\Leftrightarrow (p-2)!+(p-2)(p-3)(p-5)!+...+(p-2)(p-3)1!+(p-2)(p-3)0! \equiv 3+!p\,(3!) \pmod{p}$

$\Leftrightarrow$(p-2)(p-3)(p-5)!+...+(p-2)(p-3)1!+(p-2)(p-3)0! $\equiv$**2** +!p (3!) (mod p) /(p-4) $\equiv$**-4**

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$\Leftrightarrow$(p-2)..(p-(p-4))2!+(p-2)..(p-(p-4))1!+(p-2)..(p-(p-4))0! $\equiv$**d_{p-5}**+!p (p-4)! (mod p)/ (p-(p-3)) $\equiv$**-(p-3)**

$\Leftrightarrow$(p-2)!+(p-2)! /2+(p-2)! /2 $\equiv$ -(p-3)d_{p-5} +!p (-(p-3)!) (mod p)

$\Leftrightarrow$ (p-2)! /2+(p-2)! /2 $\equiv$ -(p-3)d_{p-5} -1 +!p (-(p-3)!) (mod p)

$\Leftrightarrow$ (p-2)! $\equiv$ -(p-3)d_{p-5} -1 +!p (-(p-3)!) (mod p)

$\Leftrightarrow$ d_{p-4} +!p (-(p-3)!)$\equiv$ (p-2)! (mod p)

$\Leftrightarrow$ d_{p-4} -1 $\equiv$!p (p-3)! (mod p) /-(p-2)

$\Leftrightarrow$ d_{p-3} -1 $\equiv$!p(- (p-2))! (mod p) /-(p-1)

$\Leftrightarrow$ d_{p-2} $\equiv$!p (p-1)! (mod p).

$\Leftrightarrow$ -d_{p-2} $\equiv$!p (mod p).

Consequence 4 For any term sequence { d^{-}_{n} } it applies:

a) d^{-}_{n} +1 $\equiv$ 0 (mod 2n-2)

b) d^{-}_{n} $\equiv$ 0 (mod 2n-1)

c) d^{-}_{n} +1 $\equiv$ 0 (mod 2n).

Proof Direct consequence of Theorem 1 and the equality $d_{2n-1}=d^{-}_{n}$.

4 $\{a_n\}$ sequence

Definition 4 The sequence of integer $\{a_n\}$ is defined by the following recurrent formula:

$a_1=0$,

$a_{n+1}=-(n+2)a_n - d_n$,

for every natural number n and $d_n \in \{d_n\}$.

The terms of sequence $\{a_n\}$ are $a_1=0$, $a_2=1$, $a_3=-6$, $a_4=39$, ...

Theorem 5 For any term of sequence $\{d_n\}$ if applies:

$$d_{j-2} \equiv t \pmod{j} \Rightarrow d_{j+k} \equiv (-1)^k j(k+1)! (t+1)+ja_k +d_k \pmod{j^2}$$

for any integer t and any natural number k, j>2.

Proof

Let $d_{j-2} \equiv t \pmod{j}$ /-j

$\Leftrightarrow$ -jd_{j-2} -1 $\equiv$ -j t-1 (mod j^2)

$\Leftrightarrow$ $d_{j-1} \equiv$ -j t-1 (mod j^2) /-(j+1)

$\Leftrightarrow$ -(j+1)d_{j-1} -1 $\equiv$ (-j t-1)(-(j+1))-1 (mod j^2)

$\Leftrightarrow$ $d_j \equiv$ (j t+1)(j+1)-1 (mod j^2)

$\Leftrightarrow d_j \equiv j(t+1) \pmod{j^2} / -(j+2)$

$\Rightarrow -(j+2)d_j - 1 \equiv j(t+1)(-(j+2)) - 1 \pmod{j^2}$

$\Rightarrow d_{j+1} \equiv -2!\, j(t+1) + 0j + (-1) \pmod{j^2} / -(j+3)$

$\Rightarrow -(j+3)d_{j+1} - 1 \equiv (j+3)2!\, j(t+1) + j + 3 - 1 \pmod{j^2}$

$\Rightarrow d_{j+2} \equiv 3!\, j(t+1) + 1j + 2 \pmod{j^2} / -(j+4)$

$\Rightarrow d_{j+3} \equiv -4!\, j(t+1) + (-6)j + (-9) \pmod{j^2} / -(j+5)$

$\Rightarrow d_{j+4} \equiv 5!\, j(t+1) + 39j + 44 \pmod{j^2} / -(j+6)$

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$\Rightarrow d_{j+k} \equiv (-1)^k\, j(k+1)!\, (t+1) + ja_k + d_k \pmod{j^2}$.

Consequence 5 For any term of sequence $\{ d_n \}$ and natural number r, $j > 2$ je:

$$d_{j-2} \equiv d_{rj-2} \pmod{j}.$$

Proof
Based on Definition 4 and Theorem 5 taking for k=j-1, k=2j-1,... k=(r-1)j-1, it is obtained in sequence $d_{j-2} \equiv d_{2j-2} \equiv d_{3j-2} \ldots \equiv d_{rj-2} \pmod{j}$.

5 $\{s_n\}$ sequence

Definition 5 The sequence of integer $\{s_n\}$ is defined by the following recurrent formula:

$s_1 = 2$,
$s_n = (n+1)(s_{n-1} + (-1)^{n-1})$,

for every natural number n.

The terms of sequence $\{s_n\}$ are $s_1=2$, $s_2=3$, $s_3=16$, $s_4=75$, $s_5=456$,...

Theorem 6 Let p be a prime number. Then:

$$!p \equiv -s_{p-2} \pmod{p},$$

where $s_{p-2} \in \{s_n\}$.

Proof
In [7] it is proved that any prime number p it applies :

$(p-2)!\,(1 - 1/2! + 1/3! - \ldots - 1/(p-3)! + 1/(p-2)!) \equiv !p \pmod{p}$

$\Leftrightarrow 1 + (p-2)!\,(-1/2! + 1/3! - \ldots - 1/(p-3)! + 1/(p-2)!) \equiv !p \pmod{p} / 2$

$\Leftrightarrow 2 - 1 + 2(p-2)!\,(1/3! - \ldots - 1/(p-3)! + 1/(p-2)!) \equiv !p\, 2! \pmod{p} / 3$

$\Leftrightarrow 3(2-1) + 1 + (3!)(p-2)!\,(-1/4! - \ldots - 1/(p-3)! + 1/(p-2)!) \equiv !p\, 3! \pmod{p}$

$\Leftrightarrow 3 + 1 + (3!)(p-2)!\,(-1/4! - \ldots - 1/(p-3)! + 1/(p-2)!) \equiv !p\, 3! \pmod{p} / 4$

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$\Leftrightarrow s_{p-4} - 1 + (p-3)!\,(p-2)!\,(1/(p-2)!) \equiv !p\,(p-3)! \pmod{p} / (p-2)$

$\Leftrightarrow s_{p-3} + 1 \equiv !p\,(p-2)! \pmod{p} / (p-1)$

$\Leftrightarrow$ $s_{p-2} \equiv !p\,(p-1)!\pmod p$

$\Leftrightarrow$ $s_{p-2} \equiv -!p \pmod p$.

6 $\{b_n\}$ sequence

Definition 6 The sequence of integer $\{b_n\}$ is defined by the following recurrent formula:

$b_1=1$,

$b_n=(2n-3)2n\, b_{n-1} +1$,

for every natural number n.

The terms of sequence $\{b_n\}$ are $b_1=1$, $b_2=5$, $b_3=91$, $b_4=3641$,...

Theorem 7 Let p be a prime number. Then:

$$!p \equiv -b_{\frac{p+1}{2}} \pmod p ,$$

where $b_{\frac{p+1}{2}} \in \{b_n\}$.

Proof

In [7] it is proved that any prime number p it applies :

$(p-2)!\,(1-1/2!+1/3!-\ldots-1/(p-3)!+1/(p-2)!) \equiv !p \pmod p$

$\Leftrightarrow$ $(p-2)!\,(1/2!+3/4!+\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p \pmod p /2$

$\Leftrightarrow$ $(p-2)!\,-1+2((p-2)!)(3/4!+5/6!\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p2-\mathbf{1} \pmod p$

$\Leftrightarrow 2((p-2)!)(3/4!+5/6!\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p2-\mathbf{1} \pmod p/\mathbf{1\cdot 4}$

$\Leftrightarrow (p-2)!-1+1\cdot 2\cdot 4\,((p-2)!)(5/6!+7/8!\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p\cdot 1\cdot 2\cdot 4-1\cdot 4-1 \pmod p$

$\Leftrightarrow 1\cdot 2\cdot 4\,((p-2)!)(5/6!+7/8!\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p\cdot 1\cdot 2\cdot 4-\mathbf{5} \pmod p / \mathbf{3\cdot 6}$

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$\Leftrightarrow 2\cdot\ldots k\cdot(k+2)((p-2)!)(\,(k+3)/(k+4)!+\ldots+(p-4)/(p-3)!+1/(p-2)!) \equiv !p\,2\cdot\ldots k\cdot(k+2)-b_{\frac{k+2}{2}} \pmod p$

za k=p-7 imamo

$\Leftrightarrow 2\cdot\ldots(p-7)\cdot(p-5)((p-2)!)(\,(p-4)/(p-3)!+1/(p-2)!) \equiv !p\,2\cdot\ldots(p-7)\cdot(p-5)\ldots-b_{\frac{p-5}{2}} \pmod p / \mathbf{(p-6)\cdot(p-3)}$

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$b_{\frac{p+1}{2}} \equiv -!p \pmod p$.

Consequence 6 For any prime number p, it applies:

$$d_{p-2} \equiv s_{p-2} \equiv b_{\frac{p+1}{2}} \pmod p.$$

Proof

Follows on the bassis of Theorems 4 , 6 i 7.

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Rezime

O $\{d_n\}$ NIZU

PETOJEVIĆ Aleksandar

Nastavljajući razmatranja tvrđenja rada [6], ovde je navedeno uopštenje ekvivalenta Kurepine hipoteze za levi faktorijel preko $\{d_n\}$ niza. Razmatrana su još dva niza i dovedena su u vezu sa Kurepinom hipotezom.

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Application of the Poisson's theorem to electron

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ABSTRACT

The Piosson's theorem about the Fundamental properties of vector field has proved that is valid for the vector field of the distribution of the electical current density inside the volume of the electron.

Keywords: Poisson'stheorem, electron

Introduction

The enormous efforts have been made by the Theoretical Physicists in this century in order to solve the some problems connected with the electron as an elementary particle. Nobody of them has been thought that the crucial idea is to bring up a question of the internal structure of the electron [3, 4].

Methods

The decisive step for solving by theoreticaly methods some experimental comfirmed results connected with the electron as are : the quantum of magnetic flux Š4Ć, Bohr's magneton, the proof for the staby!ity of the electron as a elementary particle, the proof that the Ohm's law with the Maxwell's equations and the Poisson's theorem are in effect, is the idea of entering the electron by the Schrödinger equation [2].

Results

In accordance with the Poisson's theorem the Fundamental Properties of vector field must to satisfy the following relation :

$$\iiint \nabla \times \frac{\bar{A}}{r} dV = 0 \qquad (1)$$

We will check if is applicable this theorem to vector field of the distribution of the probability electrical current density of the electron. The derived expression for its vector field is worded like this [1]:

$$\bar{J}_e = 2\frac{e^2}{m_0} A_\varphi \Psi^* \Psi \bar{e}_\varphi \qquad (2)$$

Where $\bar{A}_\varphi$ is vector potential equal

$$\bar{A}_\varphi = \frac{1}{2} B r \bar{e}_\varphi \,, \left(B = \frac{m_0 c^2}{\mu_B} = \frac{m_0 c}{x_0 e}, \mu_B = \frac{e\hbar}{2m_0}, x_0 = \frac{\hbar}{2m_0 c} \right) \qquad (3)$$

m_0 is electron's mass in the stand still

$\hbar$ is Planck's constant
c is speed of light
e is electron's charge
$\vec{r}$ is radius vector

The wave functions of the electron Ψ are equal to [1]

$$\Psi = R(r)\Phi(\varphi)Z(z)$$

$$R(r) = \frac{1}{x_o} e^{-\frac{r^2}{4x_o^2}}$$

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}}$$

$$Z(z) = \frac{1}{\sqrt{2r_o}}, \quad r_o = \frac{e^2}{4\pi\varepsilon_o m_o c^2} \tag{4}$$

$$\iiint \Psi^* \Psi \, r \, dr d\varphi dz = 1 \tag{5}$$

For the curl in the integral (1) we will use the formula :

$$\nabla \times \frac{\vec{A}}{r} = \begin{vmatrix} \frac{\vec{e}_1}{h_2 h_3} & \frac{\vec{e}_2}{h_1 h_3} & \frac{\vec{e}_3}{h_1 h_2} \\ \frac{\partial}{\partial q_1} & \frac{\partial}{\partial q_2} & \frac{\partial}{\partial q_3} \\ h_1 \frac{A_1}{r} & h_2 \frac{A_2}{r} & h_3 \frac{A_3}{r} \end{vmatrix} \tag{6}$$

Applying this formula in cylindrical coordinate system to the vector field of $\vec{J}_e$ will be :

$$\nabla \times \frac{\vec{J}_e}{r} = \begin{vmatrix} \frac{1}{r}\vec{e}_r & \vec{e}_\varphi & \frac{1}{r}\vec{e}_z \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \varphi} & \frac{\partial}{\partial z} \\ 0 & r\frac{J_e}{r} & 0 \end{vmatrix} =$$

$$= \frac{1}{r}\left[\frac{\partial}{\partial \varphi}0 - \frac{\partial}{\partial z}\left(r\frac{\vec{J}_e}{r}\right)\right]\vec{e}_r + \left(\frac{\partial}{\partial z}0 - \frac{\partial}{\partial r}0\right)\vec{e}_\varphi + \frac{1}{r}\left[\frac{\partial}{\partial r}\left(r\frac{J_e}{r}\right) - \frac{\partial}{\partial \varphi}0\right]\vec{e}_z$$

$$=\frac{1}{r}\frac{\partial}{\partial r}J_c\,\bar{e}_z=\frac{1}{r}\frac{\partial}{\partial r}(e\frac{c}{x_o}r\Psi^*\Psi)\,\bar{e}_z=\frac{ec}{x_o}\frac{1}{r}\frac{\partial}{\partial r}(r\frac{1}{x_0^2}e^{-\frac{r^2}{2x_0^2}}\frac{1}{2\pi}\frac{1}{2r_o})\bar{e}_z$$

$$=\frac{ec}{x_oV_o}\frac{1}{r}\frac{\partial}{\partial r}(re^{-\frac{r^2}{2x_0^2}})\bar{e}_z=\frac{ec}{x_o}\frac{1}{r}(1-\frac{r^2}{x_o^2})e^{-\frac{r^2}{2x_0^2}}\bar{e}_z\ ,\ V_o=(2r_o)\pi(\sqrt{2}\,x_o)^2 \qquad (7)$$

The integral for this field is

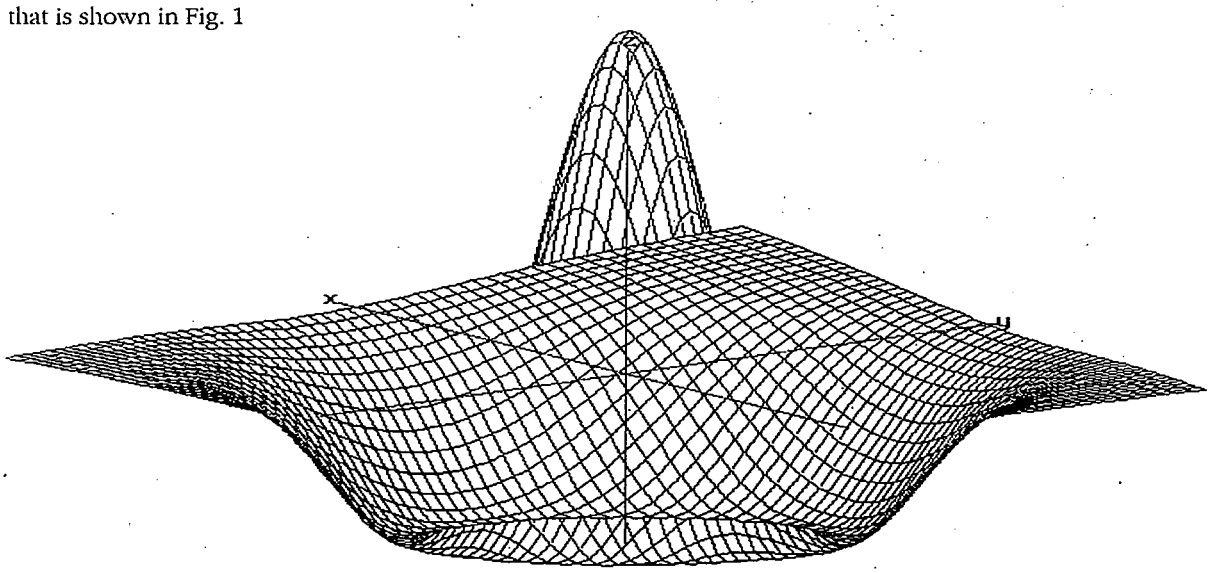
$$\iiint\nabla\times\frac{\bar{J}_e}{r}rdrd\varphi dz=\frac{ec}{x_o^3}\int_0^{\infty}(1-\frac{r^2}{x_o^2})e^{-\frac{r^2}{2x_0^2}}dr\int_0^{2\pi}\Phi^2\,d\varphi\int_0^{2r_0}Z^2dz$$

$$=\frac{ec}{x_o^3}\int_0^{\infty}(1-\frac{r^2}{x_o^2})e^{-\frac{r^2}{2x_0^2}}dr \qquad (8)$$

Before solving integral (8) we can draw the integrand function

$$f(r)=(1-\frac{r^2}{x_o^2})e^{-\frac{r^2}{2x_0^2}} \qquad (8a)$$

that is shown in Fig. 1



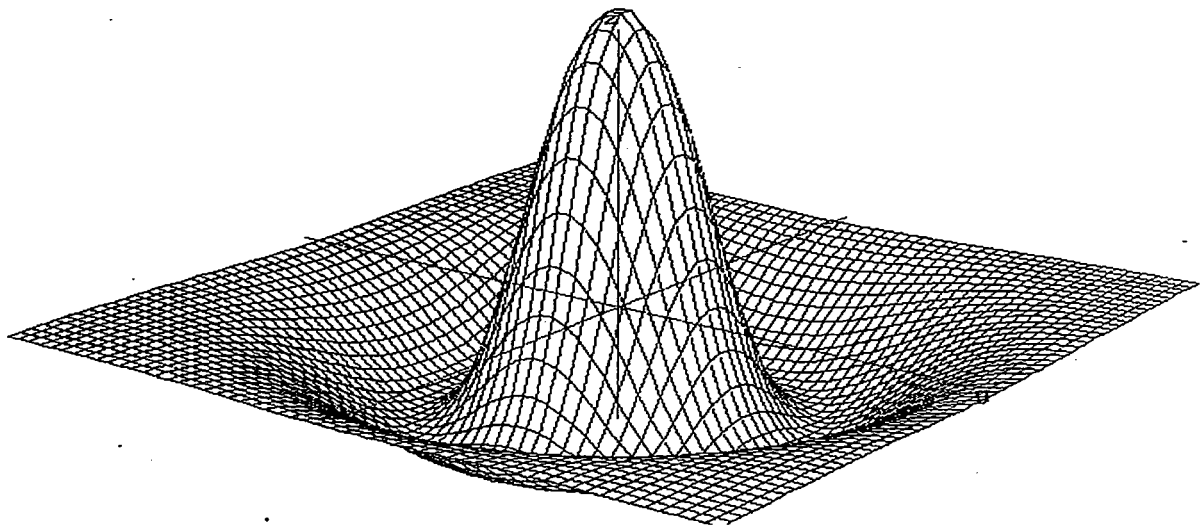


Fig.1.

In Fig.1. which represents two different projection of the equation (8a) is shown the visual representation of the Poisson's theorem. The volume integral around positive z-coordinate axis in accordance with equation (8a) is equal to that one around negative z-coordinate axis. It means that the total algebraic sum of this integral is equal to null.

The integral (8) consists of two integrals :

$$I_1 = \int_0^{\infty} e^{-\frac{r^2}{2x_0^2}}\, dr \tag{9}$$

$$I_2 = \frac{1}{x_0^2} \int_0^{\infty} r^2 e^{-\frac{r^2}{2x_0^2}}\, dr \tag{10}$$

Introducing the exchange

$$r^2 = 2x_0^2 t, \quad r = \sqrt{2}\, x_0\, t^{\frac{1}{2}}, \quad dr = \sqrt{2}\, x_0 \frac{1}{2} t^{-\frac{1}{2}}\, dt$$

the integrals (9) and (10) become :

$$I_1 = \frac{\sqrt{2}}{2} x_0 \int_0^{\infty} t^{\frac{1}{2}-1} e^{-t}\, dt = \frac{\sqrt{2}}{2} x_0\, \Gamma(\frac{1}{2}) = \frac{\sqrt{2}}{2} x_0 \sqrt{\pi} \tag{11}$$

$$I_2 = \sqrt{2}\,x_0 \int_0^{\infty} t^{\frac{3}{2}-1} e^{-t}\,dt = \sqrt{2}\,x_0\,\Gamma(\frac{3}{2}) = \sqrt{2}\,x_0\,\frac{1}{2}\Gamma(\frac{1}{2}) = \frac{\sqrt{2}}{2}x_0\sqrt{\pi} \qquad (12)$$

On the basis of obtained results (11) and (12) obviously follow that the Poisson's theorem is satisfied. So,

$$\iiint \nabla \times \frac{\vec{J}_e}{r}\,r\,dr\,d\varphi\,dz = \iiint \nabla \times 2\,\frac{\frac{e^2}{m_0}A_\varphi \Psi^* \Psi \vec{e}_\varphi}{r}\,r\,dr\,d\varphi\,dz =$$

$$= \iiint \begin{vmatrix} \frac{1}{r}\vec{e}_r & \vec{e}_\varphi & \vec{e}_z \\ \frac{\partial}{\partial r} & \frac{\partial}{\partial \varphi} & \frac{\partial}{\partial z} \\ 0 & e\omega_0 r \Psi^* \Psi & 0 \end{vmatrix} r\,dr\,d\varphi\,dz = 0 \qquad , \left(\omega_0 = \frac{c}{x_0}\right) \qquad (13)$$

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Rezime

PRIMENA PUASONOVE TEOREME NA ELEKTRON

Todorović, Z .

U ovom radu je proverena fundamentalna osobina vektorskog polja izražena u vidu Poisson-ove teoreme koja kaže da zapreminski intergal oblika

$$\iiint \nabla \times \frac{\vec{J}}{\rho} dV$$

mora biti jednak nuli.

Pošto nam formula (13) potvrđuje važenje Poisson-ove teoreme, sledi da je dobijeno vektorsko polje raspodele gustine električnih struja u unutrašnjosti elektrona jedino moguće. Ova činjenica da u stvarnosti elektron sam po sebi čini vektorsko polje gustine elementarnih struja koje cirkulišu u njegovoj zapremini $V_0 = (2r_0)\pi(\sqrt{2}\,x_0)^2$, odbacuje bilo kakve spekulacije o tome da li je elektron čestica površinski ili zapremski naelektrisan. Kao prvo, nemogućnost da se ustanovi ova priroda naelektrisanja elektrona je označavala da ta činjenica nije bila bitna za konstrukciju njegovog realnog fizičkog izgleda. Druga činjenica kojim su se poznati fizičari ovog stoleća, kao što su : Dirak, Maks Born, Fejnman, Pauli, Lorenc, zanimali odnosila se na problem količine naelektrisanja koju nosi elektron. Naime, oni su pokušavajući da odgonetnu elektron , smatrali da je ključna stvar u tome da se matematički razreši pitanje stabilnosti elektrona. Oni su ovako rezonovali : kako elementarna susedna naelektrisanja koja međusobno deluju odbojnom Kulonovom silom se ne rasprše i time učine elektron nestabilnim? Tu su pokušavali da pišu odgovorajuće diferencijalne jednačine iz klasične elektrodinamike. Krajnji rezultat njihovih istraživanja je sažeto glasio : Maksvelove jednačine treba redukovati; u prirodi bi morala postojati magnetna naelektrisanja. Međutim, kao što je poznato nijedan do sada eksperiment nije potvrdio da bi u prirodi mogla da postoje takva naelektrisanja. Pa prema tome, na svu sreću, nijne došlo do redukcije Maksvelovih jednačina , jer su one do sada odolele svim pokušajima da se ospore.

Očigledno nezadovoljavajući rezultati istraživanja pomenutih fizičara su posledica konzistentne ideje po pitanju definicje količine naelektrisanja. Njena dimenzija je Amper-sekund. Dakle, ništa drugo do dejstvo električne struje u vremenu, što je u saglasnosti sa predloženom teorijom.

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ORIGINAL SCIENTIFIC PAPER

About the Application of Maxwell's equations to the electron

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ABSTRACT

Maxwell equations have used to estimate capatitance, resistance and inductance of electron. Ohm's law to the electron has applied showing how connection as like as in resonant oscillatory circuit exist between R_e, L_e, C_e components. The voltage of the electron satisfies Faradau's law of electromagnetic induction and has shown that it plays the role like to the electromotive force. The quantum of magnetic flux has calculated is equal to that one obtained by BCS theory. However the physical maning of both fluxes is different; and obtained quantum of magnetic flux is the cause of that one obtained by BCS theory.

Keywords: Maxwell's equation, electron

Introduction

The enormous efforts have been made by the Theoretical Physicists in this century in order to solve some problems in connection with the electron as an elementary particle. None of them has thought that the crucial idea is to bring up a question of the internal structure of the electron [2, 3].

Methods

The decisive step for solving some experimentally confirmed results by theoretical methods connected with the electron such as : the quantum of magnetic flux [4], Bohr's magneton, the proof for the stability of the electron as a elementary particle, the proof that the Ohm's law with the Maxwell's equations and the Poisson's theorems are in effect, is the idea of entering the electron by the Schrödinger equation [2].

Results

The capacity of the electron can be computed by using the Poisson's equation

$$\Delta U=\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial U}{\partial\rho}\right)+\frac{1}{\rho^2}\frac{\partial^2 U}{\partial\varphi^2}+\frac{\partial^2 U}{\partial z^2}=-\frac{\rho_e}{\varepsilon_o}=\frac{e\Psi^*\Psi}{\varepsilon_o}=\frac{e}{\varepsilon_o V_o}e^{-\frac{e^2}{2x_o^2}} \qquad (1)$$

where

$\vec{\rho}$ - is radius vector of the electron in cylindrical coordinate system

U is electrical potential of electron,

$V_o=(2r_o)\pi(\sqrt{2}\,x_o)^2$ is the volume of the electron in the standstill,

e is electron charge,

ε_o is the vacuum dielectric constant

$x_o=\frac{\hbar}{2m_o c}$

$\hbar$ is Planck's constant

m_o is the electron mass in the standstill

c is speed of light

The equation (1) can be simplified if taking into account the symmetrical aspect of the electron and the idenpedence of the distribution of the charge volume density along z axis. Then it reduses to

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho\frac{\partial U}{\partial\rho}) = \frac{e}{\varepsilon_o V_o} e^{-\frac{\rho^2}{2x_o^2}} \tag{2}$$

The integral of equation (2) will be

$$\int_0^{\rho} d(\rho\frac{\partial U}{\partial\rho}) = \frac{e}{\varepsilon_o V_o}\int_0^{\rho} e^{-\frac{\rho^2}{2x_o^2}}\rho d\rho \tag{3}$$

$$\rho\frac{\partial U}{\partial\rho}\Big|_0^{\rho} = \frac{e}{4\pi\varepsilon_o r_o}(1-e^{-\frac{\rho^2}{2x_o^2}}) \tag{4}$$

Using the relation between the vector of the electrical field and the electrical potential

$$\vec{E} = -\nabla U = -(\frac{\partial}{\partial\rho}\vec{e}_\rho + \frac{1}{\rho}\frac{\partial}{\partial\varphi}\vec{e}_\varphi + \frac{\partial}{\partial z}\vec{e}_z)U \tag{5}$$

since the vector field possesses only a component in the direction of $\vec{e}_\rho$, we obtain

$$-\rho E_\rho\Big|_0^{\rho} = \frac{e}{4\pi\varepsilon_o r_o}(1-e^{-\frac{\rho^2}{2x_o^2}}) \tag{6}$$

The upper and lower limit for the value of the vector field are:

$$\lim_{\rho\to 0} E_\rho = -\frac{e}{4\pi\varepsilon_o r_o}\lim_{\rho\to 0}\frac{1-e^{-\frac{\rho^2}{2x_o^2}}}{\rho} = 0 \tag{7}$$

$$\lim_{\rho\to \infty} E_\rho = -\frac{e}{4\pi\varepsilon_o r_\infty}\lim_{\rho\to \infty}\frac{1-e^{-\frac{\rho^2}{2x_o^2}}}{\rho} = 0 \tag{8}$$

The electrical potential in the limit points is

$$\lim_{\rho\to 0}\rho\frac{dU}{d\rho} = \frac{e}{4\pi\varepsilon_o r_o}\lim_{\rho\to 0}(1-e^{-\frac{\rho^2}{2x_o^2}}) = 0 \tag{9}$$

$$\lim_{\rho\to\infty}\rho\frac{dU}{d\rho}=\frac{e}{4\pi\varepsilon_o r_o}\lim_{\rho\to\infty}(1-e^{-\frac{\rho^2}{2x_o^2}})=\frac{e}{4\pi\varepsilon_o r_o} \tag{10}$$

It means that is

$$\rho\frac{dU}{d\rho}\Big|_0^\infty=\lim_{\rho\to\infty}\rho\frac{dU}{d\rho}-\lim_{\rho\to 0}\rho\frac{dU}{d\rho}=\frac{e}{4\pi\varepsilon_o r_o} \tag{11}$$

The second way for computing the electrical potential is

$$\int_0^\infty d(\rho\frac{dU}{d\rho})=\frac{e}{\varepsilon_o V_o}\int_0^\infty e^{-\frac{\rho^2}{2x_o^2}}\rho d\rho \tag{12}$$

Since the integral of equation (12) is

$$\int_0^\infty e^{-\frac{\rho^2}{2x_o^2}}\rho d\rho = x_o^2$$

we obtain

$$\rho\frac{dU}{d\rho}\Big|_0^\infty=\frac{e\,x_o^2}{\varepsilon_o(2r_o)\pi(\sqrt{2}\,x_o)^2}=\frac{e}{4\pi\varepsilon_o r_o} \tag{13}$$

$$-\rho E_\rho\Big|_0^\infty=\frac{e}{4\pi\varepsilon_o r_o}=U_o-U_\infty=-U_\infty \tag{14}$$

The difference between potentials from the center of the electron to the boundeless distance is

$$U=U_o-(-U_\infty)=U_\infty=\frac{e}{4\pi\varepsilon_o r_o}=U_e \tag{15}$$

From this equation the capacity of the electron C_e is equal to

$$C_e=\frac{e}{U_e}=4\pi\varepsilon_o r_o \tag{16}$$

The Application of the Maxwell equations

$$\vec{B}=\operatorname{rot}\vec{A}=\frac{1}{\rho}\left(\frac{\partial A_z}{\partial\varphi}-\frac{\partial(\rho A_\varphi)}{\partial z}\right)\vec{e}_\rho+\left(\frac{\partial A_\rho}{\partial z}-\frac{\partial A_z}{\partial\rho}\right)\vec{e}_\varphi+\frac{1}{\rho}\left(\frac{\partial(A_\varphi\rho)}{\partial\rho}-\frac{\partial A_\rho}{\partial\varphi}\right)\vec{e}_z \tag{17}$$

Since is

$$A_\rho=0,\ A_z=0$$

follows

$$\vec{B}=\frac{1}{\rho}\frac{\partial}{\partial\rho}(A_\varphi\rho)\vec{e}_z \tag{18}$$

From this one obtains

$$\nabla\vec{B}=\operatorname{div}\vec{B}=\frac{\partial}{\partial z}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}(A_\rho\rho)\right]=0$$

$$A_\varphi=\frac{1}{2}B\rho\ ,\qquad \left(B=\frac{m_0c^2}{\mu_B}=\frac{m_0c}{x_0e};\ x_0=\frac{\hbar}{2m_0c}\right) \tag{19}$$

$$\operatorname{rot}\vec{H}=\vec{J}=\frac{1}{\rho}\left(\frac{\partial H_z}{\partial\varphi}-\frac{\partial(\rho H_\varphi)}{\partial z}\right)\vec{e}_\rho+\left(\frac{\partial H_\rho}{\partial z}-\frac{\partial H_z}{\partial\rho}\right)\vec{e}_\varphi+\frac{1}{\rho}\left(\frac{\partial(H_\varphi\rho)}{\partial\rho}-\frac{\partial H_\rho}{\partial\varphi}\right)\vec{e}_z=$$

$$=-\frac{i\hbar e}{2m_0}\left(\Psi^*\operatorname{grad}\Psi-\Psi\operatorname{grad}\Psi\right)-2\frac{e^2}{m_0}A_\varphi\,\Psi^*\Psi\vec{e}_\varphi \tag{20}$$

Since the wave function Ψ is real function will be :

$$\operatorname{rot}\vec{H}=-2\frac{e^2}{m_0}A_\varphi\,\Psi^*\Psi\vec{e}_\varphi\ ,\ H_\varphi=0,\ H_\rho=0 \tag{21}$$

$$-\frac{\partial H_z}{\partial\rho}=-2\frac{e^2}{m_0}A_\varphi\,\Psi^*\Psi \tag{22}$$

$$dH_z=2\frac{e^2}{m_0}A_\varphi\,\Psi^*\Psi d\rho=2\frac{e^2}{m_0}\frac{1}{2}B\rho\Psi^*\Psi d\rho=\frac{e^2}{m_0}B\rho\Psi^*\Psi d\rho \tag{23}$$

The same for magnetic field one obtains immediatly from the equation of the differential element of the electrical surrent intensity [1]:

$$dI = \vec{J}\, d\vec{\sigma} = 2\,\frac{e^2}{m_o} A_\varphi\, \Psi^*\Psi\, d\rho\, dz = dH_z\, dz \tag{24}$$

The differential element of the quantum of magnetic flux is :

$$d\Phi_o = d\vec{A}_\varphi\, d\vec{l} = \left(\frac{1}{2} dB\rho\right)(\rho\, d\varphi) \tag{25}$$

where is

$$dA_\varphi = \frac{\mu_o}{2} dH_z\, \rho = \frac{\mu_o e^2}{2 m_o} B\rho^2\, \Psi^*\Psi\, d\rho \tag{26}$$

$$d\Phi_o = \frac{\mu_o e^2}{2 m_o} B\, \Psi^*\Psi \rho^3\, d\rho\, d\varphi \tag{27}$$

and the quantum of magnetic flux

$$\Phi_o = \iint d\Phi_o = \frac{\mu_o e^2}{2 m_o} B \int_0^\infty R^2 \rho^3 d\rho \int_0^{2\pi} \Phi^2\, d\varphi\, Z^2 = \frac{1}{\varepsilon_o c^2}\, \frac{e^2}{2 m_o}\, \frac{m_o c}{x_o e}\, 2x_o^2\, \frac{1}{2r_o} =$$

$$= \frac{1}{\varepsilon_o c^2}\, \frac{e x_o c}{2}\, \frac{4\pi\varepsilon_o m_o c^2}{e^2} = \frac{2\pi x_o m_o c}{e} = \frac{2\pi}{e}\, \frac{\hbar}{2 m_o c}\, m_o c = \pi \frac{\hbar}{e} \tag{28}$$

The Stokes's theoreme

$$\oint \vec{A}_\varphi\, d\vec{l} = \iint_\sigma \mathrm{rot}\, \vec{A}_\varphi\, d\vec{\sigma} = \iint_\sigma \vec{B}\, d\vec{\sigma} = \pi \frac{\hbar}{e} = \Phi_o \tag{29}$$

The Gauss's theoreme

$$\oiint_S \vec{B}\, d\vec{\sigma} = \iiint_{D \to V_o} \mathrm{div}\vec{B}\, dV = \iiint_{D \to V_o} \nabla \vec{B}\, dV = 0 \tag{30}$$

The Application of the Ohm's law to the electron

Using the obtained capacity of the electron (16), according to the classical electrodynamics, we can compute :

$$U_e = \frac{e}{4\pi\varepsilon_0}\frac{4\pi\varepsilon_0}{e^2} m_0c^2 = \frac{m_0c^2}{e} \tag{31}$$

The electron electrical resistance

$$R_e = \frac{U}{I_c} = \frac{m_0c^2}{e}\frac{2\pi x_0}{ec} = \frac{m_0c^2}{e^2c} 2\pi \frac{\hbar}{2m_0c} = \pi\frac{\hbar}{e^2} \tag{32}$$

The quantum of magnetic flux

$$eR_e = \Phi_0 = \pi\frac{\hbar}{e} \tag{33}$$

The internal energy of the electron or the electron energy in the rest is

$$E = U_e I_e T = \frac{m_0c^2}{e}\frac{ec}{2\pi x_0}\frac{2\pi x_0}{c} = m_0c^2$$

$$(I_eT = e,\ \nu_0 = \frac{1}{T})$$

$$= I_e^2 R_e T = \left(\frac{ec}{2\pi x_0}\right)^2 \pi\frac{\hbar}{e^2}\frac{2\pi x_0}{c} = \frac{\hbar c}{2x_0} = \frac{\hbar c}{2\hbar} 2m_0c = m_0c^2 \tag{34}$$

Let us notice that the electron voltage U_e plays the role of the electromotive force of electron. Namely,

$$U_e = \left|\frac{d\Phi}{dt}\right| = \frac{\Phi_0}{T} = \pi\frac{\hbar}{e}\nu_0 = \Phi_0\nu_0 \tag{35}$$

$$= \pi\frac{\hbar}{e}\frac{\omega_0}{2\pi} = \pi\frac{\hbar}{2e}\frac{c}{x_0} = \frac{\hbar}{2e}\frac{c}{\hbar}2m_0c = \frac{m_0c^2}{e}$$

In the sense of the classical electrodynamics we can regard an electron like a resonant current currying circuit. The number components of that circuit is two. Taking into consideration the possible combination of them : R_e - C_e , R_e - L_e , L_e - C_e . The components of that circuit behave like an ideal capacitor C_e , resistor R_e and inductance L_e .

The ideal feature means that there is no waste of energy from them. A circuit performs like a resonant oscilatory circuit if fullfilled the equality of the resistance of the appropriate components. Such conditions in classical electrical circuit are expressed like these

$$R_e = \frac{1}{C_e \omega_o} \tag{36}$$

$$R_e = L_e \omega_o \tag{37}$$

$$L_e \omega_o = \frac{1}{C_e \omega_o} \tag{38}$$

Despite the classical electrical resonant circuit, here, the role of the resonant angular frequency ω_o plays the linear frequency $\nu_o = \frac{\omega_o}{2\pi}$. Namely, if we previosly computed values of the components

$$R_e = \frac{U}{I_e} = \pi \frac{\hbar}{e^2} = \frac{\Phi_o}{e} \tag{39}$$

$$L_e = 4\pi \frac{m_o}{e^2} x_o^2 = \frac{\Phi_o}{I_e} = \frac{\Phi_o}{e\nu_o} \tag{40}$$

$$C_e = \frac{e}{U} = 4\pi \varepsilon_o \nu_o = \frac{eT}{\Phi_o} = \frac{e}{\Phi_o \nu_o} \tag{41}$$

put in mutual dependence, we will obtain :

$$\nu_o = \frac{1}{R_e C_e} = \frac{R_e}{L_e} = \frac{1}{\sqrt{L_e C_e}} = \frac{1}{T} \tag{42}$$

$$R_e = \sqrt{\frac{L_e}{C_e}} \tag{43}$$

that represents the simplest possible relation on the mathematical sense.

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Rezime

O PRIMENI MAKSVELOVIH JEDNAČINA NA ELEKTRON

Todorović, Z.

Primenjujući Poisson-ovu jednačinu električnog potencijala, određen je kapacitet elektrona. Ovde treba istaći da se direktno ne određuje potencijal preko rešenja diferencijalne jednačine (1) . Naime, rešenje jednačine (1) je oblika logaritamske funkcije i po prirodi integral takve funkcije je divergentan. Zato je izbegnuto to rešenje jer nema fizičkog smisla. Potencijal je rešen preko definicije graničnih vrednosti za potencijal (7,8,9,10) i smatra se da je ovakav pristup jedino izvoran (16).

Primenom Maksvelovih jednačina (17-23) dobijena je raspodela magnetnog polja u unutrašnjosti elektrona koja ima dominantno nehomogen karakter(23).Isto tako je dat postupak određivanja kvanta magnetnog fliksa (28) koji se poklapa sa BCS teorijom. Primenom Ohm-ovog zakona na elektron izračunate su komponente za otpornost , kapacitet i induktivnost. Pokazano je da on funkcioniše kao rezonantno oscilatorno kolo i da efektivno delije kao da je sastavljen od parova komponenti RC, RL i LC.

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ORIGINAL SCIENTIFIC PAPER

A Study of the Initial Stages of the Electrochemical Deposition of Lead on Vitreous Carbon

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ABSTRACT

The initial stages of lead deposition onto vitreous carbon electrodes have been investigated using Linear Sweep Voltammetry (L.S.V.) and potential step techniques. This study included both underpotential (UPD) and overpotential (OPD) depositions in order to investigate their interdependence.

Experiments were performed on a very carefully mechanically polished vitreous carbon electrode (surface area ≈ 0.283 cm^2) in 10^{-1}M $Pb(OAC)_2$+10^{-3}M $HClO_4$ solutions.

Lead UPD on vitreous carbon was found to be the result of substrate reconstruction induced by repeated unerpotential deposition and dissolution leading to surface condition changes favoring deposition of the first layer.

The uderpotential deposition of lead on vitreous carbon and its extent was found to be of a profound influence on the nucleation and growth mechanism of the overpotential lead deposition. In the absence of pronounced lead UPD on vitreous carbon lead overpotential deposition commences and proceeds trough 3D instanteneous nucleation and growth mechanism. In the presence of pronounced lead UPD on vitreous carbon the mechanism of the initial stages of lead overpotential deposition appears to dependent on the competition between 2D and 3D nucleation and growth , subject to overpotential applied.

Key words: Underpotential deposition, Overpotential deposition, Liner sweep voltammetry, Potential step, Pb, Vitreous carbon

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 1834[1]. 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 exhibit 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 electocrystallization 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 uderpotential 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.

The techniques employed were linear sweep voltammetry and potential step.

MATERIALS AND METHODS

The experimental work described in this study can be divided into two parts:

1 .- Linear sweep voltammetry (L.S.V.) experiments.

2.- Potential step experiments: (single, double and triple potential pulses were used).

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., or 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 L.S.V. and 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 mash disc ≈ 1.5 cm^2 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

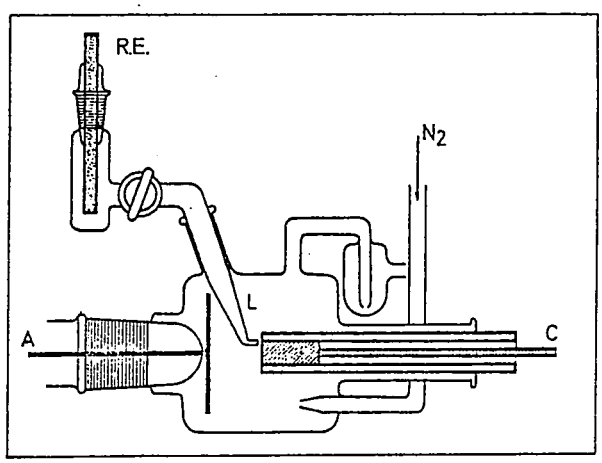

Figure 1. a) The cell used for most of the L.S.V. and potential step experiments.

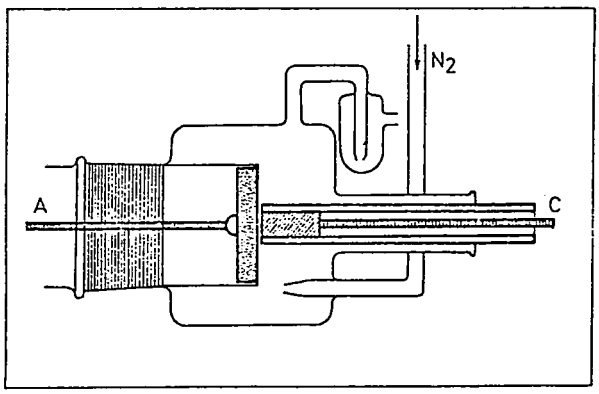

Figure 1. b) The cell used for potential step experiments on a very long time scale.

of slightly larger diameter after being wrapped with very thin $1 \cdot 10^{-4}$ cm) teflon foil.

Working electrodes were small cylinders of vitreous carbon ("Le Carbone", France 0.6 cm in diameter. These were sealed into Kel-F rod such that only the top surface of the carbon 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 mounting a carbon cylinder 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 carbon and contraction of the plastic housing ensured a very tight fit. A brass pin pressed by strong spring into the back of the vitreous carbon cylinder made electrical contact. 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%) scaled 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 zinc[18].

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for vitreous carbon 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 very careful mechanical polishing.

The electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}$ cm and $3 \cdot 10^{-4}$ cm grade, and "Banner scientific Ltd." cm and 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.

After each polishing procedure step the electrode was rinsed with tap water and eventually with triply distilled water.

These polishing processes 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 $0.20 cm^2$).

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

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.

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 picoampermeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

Voltammograms obtained on vitreous carbon electrodes in lead free solution (10^{-3} M $HClO_4$ + 0.5M $NaClO_4$), Fig. 2.a, showed only very small background currents with no structural features.

Linear sweep voltammograms recorded in the presence of lead exhibited a process of lead deposition at potentials positive to the bulk lead reversible potential, Fig. 2.b. However, the process of dissolution of this underpotentially deposited lead was not very well defined at first, but if the electrode was maintained at a potential within the UPD region for some time (in this case 4 minutes) the dissolution peak (dashed line in Fig. 2.c) became well delineated.

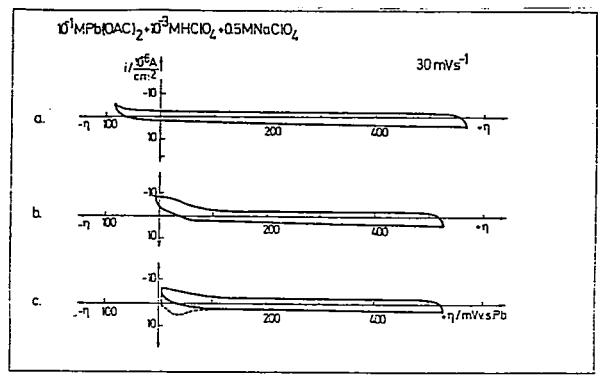

Figure 2. Behaviour of a carefully polished vitreous carbon electrode in lead free solution a, and during lead UPD b, c.

Under repetitive cycling, the UPD peaks increased in size with increasing number of cycles, Fig. 3., at first rapidly but later the change was slow. In Fig. 4. a voltammogram recorded after 30 cycles is presented. The charge associated with either the cathodic or the anodic peaks was approximately $64 \cdot 10^{-6}$ Ascm^{-2}.

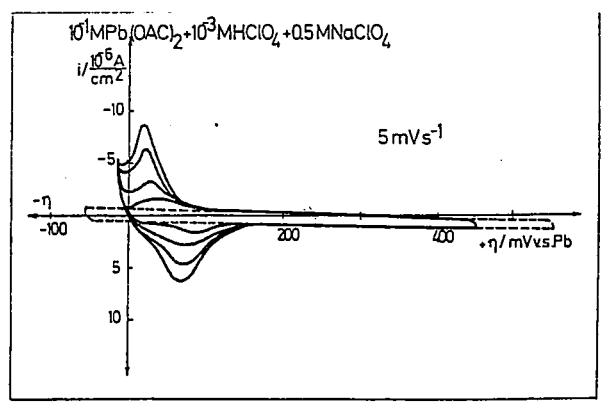

Figure 3. L.S.V. on vitreous carbon electrode under repetitive cycling showing lead UPD.

The change in substrate structure induced by UPD should have a considerable effect on the kinetics of the overpotential deposition. Therefore potential step experiments in both UPD and OPD regions were performed.

A vitreous carbon electrode in lead solutions was subjected to single and double potential steps. In the case of single potential steps, the starting potential, ES, was usually 400 mV positive to the reversible potential of lead in the given solution. The pulse potential, η, was varied such that its amplitude would correspond to potentials within the range of recorded voltammetric lead UPD peak (see Fig. 4.).

It appeared that the UPD process was relatively fast and because the amount of lead deposited were small, the i-t transients obtained did not yield data suitable for quantitative analysis.

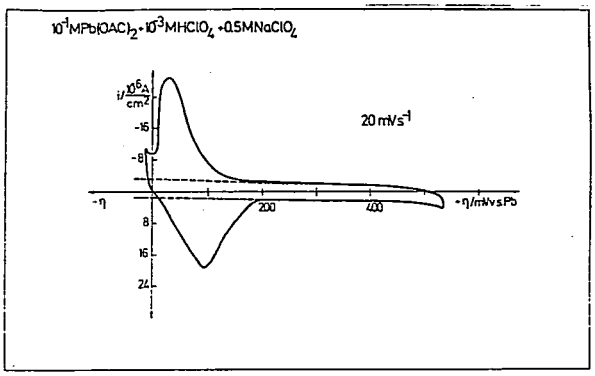

Figure 4. The voltammogram due to lead UPD on vitreous carbon recorded after 30 L.S.V. cycles.

However, when η was in the overpotential region, a variety of current-time responses were recorded.

In those cases when the electrode had not experienced repetitive cycling in the UPD region and therefore was directly subjected to a single potential pulse, η = -6 mV, the i-t response was of the form given in Fig. 5.

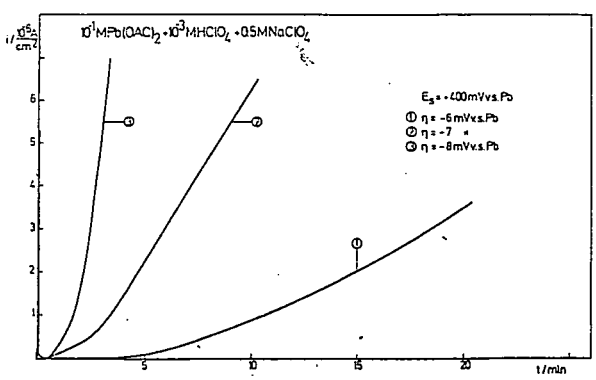

Figure 5. Current-time transients for single potential step applied into the lead overpotential deposition region

When electrode was subject to continuous cycling (30-40 cycles) prior to application of a single pulse η = -6 mV), the resulting i-t transient had the form given in Fig. 6., or sometimes the shape presented in Fig. 7.

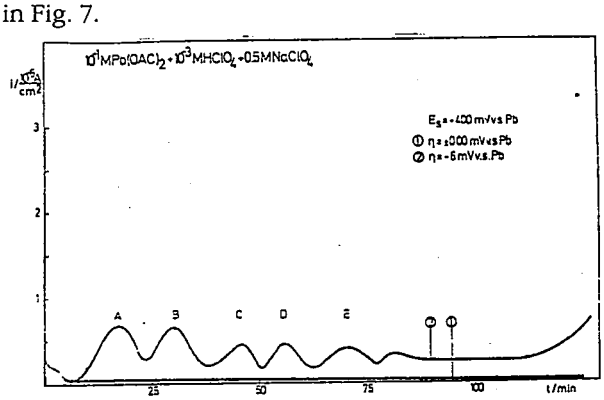

Figure 6. Current-time response to single potential step applied in lead overpotential deposition region when previous L.S.V. repetetive cycling in UPD was performed.

Curve 1 in both figures corresponds to the i-t transients obtained when a single pulse to η = 0 mV was applied.

However, when overpotentials η ≥ -7 mV were applied, typically the results given in Fig. 8. were obtained.

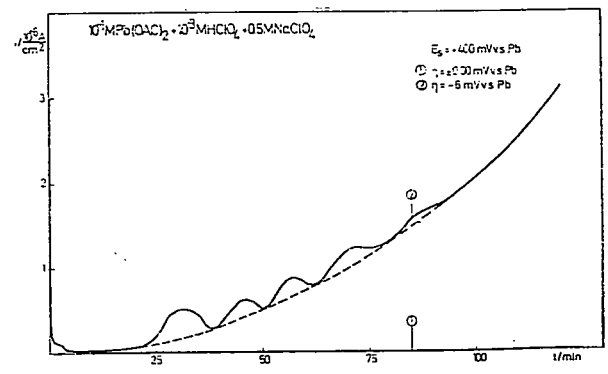

Figure 7. Current-time response to single potential step applied in lead overpotential deposition region when previous L.S.V. repetetive cycling in UPD was performed.

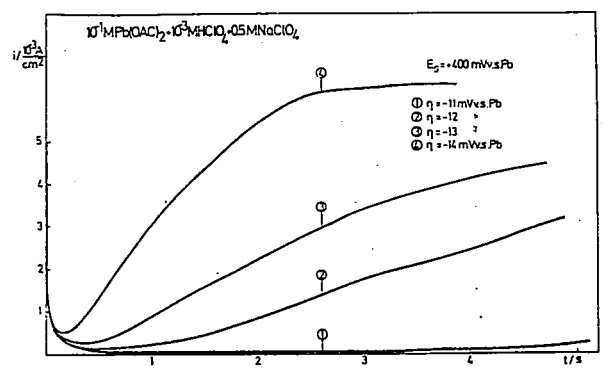

Figure 8. Current-time transients from single potential steps applied deeper into the lead overpotential deposition region when previous L.S.V. cycling in the UPD region had been performed.

Double pulse experiments were used to provide additional information on the subject. From the starting potential, Es, a first pulse η_1 of a certain duration, τ_1,

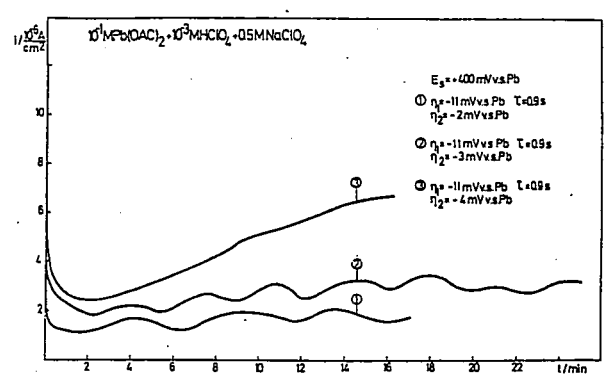

Figure 9. Current-time transients for double pulse potential steps applied into the lead overpotential deposition region.

was applied and then the electrode was maintained at the potential of the second pulse η_2, which was high enough to provide further growth of the deposit nucleated during the first pulse, but not high enough to nucleate additional growth centres. An example of vitreous carbon electrode behaviour under such a regime is presented in Fig. 9.

DISCUSSION

Since the voltammograms of lead free supporting electrolyte in a region of potentials appreciably exceeding the UPD region (Fig. 2.a and Fig. 3.) in both the cathodic and the anodic directions, did not show any reaction, it appears that changes in the UPD behaviour could well be the result of the rearrangement of the substrate surface. The lead deposited in the UPD region most probably penetrates into the substrate19, and changes the structure of the surface region of the carbon. When removed during dissolution, the lead leaves its "fingerprints" in the form of a carbon structure that promotes increasing amounts of subsequent lead deposition. As every subsequent deposition cycle increases the extent of the reconstruction, the UPD becomes pronounced.

This behaviour has some similarities to the results reported for the case of copper underpotential deposition on gold20 and for which alloy formation is probably involved.

It appears, therefore, that reconstruction of this sort is likely to occur in most of the cases when the two materials, deposit and substrate, are alloying.

When analyzed, the current-time transients for single potential steps applied into the lead overpotential deposition region without prior repetitive cycling in the UPD region (see Fig. 5.), according to the relationship for charge transfer controlled 3D instantaneous nucleation and growth[4,5,21,22]:

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

a linear relationship was obtained, Fig. 10, for i vs. t^2.

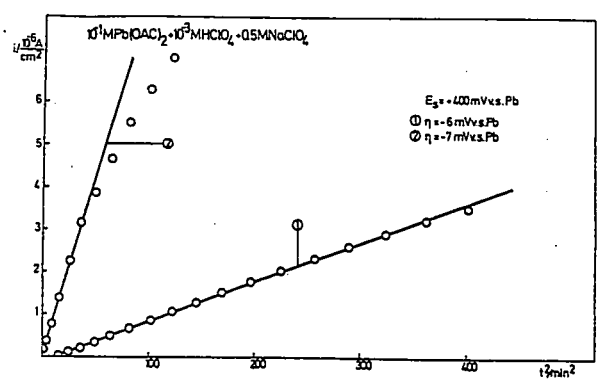

Figure 10. Plots of i vs. t^2 for transients of Fig. 5.

The initial hump occurring immediately after the current due to double layer charging (see Fig. 6 and 7), encompassed a charge $34 \cdot 10^{-6}$ Ascm^{-2}, which was a typical value obtained for the uderpotentially deposited lead during repetitive cycling.

Curve 2 in Fig. 6. Shows a charge of $\approx$ 36 Ascm^{-2} for each of the peaks A and B; and $\approx 250 \cdot 10^{-6}$ Ascm^{-2} on average for each of the subsequent peaks C, D and E. Finally, after the waves die out the current increases, following a square law with time. Having in mind that the closest-packed lead monolayer requires $\approx 310 \cdot 10^{-6}$ Ascm^{-2}, it appears that lead in this case deposits trough 2D nucleation and layer by layer growth[8,23-25]. When a 2D layer reaches a certain dimension it makes 2D nucleation and growth of the subsequent layer possible and indeed probable. It appears therefore that both 2D and 3D nucleation take place on the surface of the carbon electrode. 2D nuclei are formed more readily than 3D nuclei at low overpotentials.

At longer times, however, sufficient 3D nuclei are formed for the 3D growth mechanism to take over. Fig. 7 supports this view. It shows 3D side by side with 2D nucleation (most probably instantaneous) and layer by layer growth. When deconvoluted the curve gives a linear i vs. t^2 relationship for the dashed line[26] and a wavelike i-t function common to 2D layer by layer growth. The relative rates of 2D and 3D nucleation appear to depend upon surface preparation. Whether 2D growth preceded 3D growth for a substantial period of time, Fig. 6., or the two growth mechanisms occurred at the same time side by side on different areas of the surface, Fig. 7., depended on surface preparation. The former behaviour was more likely if extreme care was taken with the final stages of surface polishing and more cycles were carried out in the underpotential region.

It was interesting to find that overpotential lead deposition commenced at overpotentials as low as η = -6 mV, which is substantially, less than found in the literature on the subject[27-30]. Furthermore, lead deposition at this overpotential showed i-t transients different in character depending on how much of the lead UPD monolayer had previously been put down.

However, analysis of the results obtained when overpotentials $\eta \geq$ -7 mV were applied (see Fig. 8) gave a typical i-t^2 relationship for 3D instantaneous nucleation and growth of overlapping centres, Fig. 11.

It was found that η_1 = -9 mV lasting for τ_1 = 0.9s and more, was enough to nucleate centres which would then grow further at the potential η_2 = - 4 mV and -5 mV. The type of the growth and its "life" depended on τ_1 and η_2 for a given η_1. The experimental results obtained followed more or less the theoretically predicted relationships already mentioned[4,5,31-37]; the larger the value of η_1, τ_1, and η_2, the higher the current at a given time, i.e. the higher the 3D nucleation and 3D growth rates.

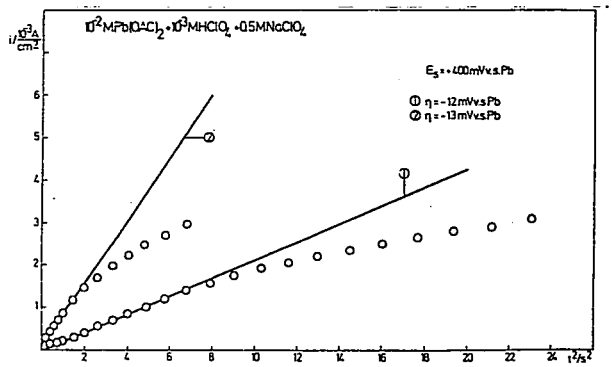

Fig. 11. Plots of i vs. t^2 for the transients of Fig. 8.

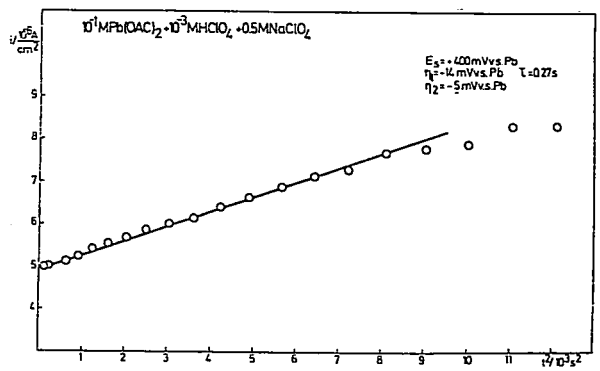

Figure 13. b) Plot of i vs. t2 for the transient of Fig. 13. a).

At lower η_1 (-9 to -11 mV), for a given τ_1, the type of growth depended on η_2 (see Fig. 9). If η_2 = -2 mV, the character of the i-t transient strongly resembled 2D layer by layer growth, although most probably accompanied by certain amount of 3D growth. This became more apparent if η_2 = -3 mV. When η_2 = -4 mV the usual i vs. t^2 linear relationship was approached, Fig. 12.

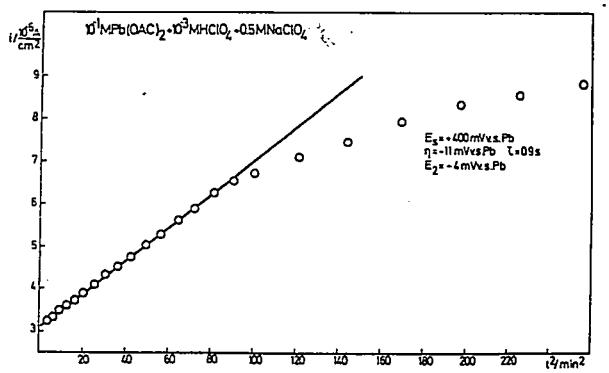

Figure 12. Plot of i vs. t^2 for transient 3 of Fig. 9.

If even higher η_1 and η_2 values were used, the familiar i-t transients reflecting 3D nucleation and growth were obtained, Fig. 13.a and b.

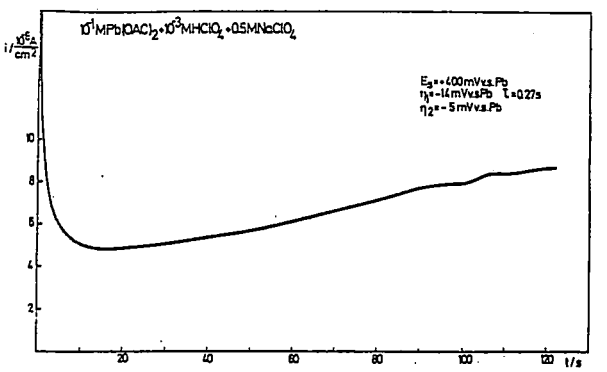

Figure 13. a) Current-time transient for a double potential step applied into the lead overpotential deposition region.

The fact that the overpotential for lead deposition on vitreous carbon was found to be such a low value is not surprising in view of the results presented. The free energy of formation for cylindrical nucleus of a height l, and radius r, is given by[4,5,23,38]:

$$\Delta G = -\frac{\pi r^2 l \rho F \eta}{M} + 2\pi r l \sigma_1 + \pi r^2 (\sigma_1 + \sigma_2 - \sigma_3)$$

where ρ is the density of the nucleus, M its molecular weight, and zFη the bulk free energy per mole at any overpotential, η, (being measured with respect to the equilibrium potential of the bulk phase).

The critical nuclear size which must be reached for growth to take place, rcrit, is:

$$r_{crit} = -\frac{l\sigma_1}{\frac{l\rho zF\eta}{M} - (\sigma_1 + \sigma_2 - \sigma_3)}$$

and ΔG_{crit} is:

$$\Delta G_{crit} = -\frac{l\sigma_1}{\frac{l\rho zF\eta}{M} - (\sigma_1 + \sigma_2 - \sigma_3)}$$

where: σ_1 is the free surface energy at the nucleus-solution, σ_2 at the nucleus-electrode, and σ_3 at the electrode-solution interfaces.

It is obvious that for all other conditions being equal, ΔG_{crit} would be smaller the larger is $\Delta\sigma = (\sigma_1 + \sigma_2 - \sigma_3)$, thus increasing the nucleation rate given as:

$$A = k \exp\left(-\frac{\Delta G_{crit}}{RT}\right)$$

In the case of lead deposition on vitreous carbon, it appears that repeated deposition and dissolution at potentials positive to the reversible potential of lead, transforms the electrode surface in such an way that σ_2 becomes lower and $\sigma_3 - (\sigma_1 + \sigma_2)$ is larger and thus 2D nucleation is favored. In this case it appears more favorable to continue 2D layer by later growth

which occurs most probably in the form of separate patches rather than full monolayers.

At higher overpotentials the bulk free energy term lpzFη/M (or the appropriate form depending upon geometry) becomes dominant and three-dimensional nucleation can readily take place.

CONSLUSIONS

There is underpotential deposition (UPD) of lead on vitreous carbon. Repetitive deposition and dissolution of lead in UPD region on vitreous carbon induces substrate surface rearrangement, thus promoting increasing amounts of lead being deposited in each subsequent UPD deposition attempt.

The vitreous carbon surface restructurion is most probably due to surface alloying of vitreous carbon by the lead deposited in UPD.

In the absence of pronounced lead UPD on vitreous carbon, the lead overpotential deposition commences and proceeds trough 3D instanteneous nucleation and growth mechanism.

In the presence of pronounced lead UPD on vitreous carbon the mechanism of the initial stages of the lead overpotential deposition appears to dependent on the competition between 2D and 3D nucleation and growth, subject to the value of the overpotential applied.

For very low overpotential values (η = -6 mV to -10 mV vs.Pb) and shorter deposition times initial stages of lead OPD are dominated by 2D nucleation and 2D . layer by layer growth. At overpotential values greater than -9 mV vs.Pb, and longer deposition times lead overpotential deposition appears to proceed predominantly by 3D nucleation and growth mechanism.

The fact that the critical overpotential for lead overpotential deposition was found to be only η = -6 mV vs.Pb can be explained as being a result of the observed phenomena; namely, that the repeated deposition and dissolution of lead in the UPD region transform the electrode surface in such an way that provokes substantial changes of the free surface energy value at the nucleus-electrode interface. When the said value becomes lower, 2D nucleation and 2D layer by layer growth is favored and thus low critical lead deposition overpotential on vitreous carbon.

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REZIME

STUDIJA POCETNIH STADIJUMA ELEKTROTALOZENJA OLOVA NA STAKLASTOM GRAFITU

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Ispitivani su početni stadijumi elektrotaleženja olova na elektrodama od staklastog grafita koristeći linearnu cikličnu promjenu potencijala elektrode (L.S.V., ciklička voltametrija) i tehnike potenciostatskog pulsa. Ovaj rad obuhvata elektrotaloženj pri potencijalima pozitivnijim od reverzibilnog (UPD) i potencijalima negativnijim od reverzibilnog potencijala olova i njihovu međusobnu međuzavisnost.

Eksperimenti su izvođeni na veoma pažljivo mehanički poliranoj elektrodi od staklastog grafita (površina poprečnog presjeka od oko 0.283 cm^2) u 10^{-1}M $Pb(OAC)_2$+10^{-3}M $HClO_4$ rastvorima.

Rezultati ispitivanja su pokazali da na staklastom grafitu dolazi do elektrotaloženja olova pri potencijalima pozitivnijim od reverzibilnog potencijala olova.

Ponavljano elektrotaloženje i rastvaranje olova na staklastom grafitu u područjima potencijala pozitivnijeg od reverzibilnog, izaziva promjene strukture površine elektrode uvećavajući u svakom narednom taloženju količinu olova istaloženog pri potencijalima pozitivnijim od reverzibilnog. Ova promjena strukture površine najvjerovatnije je rezultat površinskog legiranja staklastog grafita olovom.

Kad je količina iztaloženog olova pri potencijalima pozitivnijim od reverzibilnog na staklastom grafitu mala ili neznatna, naknadno elektrotaloženje olova uz katodne prenapetosti započinje i odvija se mehanizmom trenutne 3D nukleacije i daljeg rasta.

U prisustvu većeg elektrotaloženja olova pri potencijalima pozitivnijim od reverzibilnog na staklastom grafitu mehanizam elektrotaloženje olova uz katodne prenapetosti zavisi od konkurencije između 2D i 3D nukleacije. Za veoma male prenapetosti (η = -6 mV do -10 mV vs.Pb) i kraće trajanje elektrotaloženja, početnim stadijumima elektrotaloženja olova na staklastom grafitu dominira 2D nukleacija i rast sloj po sloj. Pri prenapetostima većim od - 9mV vs.Pb i dužim trajanjima elektrotaloženje olova na staklastom grafitu vođeno je prvenstveno mehanizmom 3D nukleacije i rasta.

Činjenica da je ustanovljena kritična prenapetost taloženja olova na staklastom grafitu svega - 6mV vs.Pb može se objasniti zapaženom pojavom da predhodno ponovljeno taloženje i rastvaranje olova pri potencijaima pozitivnijim od reverzibilnog, mijenja površinu grafita tako da izaziva promjenu vrijednosti slobodne energije površine na dodiru nukleusa i elektrode. Kada ta vrijednost postane manja favorizovana je 2D nukleacija, pa odatle i niska prenapetost taloženja olova.

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ORIGINAL SCIENTIFIC PAPER

A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART I. The Linear Sweep Voltammetry Behaviour of (111) oriented Copper Single Crystal Electrode

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ABSTRACT

The uderpotential deposition and dissolution of lead onto carefully chemically polished polycrystalline and single crystal copper (111) electrodes from acetate, nitrate and perchlorate solutions have been investigated using Linear Sweep Voltammetry (L.S.V.). The voltammetric behaviour of the polycrystalline copper electrodes was shown to be a composite of the various single crystal structures in its surface. Voltammetry results on Cu(111) single crystal electrode showed lead forming a single underpotential monolayer with closest-packed epitaxial structure. The assumption that this monolayer was formed by 2D first order phase formation is strongly supported by: extremely small half height deposition peak widths,; large deposition peak to dissolution peak potential separation, ΔE_{A-K}; the "adsorption isotherm" evaluated from L.S.V. data giving a first order discontinuity; Frumkin adsorption isotherm factor g = 3.7, very close to 4; and the lead monolayer equilibrium potential dependence on lead concentration. A model of crystalline lead closest-packed epitaxial monolayer on Cu(111) surface is proposed. Cu(111) surface reconstructs to a structure similar to Cu(100) during lead deposition/dissolution cycling in UPD region, but only if actual dissolution of copper takes place during dissolution part of the cycle.

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

INTRODUCTION

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 exhibit important differences. Nevertheless, an electrodeposition process could be divided basically into two parts[1-12]:

- 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 electocrystallization 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 copper polycrystals and single crystals. The uderpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The substrate posses high hydrogen evolution overvoltage and therefore deposition of lead is not complicated by hydrogen co-adsorption processes.

The techniques employed were linear sweep voltammetry and potential step.

MATERIALS AND METHODS

The experimental work described in this paper was done 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). The waveform generator provided 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 mash disc ≈ 1.5 cm^2 in area, positioned parallel to the working electrode.

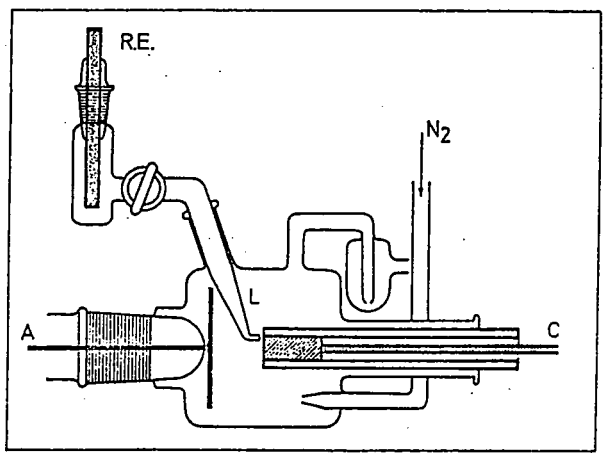

Figure 1. The cell used for most of the L.S.V. and potential step experiments

Working electrodes were small cylinders of polycrystalline ("Koch - Light Laboratories", 99.999%) or 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%) scaled 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 $KMnO4$ 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 ≈ 25 g, of amalgamated zinc[18].

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. The first stage only was applied when the vitreous carbon electrode was polished.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltdcm $5 \cdot 10^{-4}$ cm and $3 \cdot 10^{-4}$ cm grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}$ cm $3 \cdot 10^{-5}$ and 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 elsewere[19].

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 $HNO3$, 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 (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 othophosphoric 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.

These polishing processes 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 some cases 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 asses 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. 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 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 scaled 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

Distortion of the surface region introduced by mechanical polishing, however fine the grade of polishing powder is, hides real crystallographic features and produces relatively high surface roughness. Therefore, purely mechanically polished copper electrodes were not examined.

Already described chemical polishing of the copper after a careful mechanical treatment proved to be the most suitable surface preparation. Distorted layers produced by mechanical polishing, were easily removed by chemical etching In the case of the polycrystalline copper electrode this resulted in a surface showing a number of grains and their boundaries.

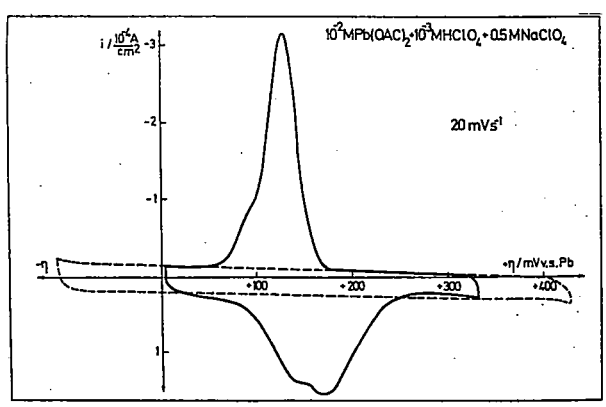

Figure 2. The voltammogram obtained for chemically polished polycrystalline copper electrode; and in a lead free solution (----------)

Voltammorgams obtained for lead UPD on polycrystalline copper therefore showed underpotential peaks covering a wide range of potentials (165 mV), Fig. 2. L.S.V. performed in the absence of lead showed only double layer charging currents (dashed curve in Fig. 2).

The total charge associated with the deposition process was $(397 \pm 15)\cdot10^{-6}$ Ascm^{-2} which, if a close packed lead monolayer is assumed ($310\cdot10^{-6}$ Ascm^{-2}), yields a surface roughness factor of 1.3. The complexity of the voltammogram does not allow any serious analysis, either qualitative or quantitative, of the nature of the lead deposit, showing once more that UPD processes cannot be investigated even on very well prepared polycrystalline surface.

The width and shape of the voltammograms are most probably the result of lead being deposited on differently crystalographically oriented substrate grains. These grains provide a variety of different lattice plans and possess sites with different adsorption energies for the adatoms which are thought to be underpotentially deposited. This is reflected in the voltammetry by the presence of more than one deposition (or stripping) peaks occurring at somewhat different potentials[20-33].

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

x M $Pb(OAC)_2$ + 10^{-2} M HOAC + 0.5M NaOAC 10^{-4}M≤x≤10^{-1}M

x M PbO + 10^{-3}M $HClO_4$ + 0.5M $NaClO_4$ 10^{-3}M≤x≤ 10^{-1}M

x M $Pb(OAC)_2$+ 10^{-3}M $HClO_4$ +0.5M $NaClO_4$ 10^{-4}M≤x≤ 10^{-1}M

x M $Pb(OAC)_2$+ 10^{-3}M $HClO_4$ +0.5M $NaNO_3$ 10^{-3}M ≤x≤ 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[181,224,225]. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2-5.5), and in such a situation:

$$PbO + H_2O + 2e^- \rightleftharpoons Pb + 2OH^-; E^o = -819 \text{ mV vs. S.C.E.}$$

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

which for different pH yields:

pH = 7	$E_{Pb/PbO}$ = -06 mV vs. S.C.E.
pH = 5.4	$E_{Pb/PbO}$ = -312 mV vs. S.C.E.
pH = 3	$E_{Pb/PbO}$ = -170 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 $a_{Pb^{+2}} = [\,Pb^{+2}\,]$. 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 high degree of complexing of lead ions by acetate anions reduces their activity to such an extent (99% of lead ions are complexed) that the deposition spectrum is moved to more negative potentials than thoseat which oxidation problems would be encountered.

Voltammograms obtained for (111) oriented copper single crystal electrode surface in all systems examined showed virtually the same features, Fig. 3. a, b, c and d, which were independent of whether the potential scan was repetitive or single.

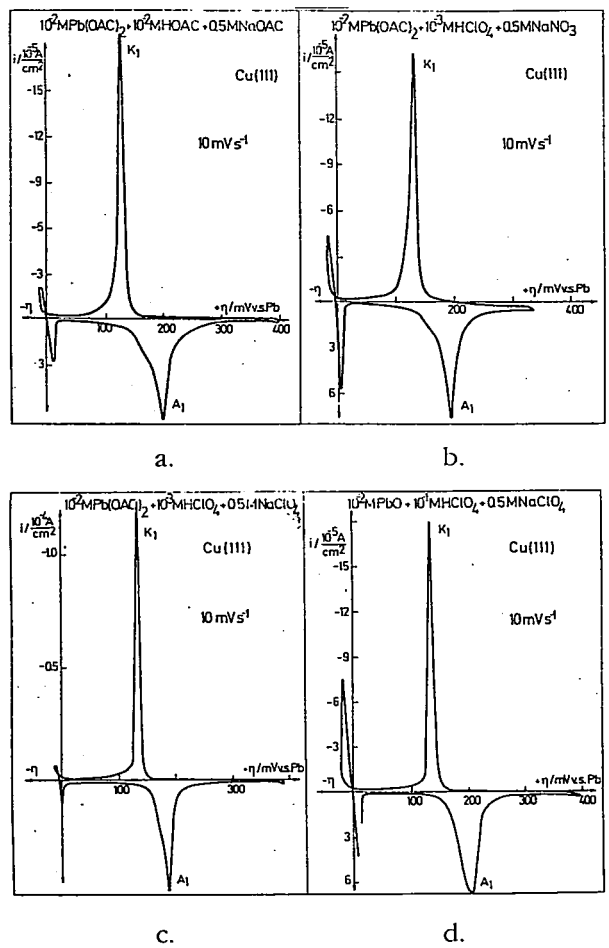

Figure 3. L.S.V. for lead UPD on the Cu(111) oriented electrode surface

The use of PbO instead of Pb(OAC)2 to prepare solutions did not produce changes in the L.S.V. recorded.

In all solutions, the lead underpotential deposition and dissolution processes occurred in the form of a very sharp deposition peak, K1, and somewhat less sharp stripping peak, A1, the two showing an asymmetry in peak positions on the potential axis.

Sometimes the two peaks, K1 and A1, were supplemented by a second peak system, K2 and A2, Fig.

4. a., b., c. and d., whose size, and therefore associated charge, was dependent upon how well the surface was prepared. The charge was typically about $(300\pm5)\cdot10^{-6}$ Ascm^{-2}, subtracting double layer charging. On continuos cycling such that the anodic limit was just 2 mV into Cu^{+2}/Cu dissolution region, this second peak system became more pronounced, while the first one (K1 and A_1) decreased in size and finally disappeared (see Fig. 4. a. to d.).These voltammograms were taken at 15 minutes intervals during the sweeping period.The new peak system, Fig. 4.d., was similar in charge values and potentials to that seen on Cu(100)[38] . It appears, therefore, that Cu(111) surface reconstructs to a structure similar to Cu(100) during cycling, but only if actual dissolution of copper takes place.

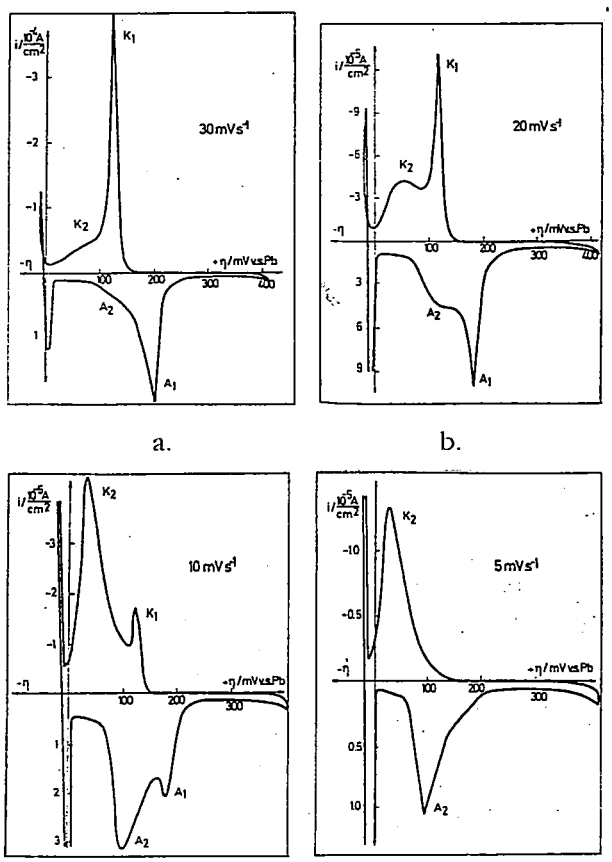

Figure 4. Reconstruction of Cu(111) surface due to cycling into copper dissolution as monitored by Lead UPD; solution $10^{-2}MPb(OAC)_2 + 10^{-3}MHClO_4 + 0.5M\ NaClO_4$

These results show that a reconstruction of the substrate surface can be readily detected on UPD voltammograms because of the great sensitivity of the energetics, kinetics and structural characteristics of underpotential layers on the substrate structure.

This also shows why the UPD characteristics are a good guide to the quality of the surface preparation.. At this point it might be interesting to note that there seems to be evidence for a related effect in the case of the Ag(111) system. Lorenz et al.28 have reported voltammograms of lead deposition onto a dislocation free, Budevski type, Ag(111) surface. This is almost free of the peaks A_1 and A_3 observed on the normal chemically polished silver single crystal electrode[28,29]. It appears, therefore, that peaks A_1 and A_3 were associated with defect structure on these crystals, as was suspected24 from the dependence of A_1 and A_3 on surface preparation.

By comparison, therefore, between Cu(111)/Pb (absence of A_1 and A_3) and Budevski type Ag(111)/Pb it can be concluded that the chemically polished Cu (111) surface is very close to ideal.

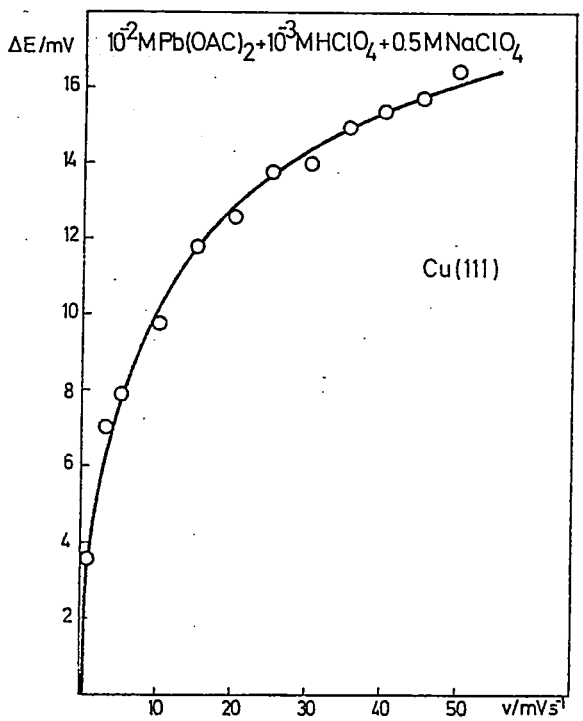

Figure 5. The dependance of the half width ΔE, on the sweep speed v.

The sharpness of the K_1 peak, measured by half peak width, ΔE, was found to increase (ΔE was becoming smaller), exponentially with decreasing sweep speed, v, tending asymptotically to zero, Fig. 5. Experimentally, this limiting value is unobtainable because of the kinetic limitations of the process discussed. Potential step experiments performed on this system[38] indicate that to obtain a voltammogram peak about 1 mV in width would require a sweep speed as low as 10^{-6} Vs^{-1}. An example of the voltammogram obtained experimentally at a sweep speed of 10- 3Vs-1 is shown in Fig. 6.

The peak potentials K_1 and A_1 changed with decreasing sweep speed, Fig. 7., K_1 becoming more positive and A_1 more negative. The change is fairly linear to start with, but at sweep speeds smaller $10\cdot10^{-3}$ Vs^{-1} the change becomes exponential. It appears, therefore, that both the deposition, K_1, and dissolution, A_1, peaks asymptotically tend to the same value of what might be called " a monolayer reversible poten-

Table. 1. Average UPD peak values for 10^{-2}M Pb solutions and v=10 mVs^{-1}

Electrode Surface Orientation	Anion	Average K_1 Peak Potential mV vs. Pb	Calculated Close-packed Layer 10^{-6} As cm^{-2}	Calculated Epitaxial Layer 10^{-6} As cm^{-2}	Measured UPD layer Charge 10^{-6} As cm^{-2}
(111)	OAC^-	+ 124 ± 2	310	212	238
(111)	NO_3^-	+ 125 ± 3	310	212	247
(111)	ClO_4^-	+ 123 ± 2	310	212	231

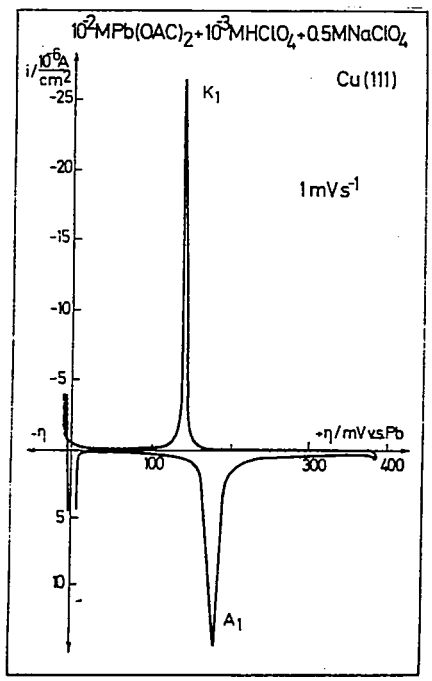

Figure 6. L.S.V. at low sweep speed v = $1Vs^{-1}$ for lead UPD on Cu(111)

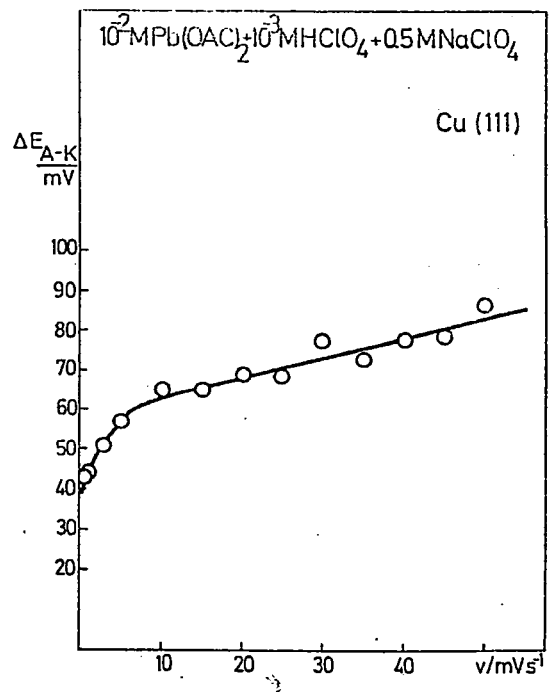

Figure 8. Dependance of the peak separation ΔE_{A-K}, on the sweep speed

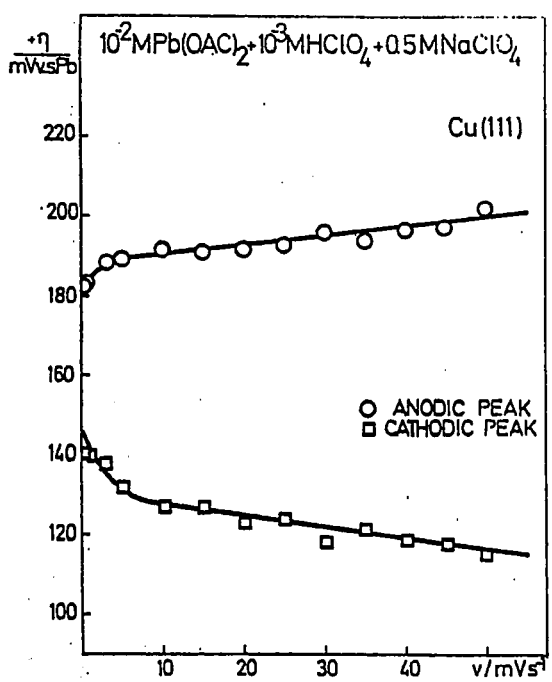

Figure 7. Dependence of peak potential on the sweep speed

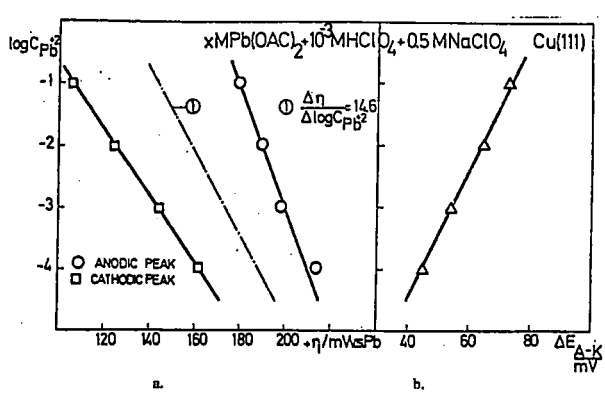

Figure 9. a) Dependence of the peak potential separation on Pb contrecation at sweep speed v = 19 mVs^{-1}
Figure 9. b) Dependance of peak potential on Pb concetration at sweep speed v = 10 mVs^{-1}

tial". Thus, the peak to peak potential separation, ΔE_{A-K}, will decrease with decreasing sweep speed, tending asymptotically to a zero value, Fig. 8.. Experimentally, however, at the sweep speed of $0.3 \cdot 10^{-3} Vs^{-1}$ ΔE_{A-K} was still 43 mV.

A change in lead concentration produces changes in the peak potentials and peak to peak potential separations as shown in Fig 9.a. and Fig. 9.b. respectively. A summary of all relevant features obtained from the L.S.V. experiments on Cu(111) electrodes is given in Table 1.

DISCUSSION

In principle there are three factors that could give rise to a multi-peak UPD voltammogram on single crystals:

1 .- The various peaks could correspond to different adsorption states; if it is assumed that the adsorption energies associated with a particular crystal structure are very different, then an unsuccessful polishing process leaving patches of the surface polycrystalline in nature would produce a multi-peak voltammetry;

2 .- If on the other hand all adsorption sites on an electrode are assumed equivalent in energy, each peak could correspond to a differently ordered structure on the surface[24,35]. If it is assumed that a distinction between an adsorbed and crystalline layer in UPD could be readily made, then the different peaks could correspond to the transformations between the different phase structures[20,47,48];

3 .- A multi-peak structure could be the result of the deposition of partial monolayers on top of one another.

Analysis of the features associated with K_1, shows that it resembles in several aspects results obtained for lead on Ag(111)[20-25]; the number of peaks and their sharpness. In this case, the authors claimed that a close packed crystalline lead monolayer is formed.

Employment of some of the simple and widely recognized diagnostic criteria for the voltammetry should yield an answer as to whether the lead layer on Cu(111) formed in UPD is crystalline or adsorbed.

For a purely adsorbed layer of metal atoms, assuming that the scan rate is sufficiently slow for the reaction to achieve equilibrium L.S.V. peaks should be exactly opposite each other36. In the case of a crystalline phase layer, however, the onset of the stripping process should not occur until the potential is equal or more positive than that at which deposition commences, the exact separation between starting potentials of stripping and deposition depending on the magnitude of any nucleation overpotential.

In Fig. 6. It was shown that at the sweep speed $v = 10^{-3} Vs^{-1}$, the separation is $\Delta E_{A-K} \geq 43$ mV.

For deposition of a monolayer of adsorbed species the expected half peak width, ΔE, for a Langmuir isotherm is 90 mV/z[33], and for a peak sharper than this some degree of attraction between the adsorbed species has to be assumed. The degree of atomic interaction is then reflected in the interaction parameter of a Frumkin isotherm, g. Peaks with low or negative values of g, (indicating repulsion), could then be ascribed to the deposition of purely adsorbed species, and they are generally wide, whereas high positive values of the interaction parameter 9 (indicating attraction) could be ascribed to the formation of a layer with mainly crystalline properties and it would produce very sharp L.S.V. peaks.

Peaks K_1 are much sharper than any of those normally associated with an adsorption process.

Starting with the form of the Frumkin adsorption isotherm[23]:

$$a_{1'} = \frac{k\theta}{(1-\theta)} \exp(-g\theta)$$

it can be easily found that for parameters $g \geq 4$, interactions within the layer would be so strong as to produce a first order phase transition (the isotherm exhibits a discontinuity at a certain value of potential). Applying the calculation[23] according to which:

$$\Delta E = -\frac{RT}{2zF} \exp(\delta^{3/2} + \delta)$$

and

$$g = 4 - \delta \quad \text{for} \quad d \leq 0.5$$

it is possible to obtain g values from the experimentally found values at the L.S.V. half peak width, ΔE.

For a number of slow sweep speed experiments ($v = 0.3; 0.5; 1 \cdot 10^{-3} Vs^{-1}$) the ΔE measured was between 3.2 - 3.5 mV. For the lower value of EMBED Equation.3 this gives g = 3.7, which is as close to the critical value of g = 4 as could be reasonably expected for a solid surface with such an area (≈ 0.502 cm^2).

Attempts made by some authors[27,28] to explain such a sharp peak by assuming an extreme form of adsorption isotherm with very large g parameters is somewhat unrealistic. In fact they have not been able so far, to provide a satisfactory physical basis for such large g parameters as were used in calculating the isotherm describing adsorbed metal monolayers[28]

Apart from the effects due to the heterogeneity of a large surface area, there are. Effects of the kinetics of the process that must be taken into account[37]. The slow kinetics of the UPD process should broaden the L.S.V. peaks recorded at sweep speeds even as low as 10^{-6} Vs^{-1}.This point will be discussed again later[38].

In view of this discussion the peak K1 observed for the Cu(111) surface could be ascribed most probably to the formation of a crystalline lead monolayer, and its counterpart A1, to the reverse dissolution process.

However, there is at least one question to be answered, namely, what is the mechanism of formation and growth of such a 2D crystalline phase.

According to results obtained in the field of 2D solid state physics[39] and surface physics of materials[40,41] phase formations (transformations) in 2D systems could be of at least two kinds: abrupt and continuous.

The better known, especially for heterogeneous systems, are abrupt, first order phase changes involving nucleation.

However, in the case of 2D crystal lattice formation it is not necessary to recourse always to arguments involving normal nucleation processes. There are continuous phase transformations which were first recognized in the homogeneous systems but which have been observed and studied to a certain degree in liquid and solid state layers on solid substrates[39,40]. They probably occur through compositional fluctuations, which grow in intensity until eventually they yield the new equilibrium phase. This sort of second and higher order transformations have been a subject of experimental and theoretical interest, particularly in the case of films physisorbed at solid surfaces[39].

In our case, the crystalline lead monolayer is most probably formed by 2D nucleation and growth, i.e. by a first order 2D phase transformation.

Experimental results obtained by the L.S.V. method alone, provide several convincing arguments in support of this statement.

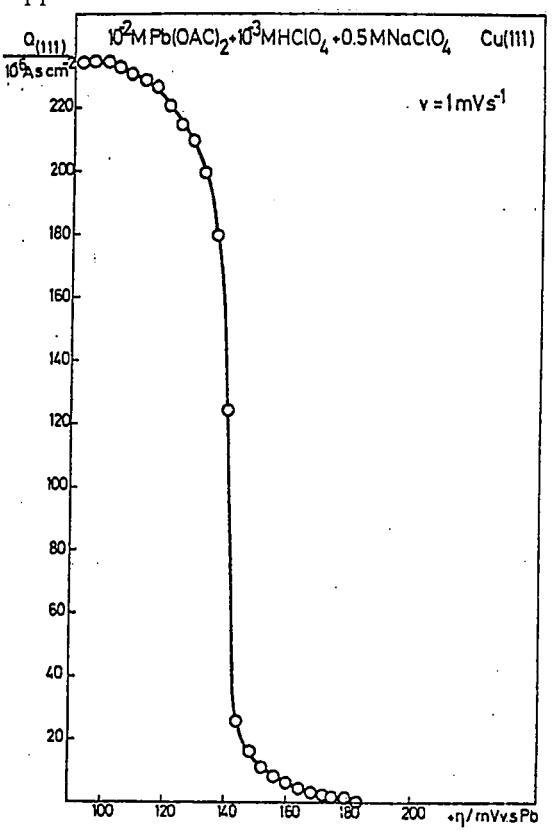

Figure 10. The isotherm obtained on the basis of the voltammogram presented in Fig. 6.

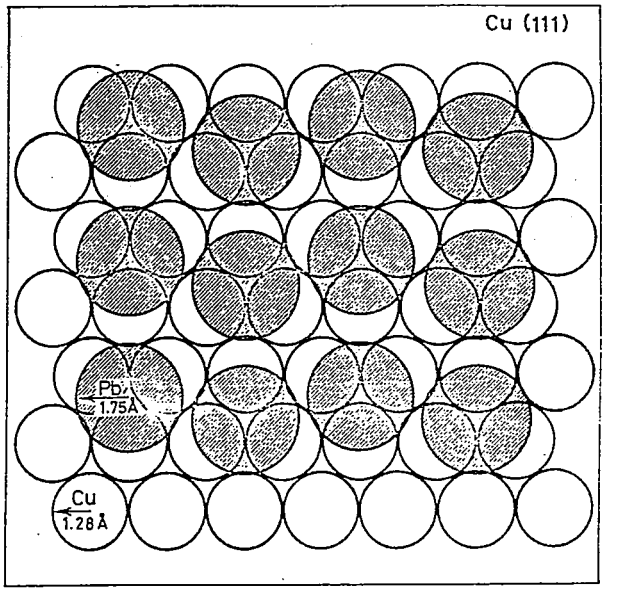

Figure 11. The structure of the closest-packed lead epitaxial monolayer on the Cu(111) surface.

Firstly, there is a separation on the potential axis of the deposition and stripping processes, $\Delta E_{A\text{-}K}$, which can be recognized as a necessary and significant feature of any mechanism incorporating a nucleation step - nucleation overpotential As already mentioned earlier, $\Delta E_{A\text{-}K}$, is typically at least 43 mV and more.

Secondly, the isotherm evaluated from L.S.V. data (e.g. that given in Fig. 6.) and presented in Fig. 10, although not showing the mathematical discontinuity predicted by the theory for first order phase transition, does show a reasonably sharp rise from 10% to 80% of the full monolayer within 7-8 mV.

Thirdly, the shift of the UPD peak potentials with change in lead concentration, presented in Fig 9.a and b. (which will be also discussed later [38]), is common basically to the crystalline UPD monolayers.

The structure of this crystalline UPD monolayer can be evaluated through the analysis of the charge encompassed by peaks, K_1 and A_1. As can be seen (Table 1.) the average measured charge corresponding to either K_1 and A_1, was $238 \cdot 10^{-6}$ Ascm^{-2}, after subtracting the double layer charge. A close-packed lead crystal plane (atomic radius r_{Pb} = $1.75 \cdot 10^{-8}$ cm) requires $310 \cdot 10^{-6}$ Ascm^{-2}. The structure of Fig. 11. Is proposed for the underpotential layer since this closest-packed epitaxial layer would need $212 \cdot 10^{-6}$ Ascm^{-2} for its deposition. Comparison with the average measured value yields a roughness factor of 1.1 which is typical for chemically polished single crystal surfaces20. In this epitaxial arrangement lead atoms are close together, more so than in any superllatice model - a monolayer consisting of metal adatoms[20,26,42] sitting on interstitial sites between surface atoms. Therefore, having in mind the relatively high electronegativity of copper and nature of UPD[43-46], it might be expected that the adlayer in this case would easily participate in

a band structure extending over the substrate and adlayer allowing the development of properties of a well-defined phase. Further deposition beyond that required for the fully formed epitaxial layer was not observed. The development of such 2D crystalline epitaxial adlayers and their existence in the case of high interaction between the substrate and the deposited monolayer (which is the very nature of the UPD phenomenon) is known in physisorption.

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.

Voltammetric behaviour of the polycrystalline copper electrodes in lead UPD region was shown to be a composite of the differently crystalographically oriented substrate grains in its substrate, revealed by careful chemical polishing (surface roughness factor estimated at 1.3).

Voltammograms on the Cu(111) oriented electrode surface (irrespective of the lead solution used) showed a very sharp deposition and somewhat less sharp dissolution peaks separated by minimum 43 mV.

The "adsorption isotherm" evaluated from such a L.S.V data showed (although not the mathematical discontinuity theoretically predicted by the theory for a first order phase transition) a reasonably sharp rise from 10% to 80% of the full monolayer within 7-8 mV.

The factor g (Frumkin adsorption isotherm repulsion/attraction factor) calculated from the deposition peak half height width obtained at slow sweep speeds (down to 10^{-3} Vs^{-1} and smaller) was g = 3.7, which is as close to the critical value of g= 4 (characteristic for crystalline phase formation) as could be reasonably expected for a solid surface in reality (electrode surface area $\approx$ cm^2).

The shift of the UPD peak potentials with change in lead concentration is common basically to the crystalline phase (in this case the lead UPD monolayer on Cu(111)).

The average measured charge, corresponding to either deposition or dissolution voltammogram peaks of lead UPD on Cu(111), was $238 \cdot 10^{-6}$ $Ascm^{-2}$ after subtracting the double layer charge The charge needed to form a layer according to the model of the closest-packed epitaxial lead UPD monolayer proposed in this paper amounts to $212 \cdot 10^{-6} Ascm^{-2}$. It is obvious that the to values mach very well taking into account the roughness factor of 1.1 for Cu(111) chemically polished surface.

All the above strongly indicate that lead forms 2D crystalline epitaxial adlayer on Cu(111) electrode surface in lead UPD region.

When exposed to repetitive deposition and dissolution L.S.V. cycling in lead UPD region the Cu(111) surface reconstructs to a structure similar to Cu(100), but only if actual dissolution of copper takes place during dissolution part of the cycle.

ACKNOWLEDGMENT

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REZIME

STUDIJA POČETNIH STADIJUMA ELEKTROTALOZENJA OLOVA NA BAKRU - I DIO PONAŠANJE BAKRNEELEKTRODE KRISTALOGRAFSKE ORJENTACIJE (111) PRI LINEARNOJ CIKLIČNOJ PROMJENI POTENCIJALA

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Ovo je prvi 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 linearnom cikličnom promjenom potencijala (L.S.V., ciklična voltametrija) bakarne polikristalne i monokristalne elektrode površinske 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.

Polikristalna bakarna površina, pri linearnoj cikločnoj promjeni potencijala (L.S.V.) u području potencijala pozitivnijih od reverzibilnog potencijala olova (UPD), daje votamogram koji predstavlja zbir karakteristika površina različitih kristalografski orijentisanih zrna, koje su pažljivim hemijskim poliranjem otkrivene i izložene elektrotaloženju olova (ustanovljen faktor rapavosti bararne poršine je bio je 1.3).

Voltamogrami dobijeni za Cu(111) orijentisanu monokristalnu površinu u istom području ispitivanih potencijala (UPD olova) pokazuju jedan veoma oštar katodni (taloženje) talas i oštar anodni (rastvaranje) talas, čiji se potencijali vrhova razlikuju međusobno za 43mV i više.

"Adsorpciona izoterma" izračunata na bazi širine poluvisine tako dobijenih talasa taložnja olova pri potencijalima 0.124V pozitivnijim od reverzibilnog potencijala olova, pokazuje oštru promjenu pravca od 10% do 80% ukupnog naboja neophodnog za elektrotaloženje jednog monosloja olova.

Faktor g (koji u Frumkinovoj adsorpcionoj izotermi odražava međusobno privlačenje/odbijanje

građevnih jedinica adsorbovanog sloja) izračunat na osnovu dobijenih širina poluvisina talasa taloženja olova pri potencijalima pozitivnijim od reverzibilnog iznosi 3.7, što je najbliže moguće teorijski predviđenoj vrijednosti g=4 (koja označava međusobno privlačenje karakteristično za kristalne faze) za realni sistem elektrodne površine cm^2.

Izmjerena promjena potencijala vrha katodnog/anodnog talasa olova u području potencijala pozitivnijeih od reverzibilnog u zavisnosti od promjene koncentracije olova u upotrebljenim rastvorima u osnovi je tipična karakteristika dobro definisanih kristalnih faza.

Srednja vrijednost sa voltamograma izmjerenog naboja koji se razmjenjuje pri elektrotaloženju ili rastvaranju olova, u području potencijala pozitivnijih od reverzibilnog, na Cu(111) površini $238 \cdot 10^{-6}$ $Ascm^{-2}$ (nakon odbitka vrijednosti za dvojni sloj). Kada se ova vrjednost uporedi sa $212 \cdot 10^{-6}$ $Ascm^{-2}$, koja je potrebna za formiranje u ovome radu predloženog modela gustopakovanog epitaksijalnog monosloja olova na Cu(111) površini, zapaža se veoma dobra saglasnost (posebno kada se uzme u obzir i faktor rapavosti od 1.1 tipičan za dobro hemijski polirane površine metala).

Sve navedeno snažno ukazuje na to da olovo na Cu(111) formira 2D kristalni epitaksijalni monosloj pri potencijalima od oko 0.125 V pozitivnijim od reverzibilnog potencijala olova u datoj sredini. Zapažena je i pojava prestrukturiranja Cu(111) površine u strukturu sličnu Cu(100) površini, međutim do toga dolazi samo kada je Cu(111) elektroda na kratko izložena malim (2 mV) prenapetostima rastvaranja u anodnom dijelu ponavljanih ciklusa taloženja i rastvaranja olova u područjima potencijala pozitivnijim od reverzibilnog.

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ORIGINAL SCIENTIFIC PAPER

A Study of the Initial Stages of the Electrochemical Deposition of Lead on Copper - PART II. The Linear Sweep Voltammetry Behaviour of (110) oriented Copper Single Crystal Electrode

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ABSTRACT

The uderpotential deposition and dissolution of lead onto carefully chemically polished single crystal copper(110) 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 (110) 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(110) starts as an adsorption and proceeds as higher order 2D transformation into close-packed crystalline monolayer. The structure of the closest-packed lead epitaxial monolayer (adsorption part of the process) on Cu(110) 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 second pair of voltammetric deposition and dissolution peaks exhibiting an cathodic potential shift with increasing lead concentration, thus showing typical trend observed for the crystalline monolayer, while the first pair behaved oppositely; the first deposition/dissolution pair of peaks showing almost no lead concentration dependence in already small peak potential separation, while the second pair exhibiting well defined dependence.

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

INTRODUCTION

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 copper polycrystals and single crystals. The uderpotential as well as overpotential deposition and their possible mutual interdependence were investigated. The substrate posses 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 mash disc ≈ 1.5 cm^2 in area, positioned parallel to the working electrode.

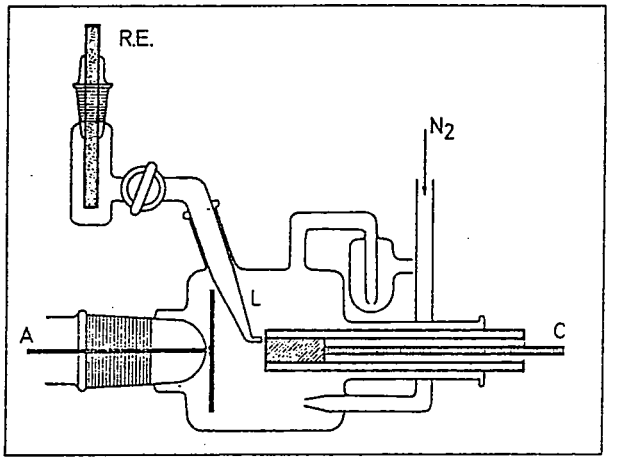

Figure 1. The cell used for most of the L.S.V. and potential step experiments

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999% ≈ 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. 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%) scaled 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 zinc[1].

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 $3 \cdot 10^{-4}$ 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 elsewere[2].

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 (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[12].

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 asses 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 scaled with a syring 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 (110) 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 $10^{-4}M \le x \le 10^{-1}$M

xM PbO + 10^{-3}M $HClO_4$ + 0.5M $NaClO_4$ $10^{-3}M \le x \le 10^{-1}$M

xM $Pb(OAC)_2$ + 10^{-3}M $HClO_4$ + 0.5M $NaClO_4$ $10^{-4}M \le x \le 10^{-1}$M

xM $Pb(OAC)_2$ + 10^{-3}M $HClO_4$ + 0.5M $NaNO_3$ $10^{-3}M \le x \le 10^{-1}$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 subject3-5. Without added acid, the pH of the solutions was effectively neutral (pH = 5.2 - 5.5), and in such a situation:

$PbO + H_2O + 2e^- \rightleftharpoons Pb + 2OH^-$; E^o = -819 mV vs. S.C.E.

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

which for different pH yields:

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

It appears that the different anions used do not change the voltammetric characteristics significantly. In Fig. 2. a., b. and c. are presented voltammograms obtained for lead underpotential deposition on Cu(110) in three different solutions.

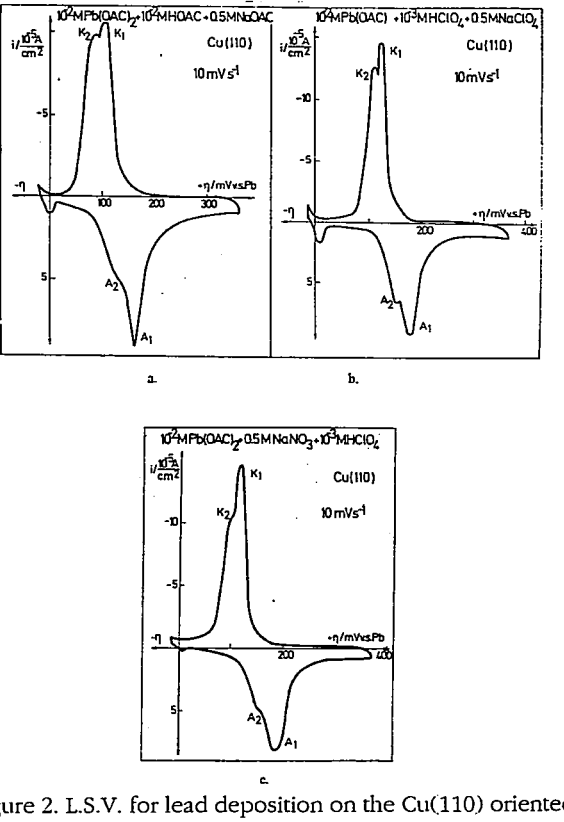

Figure 2. L.S.V. for lead deposition on the Cu(110) oriented electrode surface

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

Electrode Surface Orientation	Anion	Average Peak Potential mV vs. Pb		Calculated Close-packed Layer 10^{-6} Ascm^{-2}	Calculated Epitaxial Layer 10^{-6} Ascm^{-2}	Measured UPD Layer charge 10-6 Ascm^{-2}	
		K1	K2			K1	K1+K2
(110)	OAC^-	+117	-98	310	178	190	323
(110)	NO_3^-	-114	+95	310	178	195	329
(110)	ClO_4^-	-115	+96	310	178	190	322

The charges encompassed by the observed peaks and observed peak potentials were approximately constant, Table. 1.

The deposition and dissolution of lead in the UPD region are reflected by two cathodic, K_1 and K_2, and two anodic peaks, A_1 and A_2. Each pair of peaks is asymmetrically placed on the potential axis and the peak potential separation, $\Delta E_{A1\text{-}K1}$ and $\Delta E_{A2\text{-}K2}$, were appreciable.

If more than thirty cycles were applied, the maximum current of the first peak, K_1, would at first decrease but soon it settled at a value somewhat smaller than the maximum of the second peak, K_2. The anodic peaks, however, do not change at all either in shape or charge. The peak potentials of K_1 and K_2 became more negative, and those of A_1 and A_2 more positive as the sweep speed increased, Fig. 3.a., and thus the peak potential separation increased, Fig. 3. b.

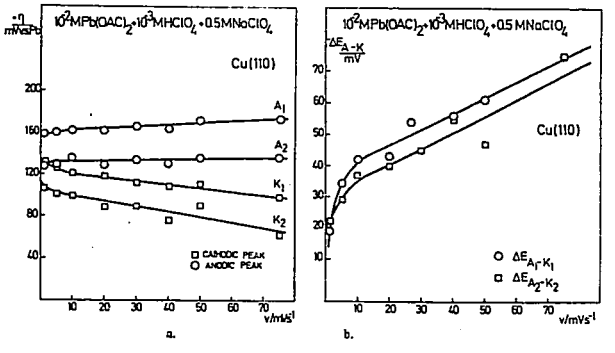

Figure 3.
a) Dependance of peak potentials on the sweep speed.
b) Dependance of peak potential separation $\Delta E_{A\text{-}K}$, on the sweep speed

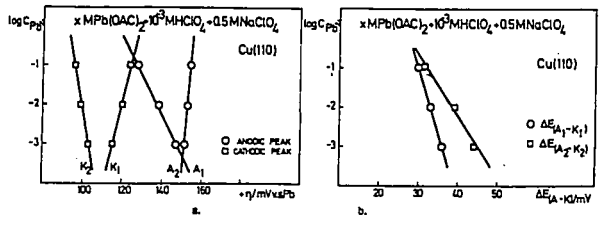

Figure 4.
a) Dependance of the peak potentials on the lead concentration at sweep speed v-10 mVs^{-1}
b) Dependance of the peak potential separation $\Delta E_{A\text{-}K}$, on the lead concebtracion at sweep speed v-10 mVs^{-1}.

The dependence of the peak potentials on lead concentration is shown in Fig. 4.a. and the dependence of the peak potential separation on lead concentration in Fig. 4.b. The different trends of the two cathodic and anodic peaks are obvious. While the potentials, K_1 and A_1 become more positive as the concentration of lead in solution increased, K_2 and A_2 behave oppositely.

DISCUSSION

The results in this case show obvious difference from those obtained for the Cu(111)/Pb system[12]: two peaks instead of one and, in addition, they are less sharp and the peak potential differences are markedly smaller.

The charges encompassed by the observed peaks and observed peak potentials were approximately constant, Table.1

The deposition and dissolution of lead in the UPD region are reflected by two cathodic, K_1 and K_2, and two anodic peaks, A_1 and A_2. Each pair of peaks is asymmetrically placed on the potential axis ant the peak potential separation $\Delta E_{A1\text{-}K1}$ and $\Delta E_{A2\text{-}K2}$, are appreciable.

If more than thirty cycles were applied, the maximum current of the first peak, K_1, would at first decrease but soon it settled at value somewhat smaller than the maximum of the second peak, K_2. The anodic peaks, however, do not change at all either in shape or charge. The peak potentials of K_1 and K_2 became more negative and those of A_1 and A_2 more positive as the sweep speed increased, Fig. 3.a. and thus the peak potential separation increased, Fig.3.b.

On the other hand a comparison with system Ag(110)/Pb[3,6-8] reveals certain similarities, e.g. in the number of peaks and the total charge under them. But, in the Cu(110)/Pb system, both peaks are relatively sharp, and K1 is definitely sharper than in the case of the Ag(110) substrate. Furthermore, the second deposition process, K_2, always starts at more positive potentials than that required for completion of the first, K_1, which was not obvious in the case of the silver substrate.

The half height peak widths for K_1 and K_2 in Fig. 2.b., are typically 19 ± 1 mV and 12 ± 1 mV respectively

in the case of the Cu(110) substrate. These values are too large even if slow kinetics of the processes involved are taken into account, to be reasonably accounted for by a first order phase formation.

However, in the case of 2D crystal lattice formation it is not necessary to recourse always to arguments involving normal nucleation processes. There are continuous phase transformations which were first recognized in homogeneous systems but which have been observed and studied to a certain degree in liquid and solid state layers on solid surfaces[9,10]. They probably occur trough compositional fluctuations, taking place more or less simultaneously in all parts of the assembly, which grow in intensity until eventually they yield the new equilibrium phase. These sort of second and higher thermodynamic order transformation have been a subject of experimental and theoretical interest, particularly in the case of films physorbed at solid surfaces[10].

Analysis of the charges associated with the peaks, Table. 1., show that the value for K_1 $(190 \pm 5)\cdot10^{-6}$ $Ascm^{-2}$ is very close to that needed for the adsorbed close-packed epitaxial layer (178 ± 10^{-6} $Ascm^{-2}$) shown in Fig. 5.. It is interesting to note that this epitaxial lead structure is similar to that of the (110) on bulk lead.

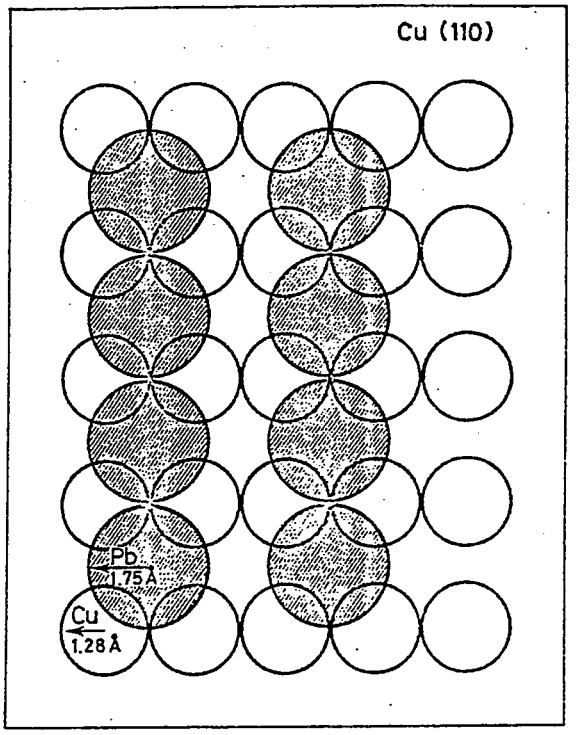

Figure 5. The structure of the closest-packed lead epitaxial monolayer on the Cu(110) surface.

The total charge encompassed by the two (cathodic) peaks on Cu(110) is approximately $322\cdot10^{-6}$ $Ascm^{-2}$, which is very close indeed to the value required to form a layer of closest-packed lead atoms ($310\cdot10^{-6}$ $Ascm^{-2}$), even disregarding the roughness factor of around 1.1. Although this close-packed lead layer is likely to be distorted by the underlying substrate, as was observed on silver in the same situation13, there is no evidence, in the present case, for the deposition of a second layer in the UPD region before the onset of bulk deposition.

The "isotherm", Fig. 6., obtained for the deposition process from the voltammogram shown in Fig. 2.b., suggests that ≈ 59% of the closest-packed lead monolayer (epitaxial monolayer presented in Fig. 5. is 59%) is deposited within a 52 mV potential range. After the structural change of the layer starts (depicted by the shoulder on the "isotherm"), the additional 40% of the monolayer is put down on the substrate within a 26 mV potential range.

It appears, therefore, that before the first layer is fully completed, it begins to reorganize into a close-packed structure.

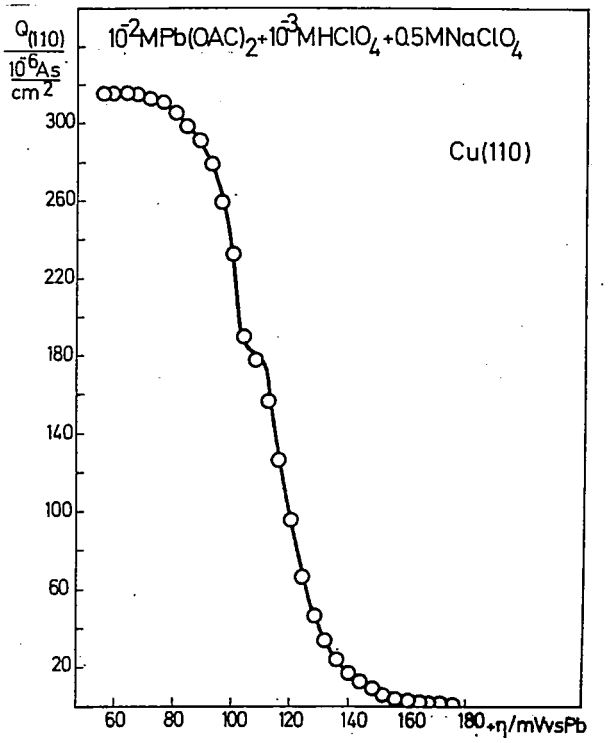

Figure 6. The "isotherm" obtained on the basis of the voltammogram presented in Fig. 2.b.

Although it might be expected that after the first epitaxial layer has been formed further material would be accommodated in the second set of chains situated between and little above the first set, the measured charge is insufficient for the completion of this process. It must be concluded, therefore, that it is energetically favorable to form a close-packed structure even though this involves a considerable loss of detailed registration. This conclusion is not entirely in agreement with the trend predicted from data on phase formation on solid surfaces from the gas phase, where the correlation between the order of the phase transformation and the degree of registration of the phase was thought to be of decisive importance[11].

However, the results obtained strongly suggest that UPD of lead on Cu(110) starts as an adsorption (K_1) and proceeds as a higher order 2D transformation into close-packed crystalline monolayer.

The influence of lead concentration on the peak potentials supports this view. The two sets of peaks, K_1 and A_1 and K_2 and A_2, behave markedly differently when the lead concentration is increased.(see Fig. 4.), clearly indicating that the less dense and the more dense monolayers are very different in character. While K_2 and A_2, corresponding to the crystalline formation process, exhibit a general trend similar to that observed for the crystalline lead monolayer on the Cu(111)[12], K_1 and A_1 behave quite oppositely. In the first layer, K_1, the lead atoms are just sufficiently far apart that their mutual interaction cannot produce features common to the crystalline layer so it behaves as an epitaxial adsorbed film. When the denser structure begins to be formed there is a reduction in the particle separation distance (at first probably at local level, but as the potential is changed the tendency spreads over the entire layer) which could allow it to participate in a band structure with the substrate, thus developing metal-like crystalline characteristics.

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.

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, voltammogram peaks. K1 peak potential average value was (+115 ± 4) mV vs.Pb, and K_2 peak potential value was (+96 ± 4)mV vs.Pb in the systems investigated. The first peak pair's potentials, K_1/A_1, became more anodic and the second peak pair potentials, K_2/A_2 more cathodic with increasing lead concentration.

The charge encompassed by K_1/A_1 was (190 ± 5)·10^{-6} Ascm^{-2}, and the charge under K_2/A_2 peaks was (132 ± 3)·10^{-6} Ascm^{-2} (the sum of the two being (322 ± 3)·10^{-6} Ascm^{-2}.

Peak potential separation, $\Delta E_{A1\text{-}K1}$, was 35 mV at 10^{-3}MPb and became smaller much faster with increasing lead concentration than, $\Delta E_{A2\text{-}K2}$, which was 43 mV at 10^{-3} MPb.

The "adsorption isotherm" evaluated from the uderpotential deposition voltammograms experimentally obtained have shown that 59% of the total cathodic peaks ($K_1 + K_2$) charge was deposited within 52mV potential rangein (a charge very close to 178 ·10^{-6} Ascm^{-2} needed for the adsorbed close-packed epitaxial layer of lead on Cu(110) surface), the additional 40% following the structural change start of the monolayer depicted by the "shoulder" (until full charge of 322·10^{-6} Ascm^{-2} was reached). It appeared therefore that before the first layer is fully completed it begins reorganization into a close-packed structure.

The experimental results obtained strongly suggest that UPD of lead on Cu(110) 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 adsorption process) on the Cu(110) surface was also presented.

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REZIME

STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA OLOVA- III DIO PONAŠANJE BAKARNE ELEKTRODE KRISTALOGRAFSKE ORIJENTACIJE (100) PRI LINEARNIOJ CIKLIČKOJ POMJENI POTENCIJALA

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Ovo je drugi 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 kristalografske orijentacije (110) 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 monokritalnoj bakarnoj površini kristalografske orijentacije (110) odražva 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_1 iznosi (+115±4) mV vs.Pb, a vrha K_2 talasa (+96±4) mV vs.Pb u svim ispitivanim rastvorima. Vrijednosti potencijala vrhova talasa K_1 i A_1 postajali su anodniji, a vrhova talasa K_2 i A_2 katodniji sa porastom koncentracije olova u upotrebljenim elektrolitima. Ponašanje prvog para talasa karakteristično je za ponašanje adsorbovanih , a drugog para talasa za ponašanje kristalne monoslojeva.

Razlika u potencijalima vrhova talasa prvoga para $\Delta E_{A1\text{-}K1}$ (iznosila je 35 mV pri 10^{-3}MPb) smanjivala se sa povećanjem koncentracije olova u upotrebljenom elektrolitu mnogo brže nego $\Delta E_{A2\text{-}K2}$ drugog para talasa (iznosila je 43 mV at 10^{-3} MPb).

Električni naboj ograničen talasima (K_1 ili A_1) iznosio je $(190\pm5)\cdot10^{-6}$Ascm^{-2} električni naboj pod drugim parom (K_2 ili A_2) iznosio je $(132\pm3)\cdot10^{-6}$Ascm^{-2}, dok je suma (K_1+K_2), odnosno (A_1+A_2) iznosila $(322\pm3)\cdot10^{-6}$ Ascm^{-2}.

"Adsorpciona izoterma" izračunata na osnovu voltamograma za proces elektrotaloženja olova, u području potencijala pozitivnijih od reverzibilnog potencijala olova, pokazala je da se 59% ukupnog električnog naboja, (K_1+K_2), razmijeni uz promjenu potencijala Cu(110) od 52mV (vrijednost veoma bliska vrijednosti od $(178\pm3)\cdot10^{-6}$Ascm^{-2}, potrebnih za formiranje adsorbovanog najgušće pakovanog epitaksijalnog sloja olova na Cu(110) površini); a da preostalih 40% slijedi nakon započinanja strukturnih promjena u monosloju odraženih na izotermi "stepenicom" (dok se ne razmijeni puni iznos električnog naboja od $(322\pm3)\cdot10^{-6}$Ascm^{-2}). Izgleda da do reorganizacije gustopakovane strukture prvog sloja dolazi i prije nego što će se cio epitaksijalno adsorbuje.

Navedeni rezultati iztraživanja snažno upućuju na to da elektrotaloženje olova na (110) površini bakarne elektrode, pri potencijalima pozitivnijim od reverzibilnog potencijala olova u datom elekjtrolitu, započinje adsorpcijom, K_1, a nastavlja se 2D faznom transformacijom višeg reda, K_2, u gustopakovani kristalni monosloj.

Predložen je model strukture najgušće pakovanog epitaksijalnog olovnog sloja (nastalog adsorpcijom) na Cu(110) površini elektrode nastalog elektrotaloženjem olova pri potencijalima pozitivnijim od reverzibilnog potencijala olova.

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ORIGINAL SCIENTIFIC PAPER

A New Kinetic Method for Determination of Indium (III) in Solution

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ABSTRACT

Oxidation reaction of 4-hydroxycoumarin by potassium permanganate in acidic media of acetate buffer, is catalyzed by In(III) ions, which was used for development of a new and the first known homogeno-cathalytic method for determination of unknown quantities of indium in solutions. Using this method under optimum conditions (C_{MnO4}=2·10^{-4}mol/dm^3, C_{coum}= 2·10^{-4} mol/dm^3, pH=3.8, at 298°C) it was possible to determine In(III) quantities in solutions containing between 0.05-1.5μg/cm^3, with probable relative error of 2.5 to 11.5%.The kinetic data obtained were processedusing the differential variation of the fixed time method. Rate of the reaction was recorded spectrophotometrically using wave length of 525nm, on the absorption layer 1cm thick.The calibration curves were constructed using the In(III) reaction rate dependence on the In(III) concentration for different preset temperatures, and application of the method of the least quadrate yielded the equations for In(III) concentration evaluation. Appropriate kinetic equations for both catalytic and noncatalytic processes were derived and were used for the conditional constants of this processes to be evaluated for the temperatures of 289K, 298K, 303K and 313K. Activation energies and other thermodynamic parameters of the noncatalytic (E*= 12.71kJmol^{-1}) and the catalytic (E*= 1.55kJmol^{-1}) processes were evaluated. Selectivity of the method was tested using some other ions influence , and it was concluded that the test reaction is disturbed by Mn(II), Co(II), Fe(III), Zn(II), citrate, thiocyanate, phosphate and other ions oxidable by permanganate.

Key words: Kinetic method, 4-hydroxycoumarin, In(III) determination

INTRODUCTION

In(III) ion electronic structure does not exhibit classical catalyst characteristics, which should account for the fact that no kinetic method for In(III) quantitative determination based on homogeneous catalysis was known. However, In(III) catalytic activity was observed (Simonović, 1995) in the reaction of 4-hydroxycoumarin with permanganate. The fact that the number of quantitative determination methods for In(III) was restricted made this reaction the subject of this investigation.

Catalytic mechanism of the elements changing their valence state during redox reactions are not well understood. Usual explanation are either the polarization influence of a catalyst onto chemical bond of the reacting substance, or catalysts' ability to attract and orient reacting substances and thus enabling the process to proceed with smaller reacting energies (N.J. Langenbeck, 1962).

What ever the mechanism of In(III) catalytic influence on the reaction of peramnganate oxidation of 4-hydroxycoumarin in acetate buffer acidic media, pH=3.8, might be, it is obviously very pronounced and it can be recorded for quantities greater than 5·10^{-8}g/cm^3.

MATERIAL AND METHODS

The reaction kinetics was followed using spectrophotometry, recording the indicating substance (permanganate) concentration decrease on wave length of 525nm and absorption layer 1cm thick, temperature was 298K.

The rate of the chemical reaction, i.e. the absorbency, A, versus time, t, was recorded on SPEKTROFOTOMETAR MA9524 SPEKOL221, programmed for kinetic measurements. This apparatus contains a monochromator Type Czerny-Turner (335-800 nm), with setting sensitivity 0.5 nm, light dispersion of 0.1% (at 340 nm), photoelectric sensitivity of 0.0002 units of A. The smallest sample allowed was 0.2 cm^3.

PH-METER-MA-5722 "Iskra", sensitivity 0.01pH unit, was used to control acidity of the solutions used.

The sample spectrophotometer quivette was thermostated by ultrathermostat Type U10.

Thermostat "Sutjeska" with water blanket served for continuous thermostating of all reactants, water and glassware used. The water used for all reactants preparation was purified through ion-exchange column, showing electroconductivity between 0.4-0.8 μS.

Prior to the initial 10^{-3} mol/dm^3 solution preparation, 4-hydroxycoumarin was recrystallized from 3:1 water-ethanol mixture and dried at 105°C. To increase its water solubility, insoluble coumarin was transferred into a soluble salt using equimolar quantity of NaOH (Kurzecova, 1967).

The potassium permanganate standard solution, 0.02 mol/dm^3 concentration, was prepared from "Merck" ampoule. The less concentrated solutions were prepared immediately before the experiment started.

The initial In(III) solution (500 μg/cm^3) was made dissolving 0.500g of pure (99.999%) In metal in 50cm^3 of 2 mol/dm^3 HCl (Hem.Teh.Priručnik, 1986). This was subsequently diluted with water to 1000cm^3 solution. Solutions concentration was tested and determined gravimetrically.

Acetate buffer solution used was prepared from 0.2 mol/dm^3 acetic acid and 1 mol/dm^3 NaOH, always from p.a. "Merck" chemicals.When optimum ratio of all experimentally obtained reaction parameters was reached the catalyst concentration was evaluated in the following way:

- a mixture of the 4-hydroxycoumarin and the buffer was made in a polyethylene glass, taking care that their ratio was two times grater than the calculated optimum concentration of the reducing agent,
- using always the same 5ml pipette the mixture was distributed into several polyethylene glasses,
- different quantities of the catalyst were then added to each of the said polyethylene glasses and topped up with water to 9.5 ml,
- these solutions are thermostated to the working temperature, and immediately before taking the measurement 0.5 ml of the permanganate solution (the oxidizing agent) was added,
- at the moment of permanganate addition to the sample the time recording was started and a sample is sucked into spectrophotometer quivette. The absorbance change, A, was recorded after 180 seconds.

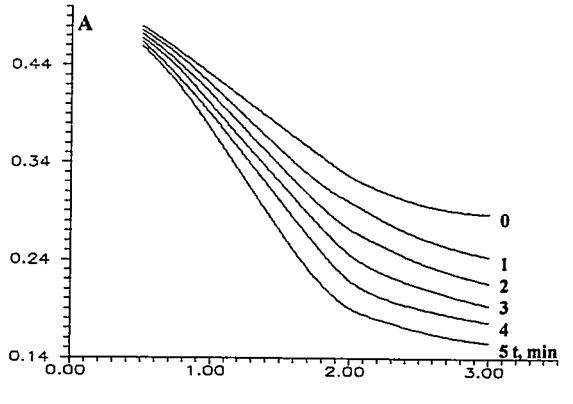

Figure. 1.- Absorbance change with time for different In(III) concentrations. Initial concentration: C_{MnO4} =2·10^{-4} mol/dm^3, C_{coum}= 2·10^{-4} mol/dm^3, pH=3.8, T=298 K and In(III) concentrations: 0-0, 1-0.3, 2-0.6, 3-0.9, 4-1.2, 5-1.5 (μg/cm^3)

The differential variation of mixed time method was used for data processing (Jacimirskii, 1967., Miller, 1983) because there existed small induction period, and a very small difference between catalytic and noncatalytic reactions particularly during their initial periods, Fig. 1.

RESULTS AND DISCUSSION

In order to establish the optimum ratio for all the reaction parameters (defined as the greatest catalyst influence on the reaction rate) it was necessary to undertake the determination of each of the equilibrium parameters.

The reaction rate dependence on 4-hydroxycoumarin concentration (ranging from 5·10^{-5} to 4·10^{-4} mol/dm^3), permanganate, buffer and hydrogen ions initial concentrations remaining constant, is given in Fig. 2. It appears that both reactions, the catalytic and noncatalytic, exhibit a change of reaction order with 4-hydroxycoumarin concentration. It also appears that the catalytic reaction was of the first order for 4-hydroxycoumarin concentrations ranging between 5·10^{-5} and 2.2·10^{-4} mol/dm^3, as well as the noncatalytic reaction for 4-hydroxycoumarin concentrations of 5·10^{-5}- 1.5·10^{-4} mol/dm^3.

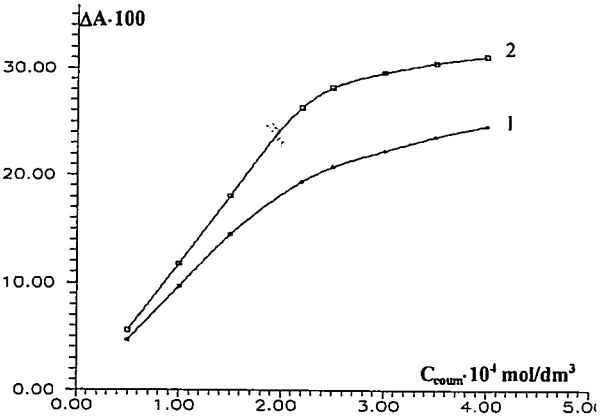

Figure 2.Dependence of the noncatalytic (1) and the catalytic (2) reaction on 4-hydroxycoumarin concentration. Initial concentration: C_{MnO4}=2·10^{-4} mol/dm^3, In(III)= 1μg/cm^3, pH=3,80, T=298 K, l=1 cm.

Fig. 3. shows (-log Δ*A*) dependence on (-log C_{coum}) for the noncatalytic reaction concentration range of 1.5·10^{-4}- 4·10^{-4} mol/dm^3). From the tangent of this linear relationship an order of the noncatalytic reaction was evaluated as being 0.7. For further experiments as the optimum 4-hydroxycoumarin concentration was established 2·10^{-4} mol/dm^3.

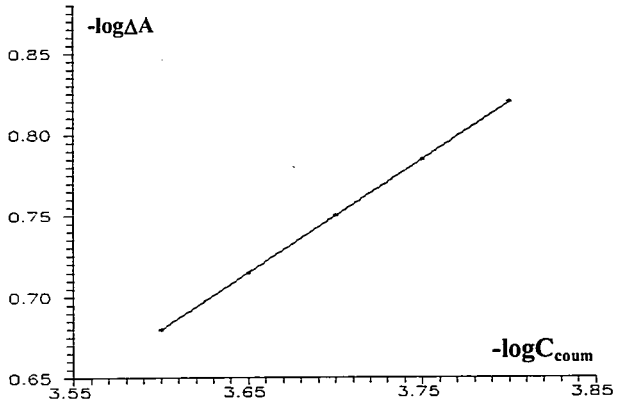

Figure 3.Dependence of (- log ΔA) = f (- log C_{coum}) for the noncatalytic . Initial concentration: C_{MnO4}=2·10^{-4} mol/dm^3, pH=3,80, T=298 K, l=1 cm.

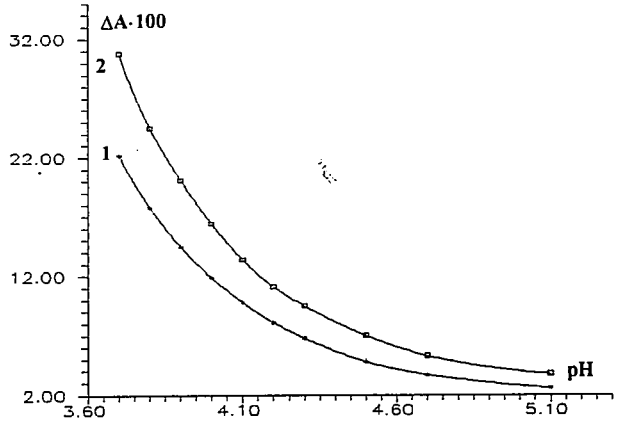

Figure 4. Dependence of the noncatalytic (1) and the catalytic (2) reaction on pH. Initial concentration: C_{MnO4}= 2·10^{-4} mol/dm^3, In(III)= 1 μg/cm^3, C_{coum} =2·10^{-4} mol/dm^3, T=298 K, l=1 cm.

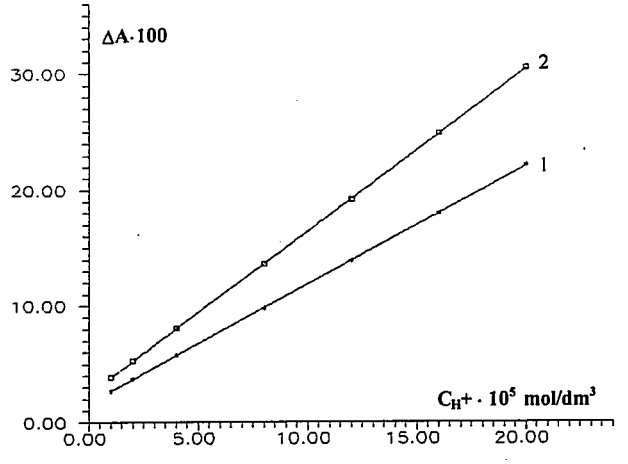

Figure 5.Dependence of the noncatalytic (1) and the catalytic (2) reaction on C_H^+. Initial concentration: C_{MNO4} = 2·10^{-4} mol/dm^3, In(III)= 1 μg/cm^3, C_{coum} =2·10^{-4} mol/dm^3, T=298 K, l=1 cm.

The logarithmic dependence of reaction rate on pH, Fig. 4., and the linear relationship of the reaction rate to the hydrogen concentration, Fig. 5., suggest that both catalytic and noncatalytic reactions were of the first order in respect to the hydrogen ions concentration ranging from 1·10^{-5} to 2·10^{-4} mol/dm^3.

The concentration of 1.58·10^{-4} mol/dm^3 (pH=3.8) was established as the optimum concentration for the subsequent experiments. This concentration was maintained using the acetate buffer.

The dependence of the noncatalytic and the catalytic reaction on the permanganate concentration is shown in Fig. 6. It appears that rates of the both reactions are of the variable order in respect to the permanganate concentrations used.

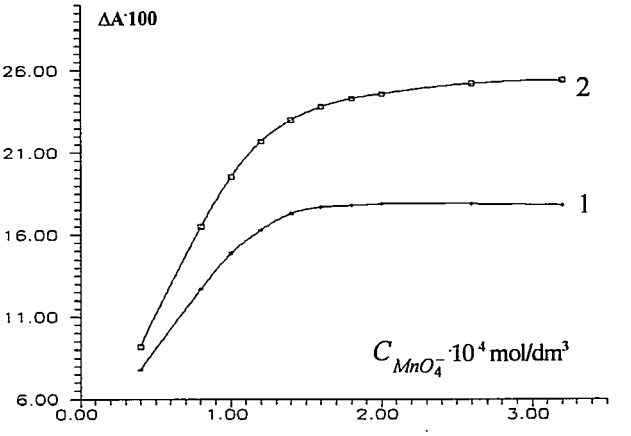

Figure 6. Dependence of the noncatalytic (1) and the catalytic (2) reaction on C_{MnO4}. Initial concentration: C_{coum} = 2·10^{-4} mol/dm^3, In(III)= 1 μg/cm^3, pH=3,80, T=298 K, l=1 cm

For permanganate concentrations ranging from 4·10^{-5} to 1·10^{-4} mol/dm^3, both reactions are of the first order, and for the greater concentrations than these reaction order becomes smaller, finally reaching a value of zero.

Permanganate concentration of 1·10^{-4} mol/dm^3 was established as the optimum concentration for the subsequent experiments. At this concentration the noncatalytic reaction is zero order and the catalytic of the 0.2 order, Fig. 7.

Influence of the acetate buffer quantity (volume) on the catalytic and noncatalytic reaction rates was also investigated, Fig. 8. It appears that for buffer volumes greater than 1.5ml, this buffer had no enough capacity (Cacetate= 3.07·10^{-3} mol/dm^3 and Cacet. Acid= 2.1·10^{-2} mol/dm^3). Cacetate= 6.14·10^{-3} mol/dm^3 and Cacet. Acid= 5.32·10^{-2} mol/dm^3 (translated into volume it amounts to 3ml of the buffer) were established as the optimum buffer concentration for the subsequent experiments.

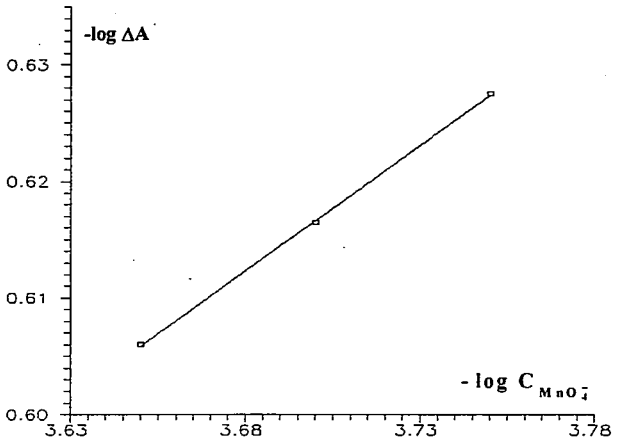

Figure 7. Dependence of (- logΔA) = f(- log C_{MnO4}-) for the noncatalytic . Initial concentration: C_{coum} = $2 \cdot 10^{-4}$ mol/dm^3, In(III)= 1 μg/cm^3, pH=3,80, T=298 K, l=1 cm.

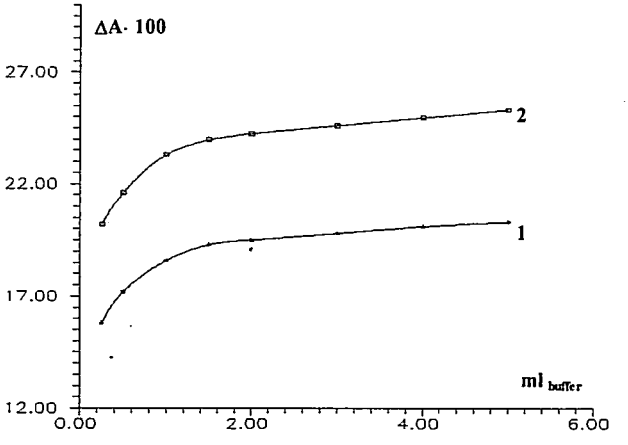

Figure 8. Dependence of the noncatalytic (1) and the catalytic (2) reaction on C_{buffer}. Initial concentration: C_{MnO4}- =$2 \cdot 10^{-4}$ mol/dm^3, In(III)= 1 μg/cm^3, C_{coum}=$2 \cdot 10^{-4}$ mol/dm^3, pH=3,80, T=298 K, l=1 cm.

Influence of In(III) on the reaction rate, optimum initial concentration of all reactants remaining constant, was examined according to the above conclusions. This investigation was conducted at different preset temperatures. The calibration curves for In(III) concentration determination were constructed applying the mathematical method of smallest quadrate (Spiridonov- Lopatkin, 1974) on the experimentally obtained data, Fig. 9. The calibration curves can be used for determination of In(III) concentration in the concentration range spanning from $5 \cdot 10^{-8}$ to $1.5 \cdot 10^{-6}$ mol/dm^3.

The ordinate secant lengths made by linear relationship (1,2,3,4) are in Fig. 9., are proportional to the reaction rate of the noncatalytic reaction for the given temperatures. An unexpected dependence of noncatalytic and catalytic reaction rates on temperature can be

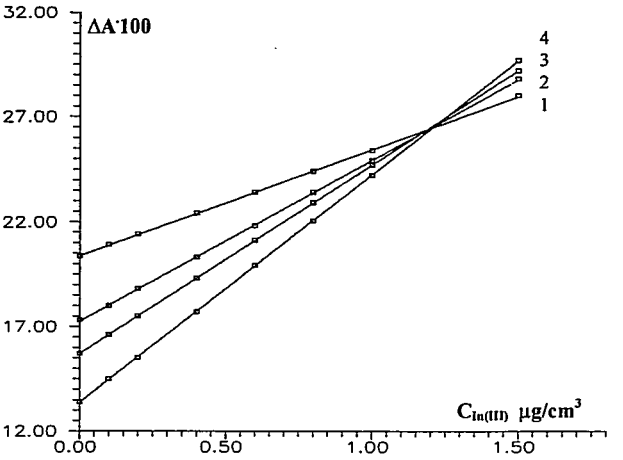

Figure. 9. Dependence of reaction rate on the catalyst In(III) concentration. Initial concentrations: C_{MnO4}-=$2 \cdot 10^{-4}$ mol/dm^3, Ccoum = $2 \cdot 10^{-4}$ mol/dm^3, pH=3,80, T=289 K (curve 1), T=298 K (curve 2), T=303 K (curve 3), T=313 K (curve 4), l=1 cm.

observed in Fig. 9. Namely, the noncatalytic reaction appeared to be slower at higher temperatures used, which was in contrast with the Arhenius equation. However, the catalytic reaction rates depend on the temperature applied for the In(III) concentrations greater than 1.2 μg/cm^3, and are in accordance with the Arhenius equation.

These observations can be explained by different products of the two kinds of observed reactions. When reaction starts with the same reactants but ends up with different products (and therefore with different temperature effects) it proceeds along different reaction mechanisms. The catalytic process was endothermic and the noncatalytic was exothermic. Since both reactions proceed at the same time (they are parallel) the opposite temperature effects are compensated. It was observed that at In(III) concentration of 1.2 μg/cm^3 the reaction rates of both kind of reactions are equal irrespective of the temperature applied (Cremer, 1955, Bond, 1962).

Linear relationships shown in Fig. 9. Can be described by:

for 289K	$\Delta A=0{,}048C_{In(III)} + 0{,}204$	(1)
for 298	$\Delta A=0{,}068C_{In(III)} + 0{,}178$	(2)
for 303K	$\Delta A=0{,}088C_{In(III)} + 0{,}150$	(3)
for 313K	$\Delta A=0{,}098C_{In(III)} + 0{,}136$	(4)

Inclinations of the linear relationships shown in Fig. 9. suggest that the calibration curve for 313K is the most suitable for the analytic purposes. On the other hand the most convenient working temperatures are 289 - 298K.

An unknown In(III) concentration can be evaluated (in μg/cm^3) using Eq. (2) for 298K, wave length of 525nm and absorption layer 1 cm thick, from

$$C_{In(III)} = \frac{\Delta A - 0{,}178}{0{,}068} \quad (\mu g/cm^3) \qquad (5)$$

The kinetic equations for the noncatalytic 4-hydroxycoumarin oxidation process by permanganate in acid media of acetate buffer, therefore can be presented as:

for C_{coum}= $5\cdot10^{-5}$ to $1{,}5\cdot10^{-4}$ mol/dm^3 and C_{MnO4^-} $4\cdot10^{-5}$ to $1\cdot10^{-4}$ mol/dm^3

$$-\frac{dC}{dt} = k_0 \cdot C_{coum} \cdot C_{H^+} \cdot C_{MnO_4^-} \qquad (6)$$

for C_{coum}= $1{,}5\cdot10^{-4}$ to $4\cdot10^{-4}$ mol/dm^3 and $C_{MnO4^-} > 1{,}6\cdot10^{-4}$ mol/dm^3

$$-\frac{dC}{dt} = k_0 \cdot C_{coum}^{0,7} \cdot C_{H^+} \qquad (7)$$

For the catalytic reaction as :

for C_{coum} from $5\cdot10^{-5}$ to $2{,}2\cdot10^{-4}$ mol/dm^3 and C_{mnO4^-} from $4\cdot10^{-5}$ to $1\cdot10^{-4}$ mol/dm^3

$$-\frac{dC}{dt} = k_1 \cdot C_{coum} \cdot C_{H^+} \cdot C_{MnO_4^-} \cdot C_{In(III)} \qquad (8)$$

for C_{coum}= from $5\cdot10^{-5}$ to $2{,}2\cdot10^{-4}$ mol/dm^3 and $C_{mnO4^-} > 1\cdot10^{-4}$ mol/dm^3

$$-\frac{dC}{dt} = k_1 \cdot C_{coum} \cdot C_{H^+} \cdot C_{MnO_4^-}^{0,2} \cdot C_{In(III)} \qquad (9)$$

where k_0 and k_1 stand for the conditional rate constants for the noncatalytic and the catalytic reactions, respectively.

Table.1. Concentration change of the indicator substance for different temperatures

$-\frac{dC}{dt}$	Catalytic process In(III)=1 μg/cm^3	$8{,}50\cdot10^{-7}$ mol/s	289 K
		$8{,}30\cdot10^{-7}$ mol/s	298 K
		$8{,}23\cdot10^{-7}$ mol/s	303 K
		$8{,}06\cdot10^{-7}$ mol/s	313 K
$-\frac{dC}{dt}$	Noncatalytic process	$6{,}79\cdot10^{-7}$ mol/s	289 K
		$5{,}78\cdot10^{-7}$ mol/s	298 K
		$5{,}24\cdot10^{-7}$ mol/s	303 K
		$4{,}44\cdot10^{-7}$ mol/s	313 K

According to the equation for the calibration curves 1-4 in Fig. 9., the conditional rate constants of the catalytic and noncatalytic reactions were evaluated, for four different temperatures used.

Table.2. Rate constants of noncatalytic reactions for different temperatures applied.

$k_0=5{,}04\pm0{,}03\cdot10^3$	T=289 K
$k_0=4{,}28\pm0{,}02\cdot10^3$	T=298 K
$k_0=3{,}89\pm0{,}03\cdot10^3$	T-303 K
$k_0=3{,}29\pm0{,}03\cdot10^3$	T=313 K

Table.3. Rate constants of catalytic reactions for different temperatures applied.

$k_1=5{,}10\pm0{,}02\cdot10^{10}$	T=289 K
$k_1=4{,}99\pm0{,}01\cdot10^{10}$	T=298 K
$k_1=4{,}94\pm0{,}03\cdot10^{10}$	T-303 K
$k_1=4{,}84\pm0{,}03\cdot10^{10}$	T=313 K

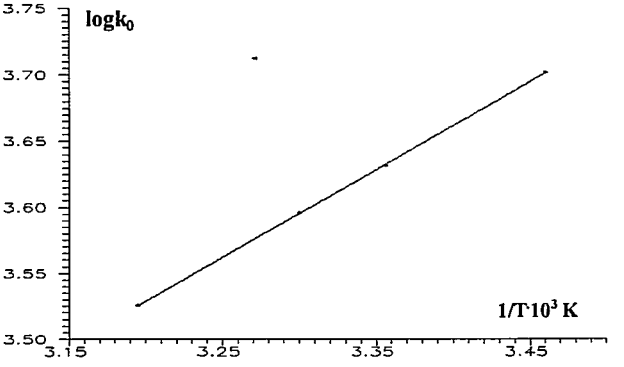

Figure. 10. Dependence of $\log k_0$ on 1/T .

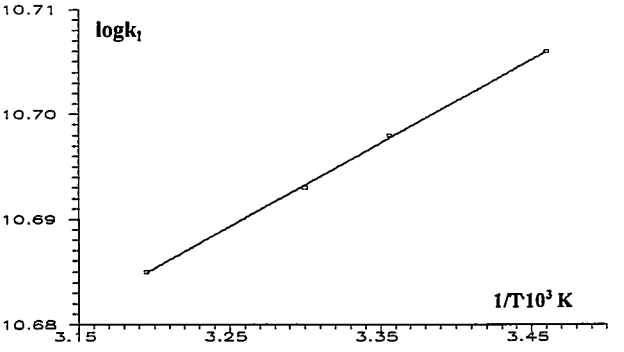

Figure. 11. Dependence of $\log k_1$ on 1/T .

In Fig. 10. and 11. the dependence of $\log k_0$ on 1/T and logk1 on 1/T, are shown for the catalytic and noncatalytic reactions, respectively. From their inclinations, thermodynamic parameters, such as: activation energy, activation enthalpy, activation entropy, free energy of activation and pK* value for active complexes (H.E.Avery,1974), Table. 4.

Table.4. Thermodynamic characteristics of activated state

Reaction	T K	E* KJmol^{-1}	ΔH* KJmol^{-1}	ΔS* KJmol^{-1}	ΔG* KJmol^{-1}	pK*
Noncatalytic	298	12,71	10,23	-132,80	49,80	8,73
Catalytic	298	1,55	-0,93	-,34,90	9,47	1,66

From Table.4. it can be seen that used catalyst substantially decreases activation energy, activation enthalpy and free energy of activation, but increases activation entropy for the same reaction observed.

To test the reproducibility and correctness of the method used, five samples with three different In(III) concentrations were prepared and determined by fixed time ΔA method. Statistical processing of experimentally obtained data yielded Table. 5. (Bautner, 1971).

Table.5. Reproducubility and correctness of the proposed In(III) concentration determination method

Weighted (μ) In(III)·10^{-7} g/cm^3	**Measured** ($\bar{x}$) In(III)·10^{-7} g/cm^3	n	S·10^8	G	$\frac{\bar{x}-\mu}{\mu}\cdot 100$
1	1,08	5	1,0	11,5	8,8
5	5,11	5	1,17	2,83	2,2
10	9,70	5	1,94	2,47	-3,0

where:

$\bar{x}$ - mean arithmetic value,

μ - exact value,

n - number of measurements.

S - standard deviation of individual measurements taken,

G - probable relative error in percentage (= 100ts/ $\bar{x}\sqrt{n}$: where n=5 and t is students confidence for 95%)

$\frac{\bar{x}-\mu}{\mu}\cdot 100$ - correctness of the method.

Probable relative error value in In(III) concentration determination in the proposed method, Table. 5., for the concentrations ranging $1\cdot10^{-7}$ to $1\cdot10^{-6}$ g/cm^3, was 2.5 to 11.5%.

Influence of several selected ions on the reaction rate of the 4-hydroxycoumarin oxidation with permanganate was used as a method selectivity test. While maintaining In(III) concentration of 1 μg/cm^3 as a constant, different quantities of different ions were added to the reaction mixture, beginning with 1:1 ratio, followed by subsequent increase. In such an way obtained results are presented in Table. 6.

Table.6. Selectivity and correctness of the proposed In(III) determination method catalyzing.

Jon	q	ΔA·10^2	Δ%	jon	q	ΔA·10^2	Δ%
-	-	24,6	-	-	-	24,6	-
NH_4^+	10^3	22,9	-6,9	Cu^{++}	10^2	25,9	5,3
Fe^{+++}	Catalysed			Cd^{++}	10^2	23,3	-5,3
K^+	10^4	25,4	3,2	Co++	Catalysed		
Mg^{++}	10^3	25,6	4,0	Sn++	10^3	22,8	-7,3
Ca^{++}	10^3	25,1	2,0	Zn++	Catalysed		
Sr^{++}	10^3	25,2	2,4	NO_3^-	10^4	26,2	6,5
Ba^{++}	10^3	25,8	4,9	Cl-	10^3	25,8	4,9
$Cr_2O_7^{2-}$	10^2	23,3	-5,3	$SO_4^=$	10^3	25,9	5,3
Pb^{++}	10^2	23,7	-3,7	PO_4^{3-}	10	30,1	22,3
Mn^{++}	Catalysed			SCN^-	5	32,2	31,3
Ni^{++}	10	26,1	6,1	Citrat	5	28,2	14,6

q - the ratio between added ion and In(III) where $C_{In(III)}$= 1 μg/cm^3.

Data listed in Table. 6. suggest that such ions as Mn(II), Co(II), Zn(II), Fe(III), citrates, thyocianates and phosphates are disturbing agents for the proposed method.

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NOVA KINETIČKA METODA ZA ODREĐIVANJE In(III) U RASTVORU

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Reakciju oksidacije 4-hidkroksikumarina kalijum permaganatom u kiseloj sredini acetatnog pufera, katalizuju joni In(III), što je iskorišćeno za razradu nove i prve poznate homogeno-katalitičke metode za određivanje nepoznate količine ovog elementa u rastvoru.

Pri optimalnim uslovima odigravanja ove katalitičke reakcije: .: C_{MnO4-}= $2\cdot10^{-4}$ mol/dm^3, C_{kum}=$2\cdot10^{-4}$ mol/dm^3, pH=3,80 , na T = 298 K, ovom metodom se može odrediti nepoznata količina In(III) u rastvoru od 0,05 - 1.5 μg/cm^3, sa verovatnom relativnom greškom od 2,5 do 11,5%.

Pri obradi kinetičkih podataka korišćena je diferencijalna varijanta metode fiksnog vremena. Brzina

reakcije je praćena spektrofotometrijski na talasnoj dužini 525 nm, pri debljini apsorpcionog sloja 1 cm.

Na osnovu zavisnosti brzine reakcije i koncentracije In(III) na različitim temperaturama, konstruisane su kalibracione krive, a metodom najmanjih kvadrata definisane su njihove jednačine za određivanje In(III) na tim temperaturama. Određene su odgovarajuće kinetičke jednačine za nekatalitički i katalitički proces, a na osnovu njih uslovne konstante ovih procesa na temperaturama od 289 K, 298 K, 303 K i 313 K. Takođe su određene energije aktivacije i ostali termodinamički parametri nekatalitičkog (E^*=12,71 $kJmol^{-1}$) i katalitičkog (E^*=1,55 $kJmol^{-1}$) procesa. Radi ocene selektivnosti metode ispitan je uticaj nekih stranih jonova na tačnost određivanja In(III) predloženom metodom, na osnovu čega je zaključeno da reakciju ometaju joni Mn(II), Co(II), Zn(II), Fe(III) citrati, tiocijanati, fosfati i drugi joni koji se mogu oksidovati permanganatom.

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ORIGINAL SCIENTIFIC PAPER

MATHEMATICAL-GEOGRAPHICAL POSITION OF SR JUGOSLAVIJA AND REPUBLIKA SRPSKA

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ABSTRACT

Mathematical-geographical position of a territory is given by determining the field of geographical coordinate net in which it fits without remnants. Percentage ratio of a territory surface and surface of corespondent field of geographical net can be named field fill. Mathematical-geographical position of the given territory is completely determined connecting a corresponding day geometry (duration of the daytime, twilight, daylight and night) to its field of geographical net.

Key words: field of geographical net, field fill, coefficient of the framed the territory, antic climate, day geometry, SR Jugoslavija, Republika Srpska.

Mathematical-geographical encirclement of SR Jugoslavija and Republika Srpska

Mathematical-geographical position of a point on Earth globe is determined by the geographical coordinates. Mathematical-geographical position of a territory is determined by the geographical coordinates of its extreme points, relative to the cardinal points - the end north point, end south point, end east point and end west point (N, S, E and W) (Fig.1). Geographical coordinates of these points for the territory of SR Jugoslavija and Republika Srpska are given in Table 1.

The end north point of SR Jugoslavija is positioned 10 km north of Subotica, the end south point is on Mala Ada at the inflow of river Bojana1 into the Adriatic Sea, the end east point is the mountain top Srebrna glava on Stara planina , while the end west point is the crossing of the roads north of Prijevor village (Miović S.D., Ćurčić P., 1996).

It could be, however, made more precise. It would be more definite if we simply indicate the field of geographical coordinate net in which the observed territory is placed. The field of geographical net is part of the sphere bordered with two given adjacent meridians and two given parallels. In that way, for SR Jugoslavija, we would say: From the mathematical-

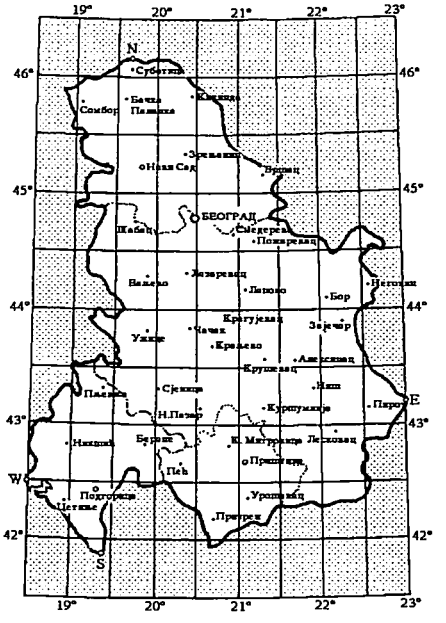

Fig 1. Contours of territory of SR Jugoslavija in the cartographic net of density $\Delta\varphi = \Delta\lambda = 30'$. Extreme points are denoted as N, S, E and W.
Slika 1. Konture teritorije SR Jugoslavije u kartografskoj mreži gustine $\Delta\varphi = \Delta\lambda = 30'$. Ekstremne tačke su označene kao N, S, E i W.

Tab.1. Geographical coordinates of extreme points of SR Jugoslavija and Republika Srpska territories. Territory, SR Jugoslavija, Republika Srpska

Territory		N	S	W	E
SR Jugoslavija	φ	46° 11' 25"	41° 50' 32"	42° 29' 35"	43° 11' 38"
	λ	19° 40' 07"	19° 22' 11"	18° 24" 04"	23° 00' 42"
Republika Srpska	φ	45° 16" 34"	42° 33' 19"		
	λ			16° 11' 06"	19° 37' 44"

1 This point remains the end south point until the definite determination of the border of SR Yugoslavia with Republika Makedonija (section in Korab mountain).

geographical point of view, the position of SR Jugoslavija is defined by the field of geographical net which is closed by the arcs of the parallels 46°11'25" and 41°50'32", with arcs of the meridians 18°24'04" and 23°00'42". The territory of SR Jugoslavija completely fits in that field. We also may say that territory of Republika Srpska fits in the field of geographical net without remains, bordered by the arcs of parallels 45°16'34" and 42°33'19" and by arcs of meridians 16°11'06" and 19°37'44".

For SR Jugoslavija the field of geographical net is the sector of spherical zone in which the base lines are $\Delta\lambda$= 4°34'38", side lines are $\Delta\varphi$ = 4°20'53" and the diagonal line is 5°27'05". Expressed in kilometers, the length of the base lines are 379.17 km and 352.34 km, side lines 483.84 km and diagonal line 606.17 km. The shortest distance between the end north and end south points of the SR Jugoslavija territory is 484.075 km, and between the end east and end west points is 381.217 km. The middle meridian of SR Jugoslavija geographical field is φ_M= 20°43'23" (meridian of Kraljevo), and the middle parallel is λ_M = 44°00'59" (parallel of Kragujevac). The middle meridian and middle parallel intersect between Gornji Milanovac and Kragujevac, in the village Grivac, 8 km north of Knić. The diagonals

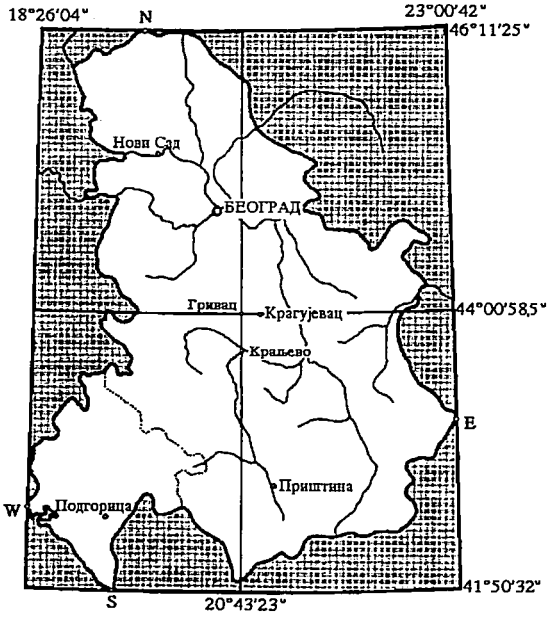

Fig.2. Field of geographical coordinate net of territory of SR Jugoslavija. The field fill is 58%.
Sl.2. Polje geografske koordinatne mreže teritorije SR Jugoslavije. Popunjenost polja je 58%.

intersect on meridian M, on latitude of 44°07'08".

For Republika Srpska the field of geographical net is a sector of spherical zone, in which the base lines are $\Delta\lambda$ = 3°26'38", side lines are $\Delta\varphi$ = 2°43'15", and diagonals are 3°40'53". Expressed in kilometers, the length of the base lines are 282.09 km and 269.47 km, side lines 302.54 km and diagonal lines are 409.35 km. The shortest distance between the end north and end south points of Republika Srpska is 325.511 km, and between end east and end west points is 292.856 km, The middle meridian of Republika Srpska geographical field is φ_M = 17°54'25", and the middle parallel is ϕ_M = 43°54'57". The diagonals intersect on meridian λ_M, on latitude 43°57'35".

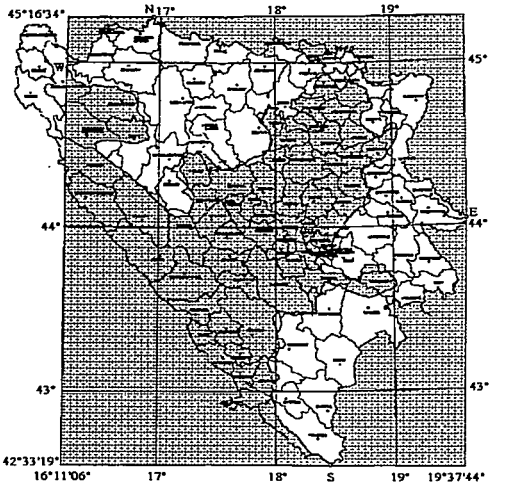

Fig.3. Field of geographical net of Republika Srpska. The field fill is 29.7%.
Sl.3. Polje geografske koordinatne mreže teritorije Republike Srpske. Popunjenost polja je 29.7%.

In the previous two sections the surfaces of the field of geographical net that encircle the territories of SR Jugoslavija and Republika Srpska are not given. For Jugoslavija, the field surface is 176 920.4 km^2. The surface of the territory of SR Jugoslavija is 102 175 km^2, which means that it occupies 58% of its geographical field. The relation of some territory and the surface of its corresponding field of geographical net, expressed in percentages, may be called *mathematical-geographical field fill* or simply *field fill.* Field fill of SR Jugoslavija is 58%.

Instead of the usual *coefficient of the form of border* you can introduce the *coefficient of the framed the territory,* like a relation beetwen the real length of state border and the perimeter of the circle which is the base of the calotte which area is aqual to area of given state territory. For the territory of SR Jugoslavija it is a calotte which the spherical radius is ρ =1°37'19, and the perimeter of the base is O=1133,01 km. The length of border line of SR Jugoslavija is 2739 km, so that the coefficient of framed its territory would be 2.42.

The surface of the geographical net field, that corresponds to the territory of Republika Srpska is 83 450 km^2. The surface of Republika Srpska territory is 24 807.9 km^2, so that the field fill is 29.7%.

From the military-geographical standpoint, according to mathematical-geographical field fill of a

territory, the conciseness of its shape may be considered as an indication of the degree of its possibilities to be defended. For example, France has the same field fill as SR Jugoslavija (57.4%), Romania has the field fill of 64.9%, Poland 70%, Australia 76% and US states Wyoming and Colorado 100%. On the other side, the poor field fill and poor conciseness of the territory have Sweden (44%), Italy (30.6%) and Norway (17%). In that group of the state territories belong Republika Srpska with the field fill of 29.7%.

Characteristics of SR Jugoslavija and Republika Srpska climate (in the antic sense of the word)

Antic and medieval geographers were not dealing with geographic coordinates but, starting with Eratosten, with climates (climata). Eratosten states 7, and Ptolemy in Almagest states 11 climates. Climates are latitude zones of ecumens separated by antic geographers according to their duration of the longest daytime. The system of antic climates starts with equator and than the climate are lined according to the extension of the daytime by half an hour. For example, Ptolemy states that parallel (climate) Lisimahia-Helespont is characterized by the longest daytime of 15 hours, Bysantium (Mesalia) is characterized by the longest daytime of 151/4 hours and Middle Pont is characterized by the longest daytime of 151/2 hours. In Geography , besides the length of the daytime, to each climate the additional entries has been added: the ratio of the shortest and longest daytime duration, the length of the longest and shortest shadow of the gnomon. In his Geography Ptolemy, for example, defines the parallel of Middle Pont in this way: It passes through the middle of Black Sea, latitude is $\varphi = 45^{\circ}01'$, the longest daytime is 15 1/2 hours long, the shortest shadow is 23 1/4 sixtieth of a gnomon, equinoctial shadow by 60, and the longest shadow is 155 sixtieth of a gnomon.

Determination of a climate by the length of daytime remained standard even after Ptolemy, in medieval age. For example, Constantin the Philosopher in its book The life of King Stephan Lazarević (Život Despota Stefana Lazarevića) describes the location of Serbia in this way: *This land (Serbian land) is full of various goods and according to writing of some geographies it sends air to the west and Helespont:* ***because day here lasts 15 hours*** *..."*

The values of the shortest and longest daytime, as well as their ratio, are given in the Table 2, as the determinant of SR Jugoslavija climate (and Republika Srpska). At the determination the extension of the daytime is considered because of the effect of astronomical refraction.

We could, therefore, say that SR Jugoslavija is situated in the climate in which the longest daytime lasts from 15^h14^m to 15^h47^m. Following the reverse order the latitudes to which the given lengths of the longest daytime correspond may be estimated (Tab. 3, Fig.3). The longest daytime is not the only characteristic of the climate, in the antique sense of the word. The climate is quitely determined when you know to its charac relation of daytime, twilight and night. In one word, when the day geometry is known. Here the day

Table 2. Determinants of climate of SR Jugoslavija (and Republika Srpska).

Point	Geographical latitude	Longest daytime (T)	Shortest daytime (T_1)	T/T_1
S	41°50'32"	$15^h13^m35^s$	$9^h08^m01^s$	1.667
	42	15 14 08	9 06 59	1.671
	43	15 21 54	9 00 16	1.706
	44	15 29 24	8 53 18	1.743
M	44°00'59"	15 29 32	8 53 11	1.743
	45	15 37 14	8 46 03	1.823
	46	15 45 25	8 38 29	1.831
N	46°11'25"	15 46 50	8 37 00	1.831

Table 3. Given duration of the longest daytime and corresponding geographical latitude

Tmax	15^h15^m	15^h20^m	15^h25^m	15^h30^m	15^h35^m	15^h40^m	15^h45^m
φ	42°02'	42°44'	43°25'	44°05'	44°43'	45°18'	45°57'

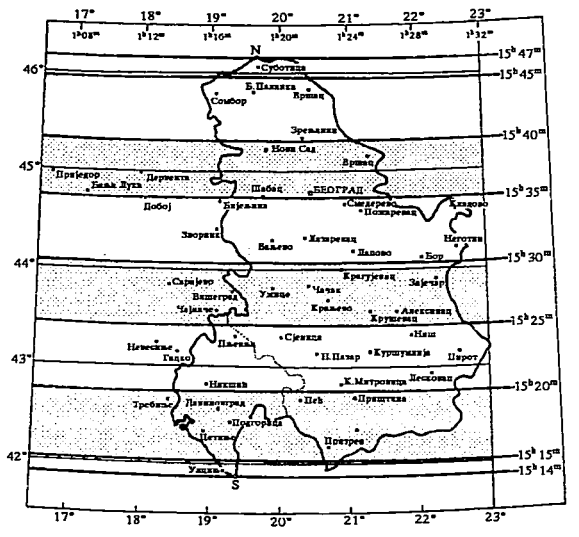

Fig.4 Climates of SR Jugoslavija
Sl.4. "Klimati" SR Jugoslavije

geometry, since we have small width dimension of the territory, will be given only for middle latitude, that can be approximated to $\varphi = 44^{\circ}$ for both SR Jugoslavija and Republika Srpska.

Here the day geometry, since we have small width dimension of the territory, will be given only for middle latitude, that can be approximated to $\varphi = 44^{\circ}$ for both SR Jugoslavija and Republika Srpska.

Day geometry as determinant of climate of SR Jugoslavija and Republika Srpska

The basic concepts and forms used for the estimation of the given values (Tadić, 1997) will not be explained here. The calculation results for the latitude will be presented only in the table form. The values in the tables may be considered as the average for the whole territory of SR Jugoslavija and Republika Srpska.

Values of the elements of the day geometry in the previous tables completely define the climate of the territory of SR Jugoslavija and Republika Srpska. They, however, characterize all the other territories that are situated in that spherical zone. Therefore, the day geometry is completely defined if the differences of the local time are stated. For the territory of SR Jugoslavija may be added that in its end east point the real noon occurs 18 minutes and 19 seconds prior the noon in its end west point, in other words, in its end east point the noon occurs 1h32m03s prior the noon in points of the Origin meridian, or 1h13m44s earlier, considering the end west point. For the territory of Republika Srpska the first mentioned difference of the local time is 13 minutes and 47 seconds, while the end east point and end west point are in advance comparing to the Greenwich noon by 1h18m44s and 1h04m44s, respectively. In this way the day geometry is correctly connected for the fields of geographical coordinate net to which SR Jugoslavija and Republika Srpska belong.

Table 4. Total duration of daytime, twilight (dusk + down) and night, given for months on $\varphi = 44^{\circ}$

	Daytime		Civil twilight		Nautical twilight		Astronomical twilight		Night (Pitch-dark night)	
	Hours	%	Hours	%	Hours	%	Hours	%	Hours	%
J	288.53	3.29	39.20	0.45	69.78	0.80	105.46	1.20	350.01	4.00
F	292.52	3.34	33.04	0.38	59.37	0.68	90.66	1.03	288.82	3.30
M	368.87	4.21	35.49	0.41	64.53	0.74	99.97	1.14	275.16	3.14
A	402.65	4.60	36.00	0.41	66.46	0.76	105.32	1.20	212.03	2.42
M	456.66	5.21	41.38	0.47	78.04	0.89	128.66	1.47	158.68	1.81
J	462.69	5.28	43.35	0.49	83.18	0.95	142.84	1.63	114.47	1.31
J	468.87	5.35	43.20	0.49	82.23	0.94	138.38	1.58	136.74	1.56
A	434.19	4.96	38.73	0.44	72.08	0.82	115.83	1.32	193.98	2.21
S	376.68	4.30	34.68	0.40	63.43	0.72	99.08	1.13	244.24	2.79
O	342.34	3.91	35.83	0.41	64.69	0.74	99.34	1.13	302.32	3.45
N	290.87	3.32	36.91	0.42	65.93	0.75	99.99	1.14	329.14	3.76
D	277.89	3.17	40.27	0.46	71.47	0.82	107.67	1.23	358.44	4.09
Y	4462.77	50.94	458.07	5.23	841.19	9.60	1333.19	15.22	2964.04	33.84

Table 5. Average length, by months, given in hours, of the daytime, twilight (dusk + down) and night on $\varphi = 44^{\circ}$

	Daytime	Civil twilight	Nautical twilight	Astronomical twilight	Night (Pitch-dark night)
J	9.31	1.26	2.25	3.40	11.29
F	10.45	1.18	2.12	3.24	10.32
M	11.90	1.14	2.08	3.22	8.88
A	13.42	1.20	2.22	3.51	7.07
M	14.73	1.33	2.52	4.15	5.12
J	15.42	1.44	2.77	4.76	3.82
J	15.12	1.39	2.65	4.46	4.41
A	14.01	1.25	2.33	3.74	6.26
S	12.56	1.16	2.11	3.30	8.14
O	11.04	1.16	2.09	3.20	9.75
N	9.70	1.23	2.20	3.33	10.97
D	8.96	1.30	2.31	3.47	11.56
Year	12.23	1.25	2.30	3.65	8.12

Table 6. Total and average values (in hours) of daytime, daylight, twilight (dusk + down) and night, given by months on $\varphi = 44^{\circ}$

M	Daytime		Daylight		Daytime + astronomical twilight		Night (Pitch-dark night)	
	Total	Average	Total	Average	Total	Average	Total	Average
J	288.53	9.31	327.73	10.57	393.99	12.71	350.01	11.39
F	292.52	10.45	325.56	11.63	383.18	13.68	288.82	10.32
M	368.87	11.90	404.36	13.04	468.84	15.12	275.16	8.88
A	402.65	13.42	438.64	14.62	507.97	16.93	212.03	7.07
M	456.66	14.73	498.04	16.07	585.32	18.88	158.68	5.12
J	462.69	15.42	506.04	16.87	605.53	20.18	114.47	3.82
J	468.87	15.12	512.08	16.52	607.26	19.59	136.74	4.41
A	434.19	14.01	472.92	15.26	550.02	17.74	193.98	6.26
S	376.68	12.56	411.36	13.71	475.76	15.86	244.24	8.14
O	342.34	11.04	378.18	12.20	441.68	14.25	302.32	9.75
N	290.87	9.70	327.78	10.93	390.86	13.03	329.14	10.97
D	277.89	8.96	318.16	10.26	385.56	12.44	358.44	11.56
Y	4462.77	12.23	4920.84	13.48	5795.96	15.88	2964.04	8.12
%	50.94		56.17		66.16		33.84	

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REZIME

MATEMATIČKO - GEOGRAFSKI POLOŽAJ SR JUGOSLAVIJE I REPUBLIKE SRPSKE

TADIĆ Milutin

Matematičko-geografski položaj neke teritorije je određen poljem geografske koordinatne mreže u koje se ona, bez ostatka uklapa, kao što je to pokazano na primjeru teritorija SR Jugoslavije i Republike Srpske (Sl.2, Sl.3). Procentualni odnos površine date teritorije i površine njoj pripadajućeg polja geografske mreže može se nazvati *matematičko-geografska popunjenost polja* ili *samo popunjenost polja.* Popunjenost polja teritorije SR Jugoslavije je 58%, a Republike Srpske 29.7%. Svakom tako određenom polju geografske mreže svojstvena je posebna geometrija dana. Na slici 4 su su ucrtani antički klimati - geografske paralele s pridruženim dužinama najduže obdanice. Svi elementi sunčeve geometrije (obdanica, sumrak i svanuće, vidjelo, mrak) dati su u tabelama 4, 5 i 6, za paralelu $\varphi = 44^{\circ}$, kao zaokruženu srednju paralelu i SR Jugoslavije i Republike Srpske. Geometrijom dana, vezanom za polje geografske mreže, u potpunosti određujemo matematičko-geografski položaj teritorije čije je to polje.

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ORIGINAL SCIENTIFIC PAPER

THE HAJLA MOUNTAIN WINTER-SPORT TOURISM MORPHOLOGIC AND CLIMATIC DEVELOPMENT CONDITIONS

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ABSTRACT

Hajla Mountain natural predisposition for the development of winter-sport tourism is the paper's subject of discussion, especially from the point of morphologic and climatic conditions.

The results of the paper are based on field research and consultations of the literature available, as well as, on the Rozaje commune tourism development plans. A number of scientific methods were used during the paper preparation (geographic, statistic, analytic-synthetic, comparative and cartographic ones).

One can clearly state, there are highly favorable morphologic and climatic conditions for the development of winter-sport and other kinds of mountain tourism on Hajla Mountain. Configuration, altitude difference and hypsometric characteristics of this high mountain enable marking out and preparation of the ski-ground suitable for alpine disciplines and all categories of skiers, respectively. Potential ski run altitude difference extends from 500 to 1000 meters, their length from 4 to 5 km and their dominant exposition is the northern one. Duration of snow for skiing extends from 4 to 5 months.

Key words: morphologic conditions, climate, Hajla, winter-sport tourism, ski-ground, snow cover.

GEOGRAPHIC-TOURIST POSITION

Hajla Mountain expands between Pecka Bistrica (Pecka Clearwater) river at south, and Gornji Ibar (Upper Ibar) and Rozaje valley at north. The mountain crest length, from Smiljevica extends to some 10 km at west, to Stedima at east,. Regarding the administration, the northern side of Hajla belongs to Rozaje commune of Monte Negro, while its southern side to Pec commune of Serbia, respectively.

A motor road, built in 1925, leads along the valleys of Pecka Bistrica and Velicka rivers, through Rugovo Gorge and over Cakor pass (1,849 m a/s/l/). The road has been categorized as highway according to its significance, although its major part is of Mac Adam surface only. The road is often inaccessible during the winter, due to snow blockade on Cakor pass. A highway, from Nis via Pristina, Pec and Podgorica to Bar port is planned, along the direction, by the year of 2010 (semi-highway in phase one), with the tunnels below Cakor and Tresnjevik. The Kosovska Mitrovica - Rozaje - Berane highway and Pec - Kula Saddle (1,871 m a/s/l/) - Rozaje regional road are of greater significance, at present, regarding the Hajle tourist evaluation. There are three forest roads leading from Rozaje toward Hajla Mountain. One of these roads, leads along the Bukeljska River valley reaching Cafa Hajla (1,884 m a/s/l/), 13 km total in length. The other leads toward the spring of Ibar River with a road branch separating in the river's vicinity and leading to a deserted village of Bandzovo on the Hajla northern slopes. The length of the road to the village mentioned is of some 10 km. The third forest road follows the Ibarac valley reaching the locality of Lomovi, at some 3.5 km to Cafa Hajla. The road leading to Ibar River spring and Bandzovo village offers the most favorable conditions for the reconstruction of the existing road into an access road of high quality to the Hajla ski grounds.

MORPHOLOGIC CHARACTERISTICS

The northern Prokletije mountain group elevates from relatively high plateau, making up a long (over 90 km) and continuing crest, in general, spreading in west - east direction. The group starts with Balja close to Andrijevica, and ends with Mokra Gora (Wet Forest) close to Kosovska Mitrovica. Hajla Mountain is the tallest and central mountain in the chain, with its tallest peak reaching 2,403 m a/s/l/.

Morphologic conditions for the development of winter-sport and summer recreational tourism in this orographic entirety depend greatly of the terrain geologic composition. Paleozoic schist dominate over the western part, consisting of Balj Mountain, Mokra Mountain, Sjekirica, Smiljevica, Hajla, Stedim, and Rusolija, and only the peaks, hills and certain crests are made of Triassic limestone. However, Triassic lime-

stone and dolomite dominate in the eastern part of the mountain chain, reaching a thickness of some 1,000 m in the Zljeb and Mokra Gora carbonic complex (Menkovic, Lj., 1978). Therefore, typical karst relief forms: waterwheels, hollows, crevices, caves and pits (Menkovic, Lj., 1978).

The regressive erosion of Pecka Bistrica and Gornji Ibar rivers created the saddles (Krstac, Cafa Hajle, Mala Gora, Kula and others) along their crests and among their peaks. Kula saddle is the only one having some traffic function at present. Mountain climber and livestock paths are the only ones leading over the rest of the saddles, while a village road leads over Cafa Hajle. The saddles with the opposite river valleys represent favorable natural routes for the construction of ski-ground access roads.

Hajla is characterized by quite steep sides and sharp crest. The southern side toward Rugovo is especially steep. The northern side, just below the limestone crest, is sharply, in places even vertically, cut due to glacial erosion. There, deep circues are cut in, keeping snow often during May and June, and in some places even during the whole summer long. The Hajla northern side is somewhat gently inclined in the zone of Paleozoic schist providing the residence for vast forests and pastures.

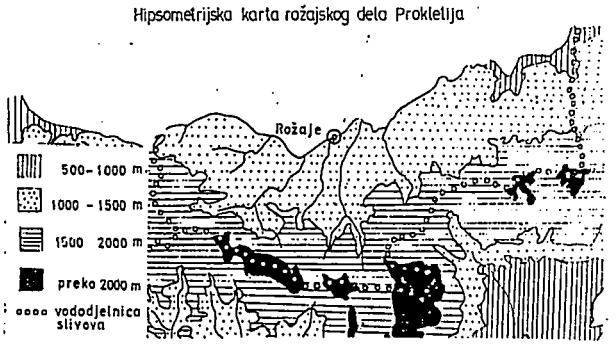


Figure 1. The hypsometric map of Rozajske Prokletije Mt.

According to hypsometric map, some 90 per cent of Rozajske Prokletije ski-grounds are located within an altitude of 1,500 to 2,000 m a/s/l/. The ski-ground inclination rate ranges from 30° to 55°.

SKI-GROUNDS

Rozaje part of Prokletije has a total altitude difference sum of potential ski-runs ranging to some 17,000 meter ("Skrivena" Investment Project). The total is twice as bigger than the one on Kopaonik, or Bjelasica, and five times bigger compared to Durmitor.

Within this part of Prokletije, three potential mountain zones could be selected with the altitude differences, as follows:

Skrivena (Smiljevica) Zone, some 3,500 m
Hajla – Stedim Zone, some 8,000 m
Beleg Zone, some 5,000 m.

The zones mentioned, together with its localities, could be united into a unique ski-complex, providing an area of some 4,000 hectare, with the distances among certain localities ranging from 2 to 10 km. Within the complex area, some highly favorable morphologic and snow conditions exist regarding the development of Nordic combinations and recreational skiing at the absolute heights of 1,200 - 1,400 m a/s/l/, as well as, for the construction of adequate tourist infrastructure (Kasalica, 1988). According to OECD Study, Hajla is disposed of 3,780 m of ski-run altitude difference, which is 3.64 per cent of total Prokletije altitude difference. However, the Amhice and Stedim ski-runs were not included into the total sum by the Study experts. In addition to altitude difference, other elements of tourist evaluation are also present, and these, apart from sport-manifestation, also suggest a recreation-excursion function of the area. The respective could be: hunting ground, mountaineer's terrain, sight-seeing spots, forest-grass complex, etc.

The highest quality area for the development of winter-sport tourism is located within the Hajle - Stedim - Rusolija complex (Knezevic, 1995). The absolute height of the complex ranges from 1,200 - 1,400 m a/s/l/, while the topographic area average inclination ranges from 13° (Amhica) to 16° (Hajla) and 20° (Rusolija) (Kasalica, 1988) (Fig. 2). The most attractive location, having the ideal conditions for the establishment and construction of the winter-sport center within the complex, is located on the vast grassy plateau, situated among Stedim (1,962 m), Amhica (2,272 m), Rusolija (2,382 m) and Crni Vrh (Black Peak 2,110 m), at the absolute heights from 1,600 - 1,800 m. Long and high quality ski-runs slope down from the mountains mentioned to the plateau, and these could be technically arranged into a unique ski-system for various ski disciplines (Knezevic, 1995).

The Hajla ski ground slopes down from the crests and the circues, over vast pastures toward Ibar and Rugovo. Its length amounts to 2 km on the Ibar side and along the pastures, while some 500 m on Rugovo side. The length could be extended to 5 and more kilometer by cutting the forest. Also, there are suitable ski grounds on the Hajla western side more than 1 km long.

The major ski-run slopes down from Hajla toward the deserted Bandzovo village. The run starts at 2,300 m a/s/l/ and ends at 1,450 m a/s/l/, thus its altitude difference is 850 m. It is 4.5 km long. The ski-run is of north-western exposition. The run goes over the pasture, except in its lower part above Bandzovo village, where it penetrates the forest 600 m in length. The terrain inclination of the starting part of the run amounts from 40 - 50°, while of the other, mostly ranges from 33 - 40°. The run ends at the younger forehead moraine in Banzovo. The northwestern side of the moraine is suitable for the construction of ski jump. Hajla - Banzovo ski-run could be technically

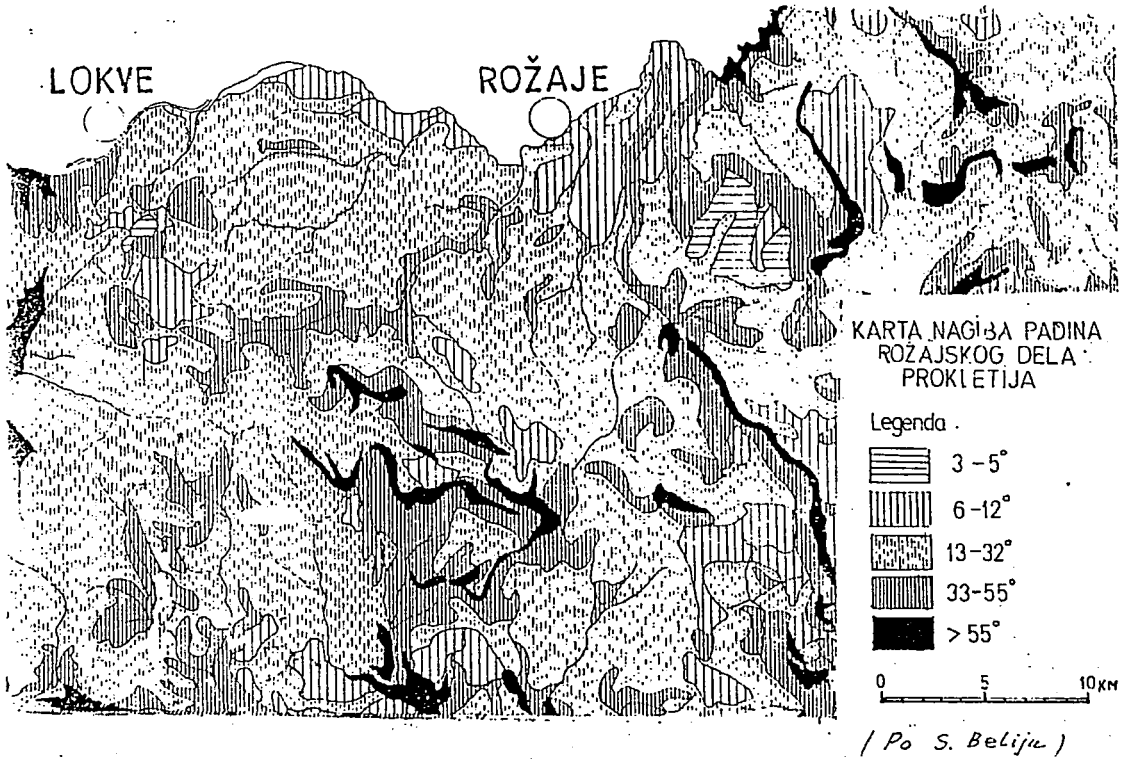


Figure 2. The topografic area average inclination of Rozajske Prokletije Mt. (Zccording to S. BELIJ)

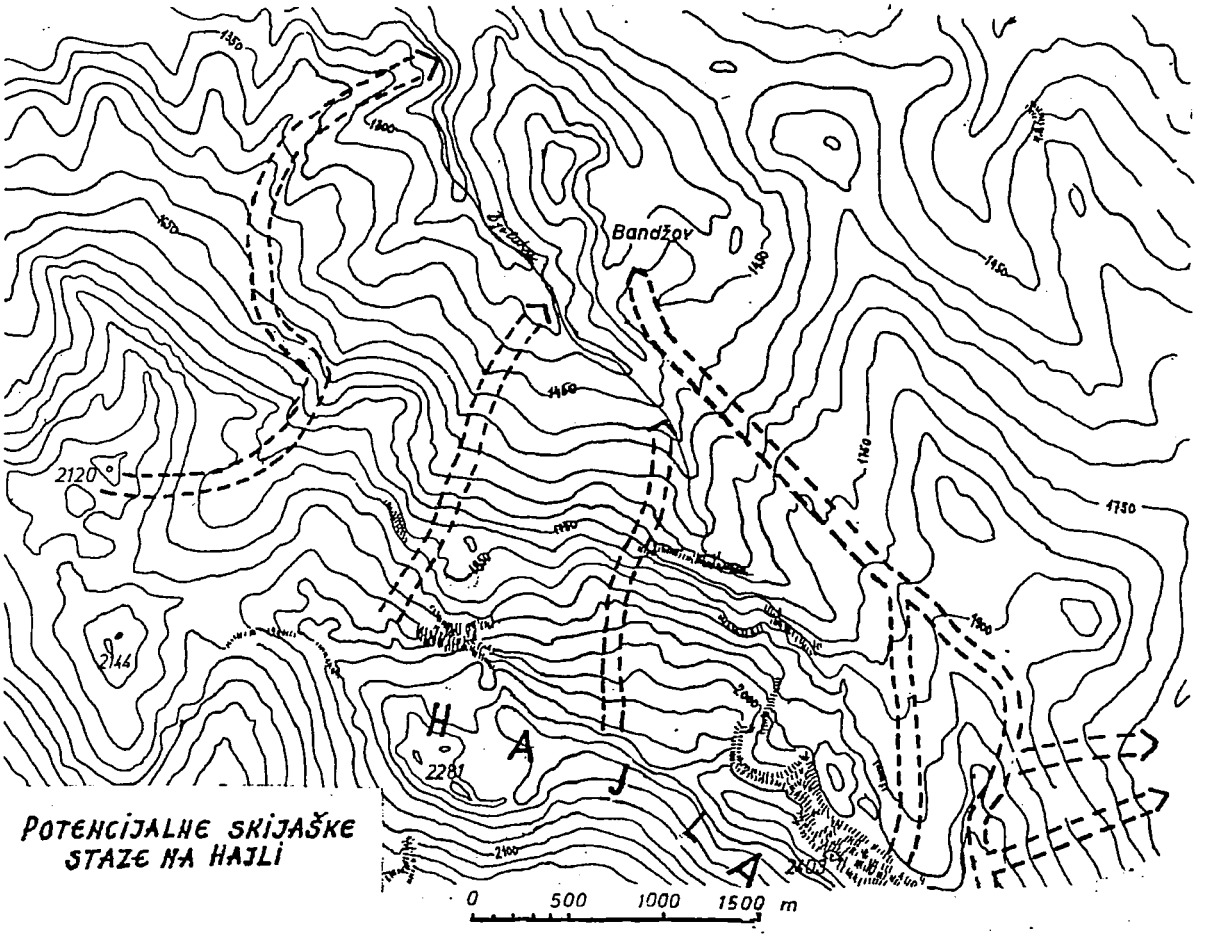


Figure 3. The potential ski-run slopes map of Rozajske Prokletije Mt.

The Rozaje Important Climate Element Mid Value (the station altitude 965 m) (1968-1980 period) (Knezevic, 1995)

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	GOD.
Temperature vazduha u °C												
-3,3	-1,6	0,9	5,8	11,2	13,3	14,5	14,3	11,1	6,0	2,0	-2,5	6,0
Relativna vlažnost vazduha u %												
81	79	78	75	77	78	76	78	83	82	84	84	76
Oblačnost ≥ 8,0												
14,7	12,0	11,4	10,2	8,5	6,5	6,2	5,5	7,7	9,0	11,8	12,8	116,3
Broj vedrih dana n ≤ 2,0												
3,5	3,8	5,6	4,5	4,3	5,8	8,9	10,0	6,6	9,0	6,5	5,1	83,6
Padavine u mm												
66	54	54	72	95	92	89	62	73	69	90	88	904
Broj dana sa snežnim pokrivačem ≥ 30 cm												
8,3	7,8	3,2	0,4	0,1	–	–	–	–	0,1	0,6	3,0	22,7

prepared for several alpine disciplines: slalom, giant-slalom and downhill (Fig. 3.).

The other runs go down from the Hajla crest towards Bjeluha river, and these are of northern exposition. They are significantly steeper than the major one, but they are also shorter. The longest one among them is the one going down from Maja Dramadol peak (2,120 m), and ending by the confluence of Bjeluha and Moraca rivers, at some 1,200 m a/s/l/. The run track is 3.5 km long with the altitude difference of 900 m.

CLIMATE CHARACTERISTICS

After relief, climate represents the most important factor for the development of mountain, especially winter-sport tourism. The air temperature, relative air humidity, the winds, quantity and distribution of precipitation, and snow cover are the climate elements of the greatest influence regarding tourist potentials evaluation for the development of winter-sport tourism.

The sub-mountain climate dominates in Rozaje valley, within the zone of 900 to 1,200 m a/s/l/, while, mountain climate dominates at greater heights, up the tallest peaks.

The sub-mountain climate is characterized with moderate warm to cool summers and with quite cold, snowy and relatively long winters.

As indicated above, annual average air temperature is 6.0°C, July average is 1.5°C, and January average - 3.3°C, respectively. Three months are with negative air temperatures (Dec., Jan. and Feb.). There are five months with air temperature of (10°C. The Rozaje annual average air temperature is 1.1°C lower than the one in Plav and Kolasin, and 1.5°C higher than on Zabljak. Average maximum air temperatures in Rozaje range from 2.5°C in January to 22.7°C in July, while, average minimum, from 7.6°C (July) to - 8.7°C (January). Within the period of 1968 - 1980, the highest absolute maximum air temperature was recorded in July of 33.0°C, and the lowest absolute minimum in December of - 28.0°C.

Due to altitude, forests and precipitation influence, relative air humidity is quite high amounting to 76 per cent annually. The highest one is in November and December (84 per cent), and the lowest in April (75 per cent). Rozaje is characterized by a higher relative air humidity compared to Plav and Berane to some 2 per cent, compared to Pec to some 7 per cent, respectively.

Annual average cloudiness (n (8.0) in Rozaje (116.3) is lower than in Plav (134.9) and berane (136.9), but is somewhat higher than on Zabljak (114.1).

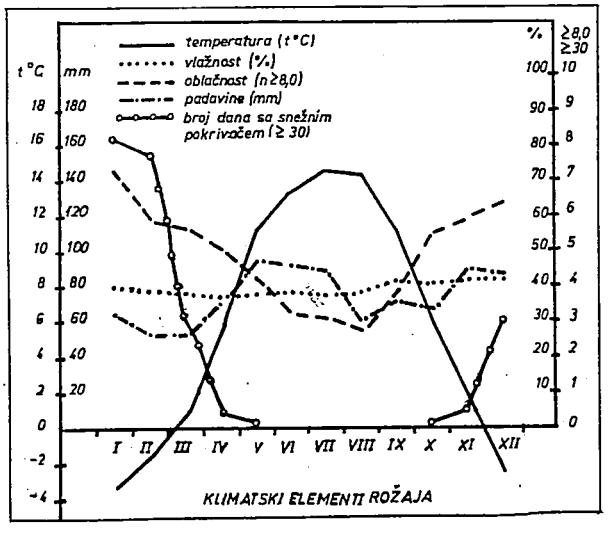
Compared to neighboring settlements, there is an outstanding priority for the development of Rozaje tourism (winter and summer), regarding the number of clear-sky days (n < 2.0). The annual number of clear-sky days (n < 2.0) in Rozaje amounts to 83.6, in Pec 60.6, in Berane 39.7, Plav 55.2 and Zabljak 63.3 (Knezevic, 1995).

According to estimates, the sun light duration in Rozaje ranges between 1,700 to 1,900 hours annually.

The winds dominating in Rozaje are from the western (15 per cent) and eastern (9 per cent) directions, and is the result of Ibar river valley direction. Insignificant appearance of northern and southern winds (1 per cent only) is caused by the orographic structure, i.e., the area being closed by mountains from all sides.

Mountain climate, that dominates on Hajla, is characterized by relatively short and cool summers, and long, cold and snowy winters. The coldest month average temperature (January or February) goes down to some - 5°C and even lower, while, the warmest one (August), 10 - 12°C, respectively. There are 70 to 100

days with snow cover > 30 cm in the zone of 1,400 - 1,800 m a/s/l/, while, at the heights above 1,800 m, up to the tallest peaks, the number of days with the above listed snow cover height, dependant of the slope exposition, ranges from 140 to 160 days. An important indicator in the evaluation of snow conditions required for the development of winter-sport tourism is mid date of the first and the last day with snow cover. Nov. 1 is mid date of the first day with snow cover existing, on Hajla, in the zone of potential ski-ground, above the altitudes of 1,300 m, while Oct. 1, refers to the heights above 2,000 meter. Apr. 16 is the mid date of the last day with snow cover at the heights of some 1,300 m, while Jun. 1, refers to the heights above 2,000 m (Knezevic, 1995) (Graphic 1.).



Graphic 1. The climagrame of Rozajske Prokletije Mt.

Northern wind is more frequent on Hajla, compared to the bottom of Rozaje valley. The wind brings small quantities of snow relatively, but the respective is of high quality and lasts longer, especially on northern side. The snow is dry powder and is suitable for skiing and sledding.

The climatic element analysis indicates that the Hajla mountain climate offers favorable conditions for the development of double season mountain tourism, but, the construction of tourist infrastructure and the preparation of ski-runs would provide the priority to winter tourist season.

The Hajla climate is also favorable for the development of health-recreational tourism. The climate provides the air with high quantities of oxygen, that also consists of ethereal oils produced by the twisting pine and other conifers resin. The inhalation of such air acts bactericide on human respiratory organs. The number of red blood cells and hemoglobin is enlarged as the altitude increases, therefore, this climate strengthens human organism.

DISCUSSION AND CONCLUSIONS

The Tourist Capacity Development Project of the Rozaje Part of Prokletije by 1980 (Economic Bureau, Belgrade, 1977), selected 8 localities that would have to make up a complete tourist offer of Rozaje commune, as follows: Djunerovica Luke, Dzakovica - Kocino, Izvor Ibra, Hajla, stedim, Kula, Beleg, Bac and Rozaje (Fig. 4.).

The priority has been given to the first and second localities in the first, already, initiated phase. The position regarding the traffic, i.e., Kosovska Mitrovica - Rozaje - Berane highway, as well as, the vicinity and accessibility of Rozaje, and the accommodation capaci-

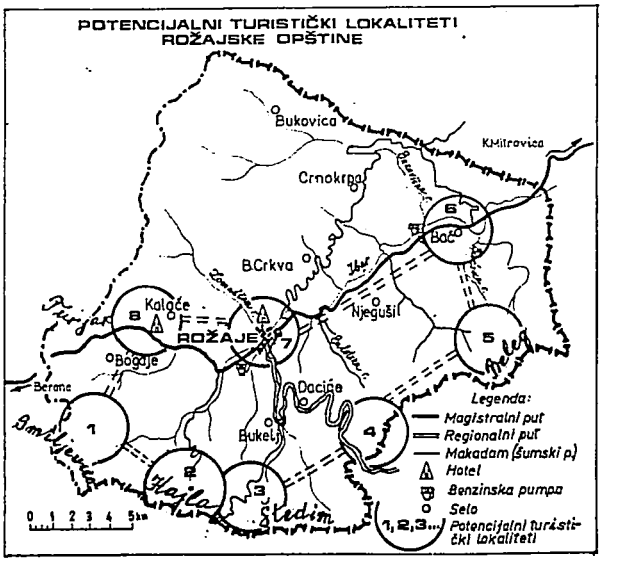


Figure 4. The potential tourist offer and capacity of Rozajske Prokletije Mt.

ties constructed previously, were the greatest influential factors, for the process of arrangement and activation of winter-sport terrain in the area, started developing in west-east direction, i.e., Smiljevica - Hajla - Rusolija - Zljeb. The respective is opposite to the proportionate winter-sport tourism potentials, especially regarding the altitude difference and potential ski-runs, that are incomparably grater in the east, than in the west part of the mountain group.

Djunerovica Luke locality covers the same name valley with the "Turjak" hotel, consisting of 110 rooms with 209 beds. The development possibilities of mass winter-sport tourism are limited here, becauseof the ski-ground's modest capacity (500 - 600) of skiers, modest altitude difference and small slopes (10 - 15°), not challenging the requests of high category skiers. Two drag lifts were already installed on the locality. Drag lift No. 1 is located next to "Turjak" hotel. It is an anchor type lift, 900 m in length, its altitude difference amounts to 135 m, and its capacity is 1,000 skiers per hour. Drag lift No. 2 is 1 km far away from the first one.

It is also an anchor type lift, 1,100 m in length, its altitude difference amounts to 205 m, and its capacity is 1,500 skiers per hour. The lift No. 2 is connected by the upper part of the ski run to the lift No. 1. In the cases of both lifts, the foundation is meadow. The run is suitable for mid and higher category skiers.

Dzakovica-Kocino locality is assigned for the development of winter-sport tourism but, here also, the possibilities of creating some larger winter-sport center are quite limited. The run altitude difference is low, ranging from 350 to 500 meters. However, thanks to the slopes, exceeding 15 to 45°, the runs could be prepared for all category skiers.

Hajla - Stedim locality should grow up into a major winter-sport center of Rozaje commune and of the whole northern Prokletije mountain group, regarding natural potentials available. The locality consists of many attractive elements for the establishment of the tourist offer. Other significant elements for winter-sport and summer recreational tourism are, as follows: winter sport suitable terrain, favorable climate, possibility of inter-connection of ski runs into a unique ski system, glacial relief and its aesthetic and recreation characteristics, mountain tours and mountain climbing terrain, forest-grass complex, hunting game, natural beauties and rarities, etc.

Considering natural resources, Hajla provides not only the possibilities for the development of winter-sport and summer-recreational, but also other types of tourism, such are: health, picnic, hunting, mountaineering, alpinism, excursion, scientific, etc.

However, the tourist arrangement and activation of Hajla requires significant investment funds, whose amount exceeds the possibilities of Rozaje commune. Therefore, it is necessary to commit banking funds (loans), private entrepreneur funds, as well as, the republic and foreign capital funds by means of good marketing activities, in order to implement the tourist development plans and programs.

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REZIME

MORFOLOŠKI I KLIMATSKI USLOVI ZA RAZVOJ ZIMSKO-SPORTSKOG TURIZMA NA PLANINI HAJLI

KNEŽEVIĆ Marko

Hajla (2.403 m. n. v.) je najviša i za zimsko-sportski turizam najperspektivnija planina severne prokletijske grupe. Njena severna strana pripada rožajskoj, a južna pećkoj opštini.

Magistralni automobislki putevi: Kosovska mirovica - Rožaje - Berane i Peć - Čakor - Murino, kao i regionalni put Peć - Kula - Rožaje, pružaju povoljnu šansu za turističko aktiviranje ove visoke planine. Od Rožaja prema Hajli vode tri šumska puta, od kojih najpogodnije terenske uslove za rekonstrukciju u kvalitetan pristupni turistički put do skijaških terena pruža onaj uz izvorišni tok Ibra do sela Bandžova, u dužini od 10 km.

Hajla raspolaže veoma povoljnim morfološkim i klimatskim uslovima, pa i izvesnim komparativnim prednostima u odnosu na Bjelasicu, Durmitor, Zlatibor i Taru, za razvoj zimsko-sportskog i letnjeg rekreacionog turizma.

Ukupan zbir denivelacija potencijalnih skijaških staza na Hajli, Štedimu i Amhici iznosi 8.000 m. Trasa glavne staze Hajla - Bandžov ima denivelaciju 850 m, dužinu 4,5 km i SZ ekspoziciju. Potencijalne staze koje se spuštaju sa Hajle prema rečici Bjeluhi su kraće i strmije.

Na Hajli je zastupljena planinska klima. Ona se odlikuje relativno kratkim i dosta svežim letima, a dugim, hladnim i snegovitim zimama. Srednja godišnja temperatura najhladnijeg meseca (januara) kreće se oko -5°C, a najtoplijeg (jula ili avgusta) 10 - 12°C. U pojasu od 1.400 m do najviših vrhova, gde se nalaze skijaški tereni, ima u proseku 70 do 160 dana sa snežnim pokrivačem ≥ 30 cm. Iznad izohipse od 1.300 m srednji datum prvog dana sa snežnim pokrivačem je 1. XI, a na visinama iznad 2.000 m 1. X, dok je srednji datum poslednjeg dana sa snežnim pokrivačem na oko 1.300 m 16. IV, a na visinama iznad 2.000 m 1. VI.

Na osnovu izloženog može se zaključiti da su se na Hajli stekli veoma povoljni morfološki, klimatski i drugi prirodni uslovi za razvoj dvosezonskog planinskog turizma, zasnovanog na sportskim aktivnostima (skijanje, planinarenje, lov i dr.), lečenju (klimatoterapija, fitoterapija) i rekreaciji.

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THE GINEVODNA LAKES ALGAE ON SAR-PLANINA

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ABSTRACT

The algae of the Ginevodna (Lost Waters) Lakes system on Sar-planina (Sar Mountain) were examined in August 1997. The material was sampled from the two sub-lacustrine springs, located in the Upper Ginevodno Lake, then, from the lake itself, as well as, from the river arm of the Lower Ginevodno Lake. Some 172 taxons total were determined, as follows: Cyanophyta - 6, Chrysophyta 1, Bacillariophyta - 141, Xanthophyta - 2, Euglenophyta - 2 and Chlorophyta - 20. Each of 4 communities examined was characterized by a various content of algae, while the quality of its water was unchanged (1.31 - 1.53), constantly indicating oligo-beta-mezzo-saprobe degree, or bonus class 1 to class 2.

Key words: Algae, The Ginevodna Lakes, Sub-Lacustrine Springs, Saprobe

INTRODUCTION

The Ginivode Lakes, located on the western branches of the Rudoka massif, in the foothill's peak elevation of 2,562 meter, represent an interesting limnological object among other numerous Sar-planina Lakes. The foothill is a plăteau, moderately lowered westward, and is named Sutman. The lakes like the Celebinsko Lake, the Upper Sutmansko Lake, the Lower Sutmansko Lake and numerous others are settled in the plateau's recesses of moderately waved surfaces. The Ginevodna Lakes settled in the part of the plateau, relatively making an isolated system with the river basin, not clearly defined. The reason for the above mentioned is in the fact that the lake's river arm, that led toward the Sutman River, is dry nowadays. Complex geologic ground of the terrain, the lake is located on, resulted in the formation of ground river arms (abysses), not yet examined regarding the direction, these draining out the water. Therefore, one could not surely state if the Ginevodna Lake water ran into the Sutman, or the Celebinska River.

The glaciers came down from the Rudoka massif, during the last glaciation thus the whole Sutman plateau was exposed to strong glaciation. Therefore, most of the plateau lakes are of glacial origin and of post-diluvial age. That is the reason, the largest number of Arctic species and of Boreal origin were found in the flora of algae of, at present, examined lakes (Urosevic, 1995).

The Ginevodna Lakes are also of glacial origin (Cukic, 1997). It is the complex of the three inter-connected lakes. The Upper Ginevodno Lake is of eastern position and is filled with water from numerous springs, the two among being the sub-lacustrine ones (Fig. 1). The lake water flows off into the Mid Ginevodno Lake and, then, toward the Lower Ginevodno Lake. However, there are two abysses between the Mid and the Lower Ginevodna Lakes, draining out the water of the lakes. The Lower Ginevodno Lake is filled with water, produced by the melting of snow from surrounding slopes, and by precipitation, respectively. The three-lake coastline is at the peak elevation of 2,250-meter a/s/l/. The lake coast is surrounded with bog, covered with well-developed clods of grass. The lake bottom is mostly muddy, only the river arm bottoms are sandy.

MATERIAL AND METHODS

Material of algae was obtained through grating of sill and straining of moss. The specimens were fixed in 4% Phormaldechide on the field. For Bacillariophyta Braune et all. (1982) method was used. The rest of peryphyton was analysed while being in fixed condition. Microscopic analysis was carried out by using the "Ergeval" microscope (Zeiss, Jena) in the laboratory of Biology Departman, Faculty of Sciences in Pristina. Determination of material was done according to following works: Cvijan & Blaženčić (1996), Dedusenko et all. (1959), Gollerbach et all. (1953), Hustedt (1930), Hustedt (1961 - 1965), Hindak et all. (1975), Komarenko et all. (1975), Lazar (1969), Patrick - Reimer (1966), Pascher (1925), Vodenicharov et all. (1971), Zabelina et all. (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 Ginevodna Lakes are of glacial origin and, compared to other Sar-planina Lakes, represent a unique hydrologic Eco-system. The specifics, making the respective differs from other lakes, are its peninsu-

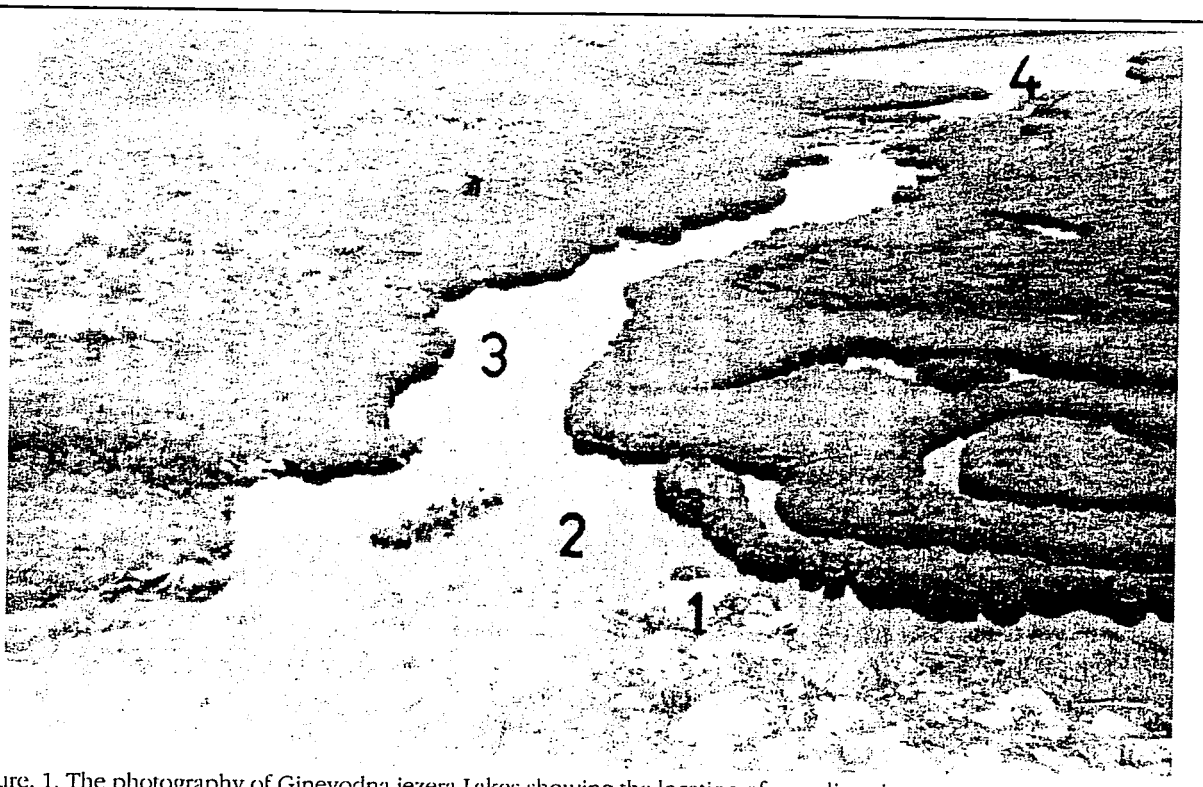

Figure. 1. The photography of Ginevodna jezera Lakes showing the location of sampling sites:
1. coastal region of Gornje Ginevodno jezero Lake, 2. first sublacustrin spring, 3. second sublacustrin spring,
4. Srednje Ginevodno jezero Lake

las, sub-lacustrine springs and the river arm of the lake lost waters. Based on the characteristics mentioned above, the lake offers variety of the conditions for the creation of the algae communities. The research proved the respective, as four of the lake localities (the coast part, sub-lacustrine spring 1, sub-lacustrine spring 2 and the river arm), determined some 172 taxons total, as follows: Cyanophyta - 6, Chrysophyta 1, Bacillariophyta - 141, Xantophyta - 2, Euglenophyta - 2 and Chlorophyta - 20 (tab. 1, Fig. 2).

The representatives of Bacillariophyta have dominated each of the lake localities, as follows: 69.7 to 96.8 per cent. Floral similarity of the communities examined was insignificant. This was proved by the presence of only seven common species: Achanthes lanceolata, Cyclotella bodanica, Cymbella cistula, Fragilaria pinnata, Meridion circulare var. constrictum, Navicula radiosa and Nitzschia vermicularis. Such community diversity could be linked with the expressed micro-ecological conditions of the four localities researched.

The Ginevodno Lake's coast part (Locality 1) represents the residence of algae with highly changing environment conditions (churning up of water, temperature and light conditions, etc.) The richest community of algae was established here, and is made of 91 taxons (Tab. 1:1, Fig. 2:1). The Bacillariophyta representatives were the most present (95.6 per cent) with the genera of: Cymbella (16 taxons), especially with highly frequent Boreal beta-mezzo-saprobe species of Cymbella. cistula, sub-dominating genus of Compho-nema (7 taxons), found in individual rare samples. Thread-like Chlorophyte, presented by the genera of Mougeotia, Spirogyra and Zygnema, are found in individual samples. The saprobe index has shown the value of 1.53, confirming the lake water, at the locality examined, belonged to the oligo-beta-mezzo-saprobe degree, or to the bonus of class 1 - 2, respectively.

Sub-lacustrine spring 1 (locality No. 2) offers more stabile conditions for the development of algae community, compared to the coast part of the Ginevodna Lakes. The environment equilibrium factor primarily refers to the spring permanent water inflow, of probable unchanged chemical content that, at the same time, limits the herbal community, adjusted to such conditions. The water samples, taken 50 cm below the lake surface, indicated high temperature values (10.2°C) and its moderate acid reaction (pH 6.7). The spring settlement was presented with 63 taxons of algae (Tab. 1:2, Fig. 2:2). The most presented division of Bacillariophyta (96.8 per cent) had the most diverse presence of genera (23) in the locality. By taxons, the most numerous among were Cymbella (8), Fragilaria, Navicula, Nitzschia and Pinnularia (each by 4 taxons). Such taxonomic diversity was not followed by the quantitative presentation. Together with the taxons mentioned, the representatives of Chrysophyta and Euglenophyta were sporadically stated. The sub-lacustrine spring 1 had no alpha-mezzo-saprobe species that, compared to the saprobe of other localities, reflects in its lowest index of saprobe (1.31). The water

a 1. The sistematic inventori of established taxons of Algae and frequency (Skale 1-5) of some species that are indicators of water bity (5) in the coastal region of Gornje Ginevodno jezero Lake (1), first sublacustrin spring (2), second sublacustrin spring (3) and t between Srednje and Donje Ginevodno jezero Lake (4)

axons	1	2	3	4	5
CYANOPHYTA					
nabaena sp.			1		
hroococcus minutus (Kütz.) Holerb.			1		o
hormidium uncinatum Gom.			3	1	a
yngbya sp.			1		
ostoc paludosum Kütz.			1		
ynechococcus aeruginosa Näg.			1		
CHRYSOPHYTA					
ydrurus phoetidus (Vill.) Trev.				5	x-o
BACILLARIOPHYTA					
chnanthes lanceolata (Bréb.) Grun.	1	1	1	1	x-o
chnanthes lanceolata f. capitata O. Müll.	1	1		1	
chnanthes lanceolata f. ventricosa Hust.	1			1	
chnanthes lanceolata var. rostrata (Østr.) Hust.	1		1	1	
chnanthes laterostrata Hust.	1				
chnanthes nodosa Cl.		1	1		
mphora ovalis Kütz	1	1		1	x-o
mphora sp.	1				
nemoeoneis zellensis (Grun.) Cl.	1				
aloneis alpestris Cl.	1	1	1		x
aloneis bacillum (Grun.) Mer.	1		1		x-o
aloneis silicula (Ehr.) Cl.	1	1	1		o-b
aloneis silicula var. alpina Cl.			1		
eratoneis arcus (Ehr.) Kütz.	1	1		5	x-o
eratoneis arcus var. amphioxys (Rabenh.) Brun.	1			1	
eratoneis arcus var. linearis Holomboe.	1	1		5	
occoneis placentula Ehr.	1	1			b
occoneis placentula var. euglypta (Ehr.) Cl.	1	1		1	
occoneis placentula var. intermedia (Herib. et				1	

Perage) Cl.					
Cyclotella bodanica Eulenst.	*1*	*1*	*1*	*1*	*o*
Cyclotella comta (Ehr.) Kütz.			*1*		*o*
Cymatopleura solea (Bréb.) W. Sm.	*1*				*b-a*
Cymbella aequalis W. Sm.	*1*	*1*			
Cymbella affinis Kütz.	*1*	*1*		*1*	*o-b*
Cymbella amphicephala Nägg.	*1*				
Cymbella aspera (Ehr.) Cl.	*1*	*1*			*b*
Cymbella cistula (Hemp.) Grun.	*5*	*1*	*1*	*3*	*b*
Cymbella cistula var. gibbosa Brun.	*1*				
Cymbella cuspidata Kütz.	*1*				
Cymbella cymbiformis (Ag.? Kütz.) V. H.	*1*	*1*			
Cymbella ehrenbergii Kütz.	*1*	*1*			*o-b*
Cymbella gracilis (Rabenh.) Cl.	*1*		*1*		*x*
Cymbella hebridica (Greg.) Grun.	*1*				
Cymbella helvetica Kütz.	*1*			*1*	*x-o*
Cymbella laevis Näg.				*1*	
Cymbella lanceolata (Ehr.) Grun.	*1*				*b*
Cymbella naviculiformis Auersw.	*1*	*1*	*1*		*b*
Cymbella sinuata Greg.	*1*	*1*			
Cymbella turgida (Greg.) Cl.			*1*	*1*	
Cymbella ventricosa Kütz.	*1*		*1*	*1*	*b*
Denticula tenuis Kütz.		*1*		*1*	*x-o*
Diatoma hiemale (Lyngb.) Heib.	*1*	*1*		*1*	*x*
Diatoma hiemale var. mesodon (Ehr.) Grun.		*1*		*1*	*x*
Diatoma vulgare Bory	*1*			*1*	*b*
Diploneis eliptica (Kütz.) Cl.	*1*	*1*	*1*		
Epithemia argus Kütz.	*1*				
Epithemia argus var. angustata Fritcke	*1*				
Epithemia argus var. longicornis Grun.	*1*				
Epithemia turgida (Ehr.) Kütz.	*1*	*1*			*b*
Epithemia zebra (Ehr.) Kütz.		*1*			
Epithemia zebra var. porcellus (Kütz.)Grun.		*1*			
Eucocconeis flexella var. gracillima Krasske	*1*	*1*	*1*		
Eunotia arcus Ehr.		*1*			
Eunotia arcus var. bidens Grun.	*1*				
Eunotia fallax var. gracillima Krasske	*1*	*1*	*1*		
Eunotia gracilis (Ehr.) Rabenh.			*1*		
Eunotia praerupta Ehr.	*1*		*1*		
Eunotia praerupta var. inflata Grun.			*1*		
Eunotia praerupta var. muscicola Boye			*1*		
Eunotia robusta var. tetraedon (Ehr.) Ralfs.			*1*		
Eunotia tenella (Grun.) Hust.	*1*		*1*		

Eunotia valida Hust.	*1*	*1*			
Fragilaria bicapitata A. Mayer	*1*				*o*
Fragilaria construens (Ehr.) Grun.		*1*		*1*	*b*
Fragilaria construens var. binodis (Ehr.) Grun.	*1*	*1*		*1*	
Fragilaria construens var. triundulata Reich.		*1*			
Fragilaria construens var. venter (Ehr.) Grun.			*1*		
Fragilaria inflata (Heid.) Hust.	*1*				
Fragilaria intermedia Grun.	*1*			*1*	
Fragilaria leptostauron (Ehr.) Hust.	*1*	*1*			
Fragilaria pinnata Ehr.	*1*	*1*	*1*	*1*	
Fragilaria pinnata var. lancettula (Schum.) Hust.	*1*				
Frustulia rhomboides var. saxonica f. undulata Hust.			*1*		
Frustulia vulgaris Thw.	*1*				*o*
Gomphonema angustatum (Kütz.) Rabenh.	*1*	*1*	*1*		*o*
Gomphonema angustatum var. productum Grun.	*1*				*b-a*
Gomphonema angustatum var. undulatum Grun.		*1*	*1*		
Gomphonema constrictum Ehr.	*1*		*1*	*1*	*b*
Gomphonema constrictum var. capitatum (Ehr.) Cl.	*1*				
Gomphonema intricatum var. pumilum Grun.	*1*			*1*	*o*
Gomphonema longiceps Ehr.			*1*		
Gomphonema longiceps var. montanum (Schum.) Cl.	*1*		*3*		*x*
Gomphonema longiceps var. subclavatum Grun.	*1*	*1*		*1*	
Gomphonema olivaceum var. minutissimum Grun.				*1*	
Gomphonema parvulum var. micropus (Kütz.) Cl.				*1*	
Gomphonema ventricosum Greg.			*1*		*x-o*
Hantzschia amphioxus f. capitata O.Müll	*1*				
Meridion circulare Ag.	*1*	*1*		*1*	*x-o*
Meridion circulare var. constrictum (Ralfs.) V.H.	*1*	*1*	*1*	*1*	
Navicula bacillum Ehr.	*1*				
Navicula cryptocephala Kütz.	*1*			*1*	*a*
Navicula cuspidata f. primigena Dipp.		*1*			
Navicula menisculus Schum.	*1*	*1*		*1*	*b-a*
Navicula pergarina (Ehr.) Kütz.				*1*	
Navicula pseudogracilis Skv.				*1*	
Navicula pupula var. elliptica Hust.	*1*				
Navicula pupula var. rectangularis (Greg.) Grun.		*1*			
Navicula radiosa Kütz.	*1*	*1*	*1*	*1*	*o-b*
Navicula viridula Kütz.				*1*	*a*
Neidium affine var. amphirhynchus (Ehr.) Cl.			*1*		
Neidium bisulcatum (Lagerst) Cl.			*1*		
Neidium dubium (Ehr.) Cl.	*1*	*1*			

Neidium iridis var. amphigomphus (Ehr.) V.H.	*1*	*1*	*1*		
Neidium iridis var. ampliatum (Ehr.) Cl.		*1*			
Neidium maximum (Cl.) Meist.		*1*			
Nitzschia gracilis var. capitata West. Et Porezky		*1*			
Nitzschia gracilis var. minor Skabitsch				*1*	
Nitzschia linearis W. Sm.	*1*	*1*			*o-l*
Nitzschia microcephala Grun.				*1*	*b*
Nitzschia sinuata (W. Sm.) Grun.	*1*	*1*			
Nitzschia thermalis var. minor Hilse	*1*				
Nitzschia vermicularis (Kütz.) Grun.	*1*	*1*	*1*	*1*	*b*
Pinnularia borealis Ehr.			*1*		*x-o*
Pinnularia dactylus Ehr.		*1*	*1*		
Pinnularia gibba Ehr.			*1*		*x*
Pinnularia lata (Bréb.) W. Sm.			*1*		
Pinnularia lata var. thueringiaca (Rabenh.) A.Mayer			*1*		
Pinnularia major (Kütz.) Cl.			*1*		*b*
Pinnularia major var. hyjalina Hust.			*1*		
Pinnularia major var. paludosa Meist.	*1*	*1*			
Pinnularia mesolepta (Ehr.) W. Sm.		*1*	*1*		*o*
Pinnularia mesolepta f. angustata Cl.			*1*		
Pinnularia microstauron (Ehr.) Cl.		*1*	*1*		*b*
Pinnularia stomatophora Cl.			*1*		
Pinnularia subcapitata Greg.			*1*		*o*
Pinnularia viridis (Nitzs.) Ehr.			*1*		*b*
Pinnularia.viridis var. fallax Cl.			*1*		
Pinnularia viridis var. rupestris (Hantzsch.) Cl.	*1*		*1*		
Rhopalodia gibba (Ehr.) O. Mull.	*1*	*1*			*o*
Stauroneis ancepa Ehr.	*1*	*1*			*b*
Stauroneis phoenicenteron Ehr.	*1*	*1*			*b*
Stauroneis phoenicenteron f. gracilis (Dipp.) Hust.			*1*		
Stauroneis smithii Grun.	*1*			*1*	
Stauroneis smithii var. karelica Wisl. et Kolbe.		*1*	*1*		
Surirella biserata Bréb.	*1*				*b*
Surirela spiralis Kütz.		*1*			*o*
Synedra ulna (Nitzsch.) Ehr.	*1*			*1*	*b*
Synedra ulna var. amphirhynchus (Ehr.) Grun.	*1*	*1*		*1*	
Tabellaria flocculosa (ROTH.) Kütz	*1*				*o - l*
Tetracyclus rupestris (A. BR.) GRUN	*1*				*x*
XANTHOPHYTA					
Tribonema sp.		*1*			
Tribonema sp.				*1*	

EUGLENOPHYTA					
hacus sp.	1				
rachelomonas volvocina var. volvocina Ehr.			1		b
CHLOROPHYTA					
osmarium crenatum var. boltianum (Gutw.) et .S. West.			1		
osmarium decedens (Reinch.) Racib.			1		
osmarium didimochondrum Nords.				1	
osmarium meneghinii Bréb.			1		
osmarium ochtodes Nords.			1		
osmarium quadratum Ralfs.			1		
osmarium quadrifolium Lund.			1		
osmarium subcrenatum Hantzsch.			1		
osmarium subprotumidum Nords.			1		
ylindrocystis brebissonii Menegh.			1		
uastrum insulare (Wittr.) Roy			1		
lougeotia sp.	1				
etrium digitus (Ehrb.) Jtzigs. et Rothe.			1		
edogonium sp.			1		
edogonium sp.			1		
enium polymorphum Perty			1		
pirogyra sp.	1				
pirogyra sp.			1		
taurastrum alternans Bréb.			1		
etmemorus laevis (Ktz.) Ralfs.			1		
ygnema sp.	1				o

acteristic remained within the limits of beta-o-saprobe degree, i.e., the bonus class 1 - 2.

The sub-lacustrine spring 2 (locality No. 3), as a rence to the previous, indicated lower water tem-ure (3.7°C), some 6.5°C lower, and lower pH (pH 4.8), some 1.9 pH units lower, respectively. above indicated the water acid reaction. The lo- had the most diverse vegetation of algae. The is presence per divisions is equal (tab. 1:3, Fig. The spring No. 2 specific refers to the least pre-d representative of Bacillariophyta (69.4 per . The respective is, at the same time, the richest in ra: Pinnularia (15 taxons) and Eunotia (7 taxons). greater presence in taxons indicates low water erature and its poor mineralization (Proskina - enko, 1974). The representatives of Cholorphyta the most present (21.4 per cent), among these, cially was the acidophilic Desmidiales (Goler-, 1977). The genus of Cosmarium (9 taxons) dis-tinguishes among the respective. This sub-lacustrine spring indicates its specifics according to the numerous representation of Cyanophyta (7.6 per cent) with its various genera: Anabaena, Chroococcus, Phormidium, Lyngbya, Nostoc and Synechococus. The two taxons dominated here quantitatively, as follows: alpha-mezzo-saprobe species of Phormidium autumnale (Cyanophyta) and Boreal xeno-saprobe Gomphonema longiceps var. montanum. Mutual comparison of similarities between the springs 1 and 2 resulted in 20 common taxons (Bacillariophyta). The saprobe index in this spring was (1.52) in the limits of oligo-beta-mezzo-saprobe degree, i.e. the water bonus class 1 and 2.

The Ginevodno Lakes' river arm (locality No. 4) water has a fast flow off, consequently, its community is the poorest one (Tab. 1:4, Fig. 2:4). Sparse species of the community (48) are probably accommodated toward the specific conditions mentioned. The respec-

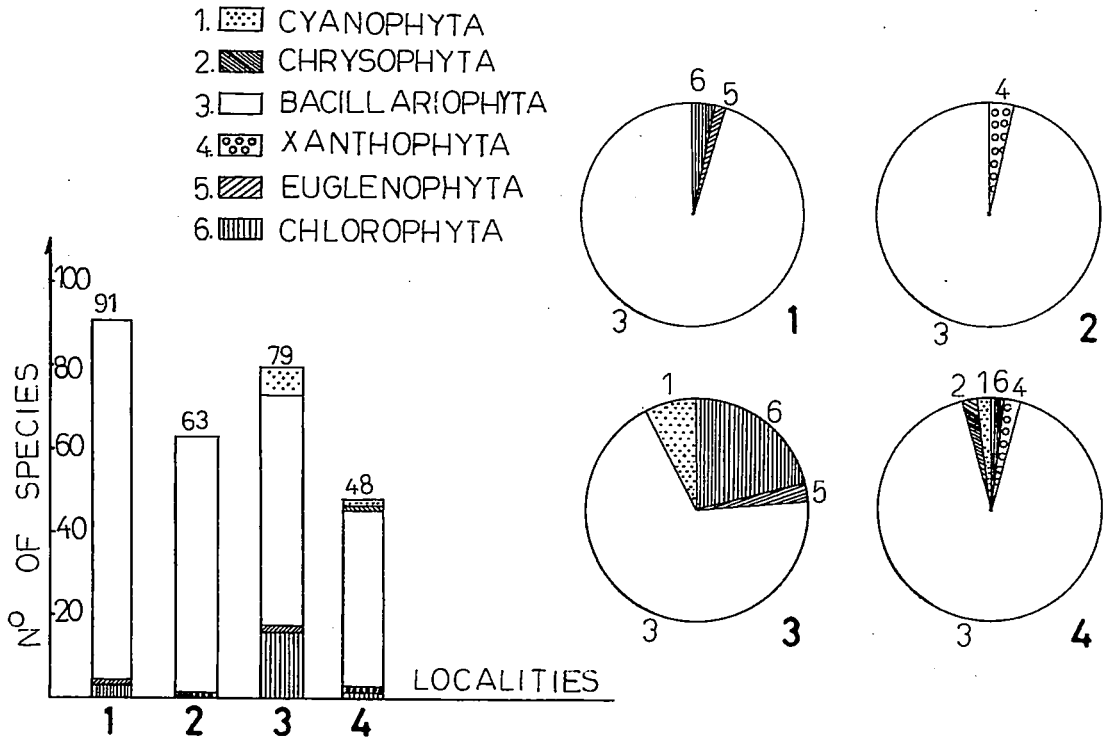

Figure 2. Number of established taxons of Algae in sampling sites.

tive is confirmed by the presence of (Bacillariophyta 94.0 per cent), the genera of Cymbella (6 taxons) and Gomphonema (5 taxons), that survive the water resistance by tidying up the rocky ground with its mucous stems. The macroscopic mucous xeno-saprobe species of Hydrurus foetidus (Chrysophyta), but on the respective, also, largely settled species of Ceratoneis arcus and Ceratoneis arcus var. linearis (Bacillariophyta) indicate additionally similar connection with its tree-like part. The Ginevodno Lake river arm water quality did not differ from the water of other localities. Its saprobe index amounted to 1.44 and indicated the oligo-beta-mezzo-saprobe degree, the water bonus class 1 and 2, respectively.

Some 61 indicative species, as follows: xeno-saprobe - 17, oligo-saprobe - 18, beta-mezzo-saprobe - 23 and alpha-mezzo-saprobe - 3, were registered from the total sum of certain indicative values. The lake as a whole shows (index 1.47) an oligo-beta-mezzo-saprobe degree, or the bonus class 1 and 2, respectively.

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REZIME

ALGE GINEVODNIH JEZERA NA ŠAR-PLANINI

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Kompleksu Šar-planinskih jezera pripadaju i Gidna jezera. Ona su smeštena na visoravni Šutman, lno od vrha masiva Rudoke (kota 2.562 m).
Ginevodna jezera čine sistem od tri jezera: e, Srednje i Donje. Za razliku od Donjeg jezera e vodom hrani topljenjem snega sa okolnih pad- padavinama Gornje vodu dodatno prima i iz lh izvora. Medju njima su dva sublakustrička iz- Gornje jezero vodu gubi otokom koja odlazi a Srednjem. Izmedju Srednjeg i Donjeg jezera su onorakojima voda navedenih jezera otiče.
Ginevodna jezera sa napred navedenim karakterma predstavljaju prirodnu retkost, koja pruža vrsne uslove za obrazovanje zajednica algi. To su dila ispitivanja obavljena (avgust 1997) na četiri teristična lokaliteta Gornjeg jezera: obalski deo, kustrički izvor I, sublakustrički izvor II i otoka jeg jezera (Fig. 1).

Sveukupni sastav algi predstavljala su 172 taksona: Cyanophyta - 6, Chrysophyta - 1, Bacillariophyta - 141, Xanthophyta - 2, Euglenophyta - 2 i Chlorophyta - 20 (Tab. 1, Fig. 2).

Na svakom jezerskom lokalitetu dominirali su predstavnici Bacillariophyta, zastupljeni od 69,4 do 96,8%. Florna sličnost ispitanih zajednica bila je neznatna i sastojala se samo od 7 zajedničkih taksona: Achnanthes lanceolata, Cyclotella bodanica, Cymbella cistula, Meridion circulare var. constrictum, Navicula radiosa, Nitzschia vermicularis i Fragilaria pinnata (Bacillariophyta).

Obalski deo jezera (91 takson) i otoka (48 taksona) predstavljaju staništa algi sa promenljivim ekološkim uslovima (talasanje, brzi protok vode, svetlost, temperatura) čije dejstvo se verovatno ispoljava na obrazovanje zajednica prilagodjenih za specifična staništa. U prilog tome navodimo da su rodovi Cymbella (16, odnosno 7 taksona) i Gomphonema (6, odnosno 5 taksona) taksonima bili najzastupljeniji. Vrsta Cymbella cistula imala je i kvantitativnu dominaciju na oba lokaliteta. Brojna prisutnost taksona navedenih rodova može se dovesti u vezu sa galeretnim drškama kojima pričvršćene za supstrat ove vrste daju otpor vodi. I makroskopska sluzava ksenosaprobna vrsta Hydrurus phoetidus (Chrysophyta) je nadjena na najprotočnijem delu (otoka), osnovom talusa pričvršćena za kamenitu podlogu, kao i za nju vezane odlično učestale vrste Ceratoneis arcus i Ceratoneis arcus var. linearis (Bacillariophyta).

Sublakustrički izvor I (63 taksona) i sublakustrički izvor II (79 taksona) su staništa algi sa stabilnijim fizičko-hemijskim uslovima (stalni priliv vode, verovatno hemijski nepromenjenog sastava) koji pružaju nove mogućnosti za obrazovanja zajednica.

Sublakustrički izvor I od ostalih ispitanih lokaliteta razlikuje se po najsiromašnijoj vegetaciji (Xanthophyta i Bacillariophyta) i pojedinačno učestalim taksonima samo na ovom staništu.

Sublakustrički izvor II u odnosu na ostale ispitane lokalitete ima najravnomernije zastupljenu floru algi u okviru četiri razdela: najmanju zastupljenost predstavnika Bacillariophyta (69,4%), najbrojniju zastupljenost Chlorophyta (21,6%), najbrojniju zastupljenost Cyanophyta (7,6%) i neznatno učestale predstavnike Euglenophyta (1,4%).

Uprkos četiri florno i vegetacijski raznovrsne zajednice, indikatorske vrste trajno su pokazivale indeks (1,31 - 1,53) koji potvrdjuje dobar kvalitet i pripadnost ispitanih Ginevodnih jezera oligobetamezosaprobnom stupnju, ili I - II klase boniteta.

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ORIGINAL SCIENTIFIC PAPER

inetum mughi - Geum bulgaricum, New Association f the Mountain Pine (*Pinus mugo* Turra) on Prokletije ountain

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ABSTRACT

The zone of high-mountain species of *Pinus go* is highly degraded on the territory of Prokje due to long duration of negative anthropoiic influence. However, it succeeded in preserving its specifics and florist resource. Phyto-cenologic research of Nedzinat, one of the numerous Prokletije massifs, also witness the respective.

words: Prokletije, *Pinus mugo*, New Association

INTRODUCTION

Twisting pine (*Pinus mugo* Turra) makes up spe-, the highest zone of high-mountain woody vege-on of the mountains of Mid and Southern Europe, ching Central Apennines toward the south, and the kan mountains along the line of Jakupica - western dope. In Serbia, it appears on Stara Planina (Old ntain), occupying small area and is known as *netum mugi* prov. Misic et all. 1978). Then, it aprs on Suva Planina (Dry Mountain), known as *rbo - Pinetum mugo* Jovanovic, 1953), on the Sarina (Sar-Mountain) branch of Ostrovica, known as *lotricho - Bruckenthalio - Pinetum mugo* Jankovic Bogojevic, 1976), on Osljak, known as (*Achileo - etum mughi* Rexhepi, 1983), on the Sar-planina thern slopes in the Jazinacko lake circue, known as *ugo - Pinetum peucis mugetosum* Stevanovic, anovic et Jankovic, 1994), on the Prokletije massif Koprivnik, Streocke mountains, Starac (Old Man) Maja Rusolija, known as (*Wulfenio - Pinetum ghi* Jankovic et Bogojevic, 1974), but it also appears Nedzinat, Lumbardske mountains, Djeravica, icke mountains, Pastrik and Koritnik.

The presence of, so far, unregistered community his high-mountain pine has been determined on lzinat, that is one of numerous Prokletije massifs. ording to preliminary research, it is located in a very ilar form on Lumbardske Mountains. The commuassigned as *Pinetum mughi - Geum bulgaricum* , new, according to its florist composition, signifitly differs from the one described above, that is also Prokletije community *Wulfenio - Pinetum mughi* c. et Bog. 1967, which depicts the heterogeny of its e on Prokletije, primarily conditioned by the posiof certain massifs and local ecological conditions.

MATERIAL AND METHODS

Florist and vegetation research were made by the beginning of July 1996 on Nedzinat. The herbal material collected was determined on the basis of voluminous literature (Hayek, A., 1929 - 1931, Javorka, S. et Ksapody, V., 1934, Tutin, T.G. ed., 1969 - 1980, Jordanov, D. ed. 1970 - 1982, Josifovic, M. ed., 1970 - 1977, Saric, M. ed., 1986, Saric, M. ed., 1992). Phytocenologic research used standard method of Zurich - Mont Pellier school (Braun - Blanquet, J., 1932), the analysis of floral elements was made on the basis of Gajic division (Gajic, M., 1980), modified by Stevanovic division (Stevanovic, B., 1992), and the plant living forms were given according to Ellenberg & Mueller - Dambois (1967).

THE PAPER RESULTS AND DISCUSSION

Nedzinat with Koprivnik, Streocke Mountains, Lumbardske Mountains, Starac and Cakor with Planinica, belong to Mid group of Yugoslav, northwestern Prokletije, respectively. Its sharp, continuing crest (2,341 m a/s/l/) occupies southeastern - northwestern direction of spreading, further extending over vast saddle on Lumbardske Mountains eastward.

The twisting pine community mainly occupies northeastern slopes, greatly inclined toward the vast circue with the Nedzinat lakes (1,920 m a/s/l/) settled in. From the geologic point, the area is made of limestone - dolomite rocks with the presence of glacial material layers going up the crest part of the massif (Mijovic, 1997). The slopes larger area is covered by brown shallow soil, out of which, bare rocky masses with poor chasm-phyte vegetation peer out. The whole zone of mountain pine, densely covering this part of Nedzinat, is under the influence of Prokletije variety of forest - tundra eco-climate type. Annual mid

ASOCIJACIJA PINETUM MUGHI - GEUM BULGARICUM Ass.nova

NUMBER OF STAND REDNI BROJ SNIMKA	1	2	3	4	5	6	7	8	9	10	11	12	13
LOCALIY LOKALITET	NEDŽINAT												
SIZE OF STAND (m^2) VELIČINA SNIMKA (m^2)	30	30	30	30	30	30	30	30	30	30	30	30	30
ALTITUDE (m) NADMORSKA VISINA(m)	2020	2030	2050	2060	2080	2100	2120	2180	2220	2250	2335	2341	2340
SLOPE (n^o) NAGIB TERENA (n^o)	5°	10°	30°	60°	5°	75°	70°	20°	10°	5°	5°	10°	5°
EXPOSURE EKSPOZICIJA	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	E	SE	SE
GEOLOGIC GROUND GEOLOŠKA PODLOGA	CARBONATE (KARBONATI)												
GENERAL COVERAGE (%) OPŠTA POKROVNOST (%)	70	90	90	90	70	80	80	50	100	50	60	100	80

CHARACTERISTIC COMBINATION OF SPECIES KARAKTERISTIČNA KOMBINACIJA VRSTA														LIFE FORM (ŽIVOTNA FORMA)	CONSTANCY CLASS (PRISUTNOST)	FLORISTIC ELEMENT (FLORNI ELEMENTI)
Pinus mugo Turra	3.3	4.4	4.4	4.4	3.3	4.4	4.4	1.2	5.5	1.2	2.2	5.5	3.3	MIP	V	SJEP
Geum bulgaricum Panč.	1.1	3.3	3.3	2.2	1.1	2.2	3.3	2.2	1.1	+	+			G	V	END.
Helianthemum alpestre (Jacq.) Brentr	+	2.2	+	1.1	2.2		+	1.1	+	2.2	+			Ch	V	ALP-BALK
Vaccinium uliginosum L.	1.1	1.1	1.1	3.3	2.2	3.3	2.2		1.2			1.2		NP	V	BOR-CIRK
Vaccinium myrtillus L.	1.1	+	1.1	3.3	2.2	2.2	2.2		1.2			1.2		Ch	V	BOR-CIRK
OTHER SPECIES OSTALE VRSTE																
Poa ursina Vel.	1.2	1.2	1.2	1.2	+.1			1.2	1.2	1.2				H	IV	END.
Gentiana verna L.	+	+	+		+		1.1	1.1	+		+			H	IV	EVR.
Calamintha alpina (L.) Lam. ssp.alpina	+	1.1	+				1.2	+	+	1.1	+			H	IV	SJEP.
Armeria canescens Host.	+	+	+				+	2.2	+	+	+			H	IV	END.
Saxifraga adscendens L.ssp. adscendens		1.1	+				1.1	1.1		+	+	+	+	H	IV	ARKT.
Linum capitatum Kit.			1.1	1.1	2.2	2.2	+	+	+	1.1				H	IV	BALK.-AP.
Geranium sanguineum L.	1.1	+	1.1	+		1.1	+		+					H	III	SUBPONT
Sorbus aucuparia L	+	+	+	+	+		+							MIP	III	SUBSE
Veratrum album L.	+	1.1	+	+			+		+					G	III	EVR.
Edraianthus montenegrinus Horak.	+	1.1			+				+	+				H	III	END.
Myosotis silvatica Hoffm.ssp.silvatica	+	+			+		+	1.2		+				H	III	SUBEVR.
Polygala alpestris Rchb.	2.2	1.1	1.1		1.1	+				+				G	III	SJEP.
Allysum scardicum (Wettst.) Hay.	1.1	2.2	1.1						+	+	+			Ch	III	END.
Hypericum alpinum W.K.	+	+	+				2.2	+			+			Ch	III	SJEP.
Thymus longicaulis Presl.		1.1	1.1		1.1		1.1			2.2	+			Ch	III	BALK-AP.
Galium anisophyllum Vill.		1.1			+		+	1.1	+			+		H	III	SJEP.

Geum montanum L.	+						+		1.1		+	+	+	H	III	SJEP.
Lotus corniculatus L.	+		+		1.1	1.1					+		+	H	III	SUBEVR.
Thymus longicaulis Presl.		1.1	1.1		1.1		1.1			2.2	+			Ch	III	BALK-AP.
Galium anisophyllum Vill.		1.1			+		+	1.1	+			+		H	III	SJEP.
Phleum alpinum L.		1.2			+				1.1		+	+		H	III	CIRK.
Ranunculus carinthiacus Hoppe.		+		+		1.1		+				+	+	H	III	JEP.
Primula elatior (L.) Grufb.			1.1	+		1.2	1.2	+	+					H	III	SE
Salix waldsteiniana Willd			+.2		+.2		2.3	1.2	+		+			NP	III	SJEP.
Juniperus sibirica Burgs.			+		+	+		+		+.2	+			NP	III	ARKT.
Valeriana montana L.			+		+	+		+		+	+			Ch	III	SE.
Arabis alpina L.ssp. flavescens			+	+			+		+	+	+			H	III	END.
Gentiana kochiana Perr.et Song			+	2.2	+			1.1		3.3		+		H	III	SJEP.
Dryas octopetala L.			+				2.2	1.2			+	+	1.2	Ch	III	ARKT.
Anemone narcissiflora L.					+	2.2	1.1	+				+	+	G	III	CIRK.
Carex laevis Kit.					+.2				1.1	2.2	+.1	+.1	+.1	H	III	JEP.
Phyteuma confusum A.Kern.					+	+	+		+	+			+	H	III	ALP-BALK
Anthyllis pulchella (Vis.)Bornm.(ssp)					+	+		+		+	+		+	Ch	III	SUBBALK.
Festuca violaceae Gaud.						1.2	+.1	2.2	+.1	3.3	+.1			H	III	SJEP.
Trifolium noricum Wulf.						+.1		1.1	+	1.1	1.1		1.2	H	III	SUBBALK.
Festuca rubra Lssp.fallax						+.2		2.2	+.1	2.2	+		+.1	H	III	CIRK.
Nordus stricta L.							+	3.3		2.2	3.3	+.2	+.1	H	III	BOR.-EVR.
Pinus peuce Gris.	1.1	2.2	1.1	+										MIP	II	END.
Asplenium trichomanes L.	+	1.1	1.1		+									H	II	KOS.
Aquilegia blecicii Pod.	+	+	1.1		+									H	II	END.
Salix caprea L.	+		+		+									NP	II	EVR.
Asplenium ruta - muraria L.	+	+	+											Ch	II	CIRK.HOL.
Achillea abrotinoides Vis.	1.1							+	+					H	II	END.
Cetraria islandica (L.)Ach		+.2							4.4	3.3				/	II	ARKT.
Potentilla crantzii (Crantz.) Beck.		+.1								+	+			H	II	ARKT.
Cardamine glauca Spreng.			+.2		1.1			+						H	II	ALP.-BALK.
Pedicularis brachyodonta Schl.et Vuk			+		+								+	H	II	END.
Onobrychis scardica (Gris.)P.W.Ball.				+	+	+								H	II	END.
Crepis dinarica (Beck.) Hay.					1.1			+			1.1			H	II	END.
Globularia cordifolia L.					+									H	II	SJEP.
Nigritella nigra (L.) Rchb.					+			+					1.1	G	II	SJEP.
Anthoxanthum odoratum L.						+.2	+	+						N	II	CIRK.
Silene acaulis L.							1.2	+.2		+.2				Ch	II	ARKT.
Paronychia kapela (Hacq.) Kern.								1.2		+.2			1.2	Ch	II	JEP.
Viola zoysii Wulf.								+			+		+	H	II	END.
Draba scardica (Gris.) Deg.et Dorf.								+	+				+	H	II	END.
Aster alpinus L.									+		+		+	H	II	ARKT.
Thymus albanus H.Braun.										1.1	1.1		+	Ch	II	END.
Saxifraga sempervivum C.Koch.										+	+		+	H	II	END.
Geranium silvaticum L.	1.1	2.2												H	I	BOR.-EVR.
Poa bulbosa f.vivipara Koch.	1.1	2.2												H	I	SUBEVR.
Polystichum lonchitis (L.) Roth.	1.1	1.2												Ch.	I	BOR.-CIRK.
Cystopteris fragilis (L.) Bernh.	1.1	1.1												H	I	BOR.-CIRK.
Rumex acetosa L.	1.1	1.1												G	I	EVR.
Ajuga genevensis L.	1.1	1.1												H	I	EVR.
Carex pallescens L.	1.1	1.2												H	I	BOR.-CIRK.
Picea abies (L.) Karst.	+	+												MIP	I	BOR.-EVR.
Dryopteris filix - mas (L.) Schott.	+	+												G	I	BOR.-CIRK.
Geum molle Vis. et Panč.		2.2	1.1											G	I	BALK.-AP.
Saxifraga rotundifolia L.		1.1	1.2											H	I	SJEP.
Scilla bifolia L.		+	+											G	I	SJEP-PONT.
Antennaria dioica (L.) Gaertn.	+								1.2					H	I	CIRK.
Helianthemum nummulariuum(L)Mill			+		1.1									Ch	I	SUBSE.
Verbascum nicolai Rohl.			+		+									H	I	END.
Trinia delachampii (Ten.) Jan.			+		+									T	I	BALK.-AP.
Anthemis montana L.			+		+									Ch	I	JEP.
Lilium albanicum Gris.				+	2.2									G	I	END.
Carex ornithopoda Willd.				+.1	+.2									H	I	SJEP.
Potentilla speciosa Willd.				+	2.2									Ch	I	END.
Hieracium murorum L.				+	+									H	I	SUBSE.
Soldanella alpina L.				+							+			H	I	SJEP.
Hieracium bauhini Bess. (ssp.)					+	+								H	I	SUBSE.
Silene sendtneri Boiss.					+	+								H	I	END.
Gentiana punctata L.					+		+							H	I	SJEP.
Minuartia bosniaca (Beck.) K. Maly					+.2			+.2						Ch	I	END.
Wulfenia blecicii Lak.						+.2			+.2					G	I	END.
Luzula sudetica (Willd.) DC.						+.2	2.2							H	I	SUBEVR.
Anemone nemorosa L.						1.1	+							G	I	CIRK.
Valeriana pancicii Hal.et Bald.						+	1.1							G	I	END.
Amphoricarpus neumayeri Vis.						+	+							H	I	END.
Doronicum columnae Ten.						+	+							G	I	SJEP.
Veronica orsiniana Ten.						+			+					G	I	END.
Saxifraga aizoon Jacq.						+				+				H	I	CIRK.
Polygonum viviparum L.							1.1	+						H	I	HOLARKT.
Ligusticum mutellina (L.) Crantz.							1.2				+			H	I	SJEP.
Achillea lingulata W.K.								+	+					H	I	BAL-KARP.
Iberis sempervirens L.								+			+			H	I	JEP.
Thlaspi cuncifolium Gris.								+				+		Ch	I	END.
Luzula campestris (L.) Lam.									1.1		+			H	I	KOS.
Rubus idaeus L.									+		+			NP	I	CIRK.
Plantago atrata Hoppe										2.2		+.1		H	I	EVR.
Botrichium lunaria (L.)										+		+		G	I	BOR.-CIRK.
Pedicularis verticillata L.											+		+	H	I	CIRK.
Myosotis alpestris (Schm.) Rohl.											+		1.1	H	I	SJEP.
Androsace villosa L.												+	2.3	H	I	EVR.

Vrste zabeležene samo u jednom snimku (Species occuring in one stand only):
Luzula luzuloides (Lam.) Dandy et Wilm. 1 (+.1), Trollius europaeus L. 1 (+.1), Vicia incana Gouan 2 (+), Dianthus petreus W.K. 5 (+), Avena versicolor Vill. 6 (+.1), Sedum acre L. 8 (+.1).

temperatures range between 2 and 4°C, the absolute minimum to - 45°C, with the absolute maximum never exceeding 25°C (Lakusic, 1985).

The community of *Pinetum mughi - Geum bulgaricum* ass., new, mainly occupies northeastern expositions within the altitude range of 2,020 to 2,341 m a/s/l/, climbing up east toward the tallest point of Nedzinat massif. It is developed on shallow soil and bare rocky mass with the inclination of 5 to 75°, reaching general coverage of 50 to 100 per cent.

An exceptional florist resource is one of the community specifics. Namely, the presence of 108 species were registered during 13 phyto-cenologic surveys of the floor of high and low bush, and herbaceous vegetation with *Pinus mugo - Geum bulgaricum* as the community's major creator.

Pinus mugo represents, by far, the most dominant species on the first floor, made of high bush. In addition, the floor is sporadically made of low tree species of *Sorbus aucuparia, Pinus peuce* and *Picea abies*, not exceeding the height of 3 m. The twisting pine itself, reaches from 2.5 m at lower altitudes, to 70 cm on the crest part of the massif, where, the most severe micro-climatic conditions are present, providing the zone of struggle between the woody and herbaceous high-mountain vegetation. This pine exactly, that belongs to Mid - South European mountain floral element, represents the symbol of the struggle framing the upper forest border by a gradual transfer into the zone of high-mountain bushy vegetation. Unfortunately, its past powerful zone, that played an exceptional anti-avalanche and anti-erosion role, is alarmingly degraded because of destructive anthropogenic influence on our mountains and, even, on Nedzinat itself.

Geum bulgaricum represents the species that dominates in the floor of herbaceous flora. It belongs to the group of the Balkan endemic, occupying certain limestone massifs of Bosnia and Herzegovina, Monte Negro, Serbia, Macedonia, Albania and Bulgaria. In Yugoslavia, the community is registered only on Prokletije within the frame of association of *Geetum bulgarici* Lakusic 1968, although it could be seen within the frame of other associations on limestone substrates. Its significant presence in the community of the twisting pine, not only on Nedzinat, confirms that its biologic optimum is in the conditions of somewhat higher humidity.

In addition to the species mentioned above, *Helianthemum alpestre*, Alpine - Balkan species, also very much present in the floor of herbaceous plants, as well as, *Vaccinium uliginosum* and *Vaccinium myrtillus*, herbaceous species of Boreal - Circum-Polar dispersion, dominant in the floor of low bush, make up a characteristic combination of the species within the community.

General characteristic and the greatest value of the community of *Pinetum mughi - Geum bulgaricum* is given by numerous endemic that are more presented than other flora elements. In fact, some 26 endemic were registered in the community, making up 24.07 per cent of the total number of the species evidenced. These are as follows: *Geum bulgaricum, Poa ursina, Armeria canescens, Pinus peuce, Achillea abrotinoides, Onobrychis scardica, Draba scardica, Thymus albanus, Lilium albanicum, Silene sendtneri, Wulfenia blecicii, Veronica orsiniana, Thlaspi cuneifolium, Verbascum nicolai, and Amphoricarpus neumayeri* - the Balkan endemic, *Edraianthus montenegrinus, Allysum scardicum, Arabis flavescens, Minuartia bosniaca* - the Central Balkan endemic, *Saxifraga sempervivum and Potentilla speciosa - the South-Balkan endemic, Viola zoysii* - the Alpine-Dinaride endemic, *Aquilegia blecicii, Pedicularis brachiodonta and Crepis dinarica* - the Dinaride endemic, as well as, *Valeria pancicii* - the Prokletije endemic.

The group of endemic is joined by the sub-endemic species making up 9.26 per cent in the community. These are as follows: *Helianthemum alpestre, Phyteuma confusum* and *Cardamine glauca* - the Alpine - Balkan species, *Linum capitatum, Thymus longicaulis, Geum molle and Trinia delachampii* - the Balkan - Apennine species, *Trifolium noricum* - the Balkan - Apennine - East Alpine, and *Anthylis pelchella* - the Balkan Pontic species.

In addition to endemic and species taxa, the Mid - South-European mountain geo-elements of flora (MSEM) are greatly present. Their presence in the community amounts to 17.59 per cent, 18 species respectively, as follows: *Pinus mugo, Calamintha alpina, Polygala alpestris, Hypericum alpinum, Geum montanum, Galium anisophyllum, Salix waldsteiniana, Gentiana kochiana, Festuca violaceae, Globularia cordifolia, Nigritella nigra, Saxifraga rotundifolia, Ligusticum mutellina* and *Myosotis alpestris.*

In addition to the most present ones, the community also consists of Circum - Polar (8.33 per cent), Boreal - Circumpolar (6.48 per cent), Arctic (6.48 per cent), South-European - Mountainous (SEM - 6.48 per cent), Sub-Euro-Asian, Mid-European, Cosmopolitan (1.84 per cent), Sub-Pontic, Sub-Mid-European, Boreal - European and Hol-Arctic (0.92 per cent) flora elements.

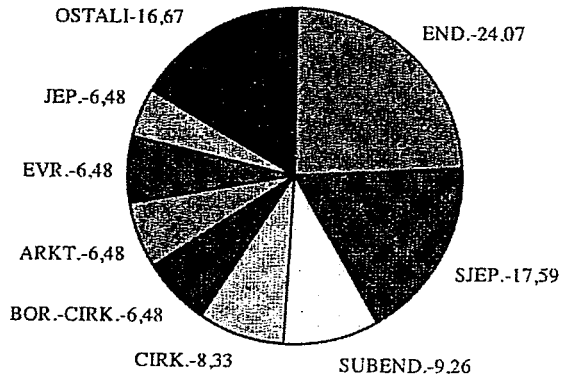
The analysis of floral element spectrum (Figure 1) depicts the community of *Pinetum mughi - Geum bulgaricum* has an expressed endemic character. The endemic (24.07 per cent), together with the sub-endemic (9.32 per cent) make up 33.93 per cent, that represents one third of the total number of species. This group can be also joined by South-European mountain species (6.48 per cent), that also represent the endemic of somewhat more dispersed area. Significant presence of Mid-European mountainous (MSEM), the Alpine elements generally (17.59 per cent) respec-

tively, as well as, the Arctic species (6.48 per cent), in addition to primary endemic, the above mentioned give the community the Arctic - Alpine characteristics too, indicating a complex action of the ecological conditions, but also a strong influence of the last glaciation period.

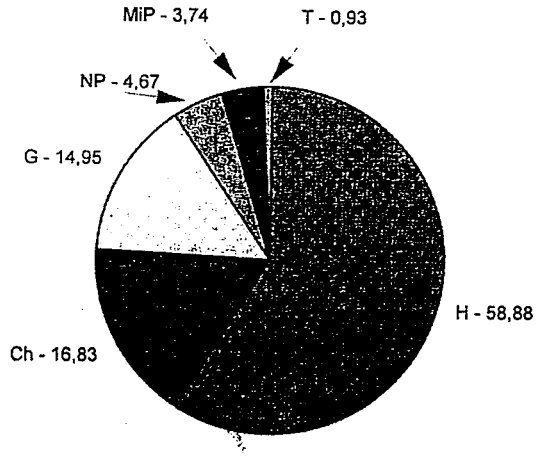
The living form spectrum (Figure 2) indicates that, by far, the most present form is the chemi-crypto-phyte (Ch - 58.88 per cent), although there are chamae-phyte too (Ch - 16.83 per cent), geo-phyte (G - 14.95 per cent), nano-phanero-phyte (NP - 4.67 per cent), mycro-phanero-phyte (MyP - 3.74 per cent), and terra-phyte (T - 0.93 per cent). Such a spectrum indicates that the community of *Pinetum mughi - Geum bulgaricum* is of chemi-crypto-phyte character with chamae-phyte - geo-phyte elements, largely depicting all the extremity of the high-mountain climate conditions of Prokletije. An insignificant participation of nano-phanero-phyte, mycro-phanero-phyte and terra-phyte, followed by complete absence of mezzo-phanero-phyte (MezP) and terra-phyte (T) indicate an extreme severity of climate.

From the sin-taxonomic point, the community of *Pinetum mughi - Geum bulgaricum* belongs to the taxon of *Pinion mugi* Pawl. 1928, the order of *Vaccinio - Piceetalia* Br. - Bl. 1939, the class of *Vaccinio Piceetea* B. - Bl. 1939, uniting the vegetation of dark coniferous forests.

By comparing the community of *Pinetum mughi - Geum bulgaricum* ass. new with, according to area, also close Prokletije community of twisting pine, *Wulfenio - Pinetum mughi* Jank. et Bog. 1967, from Koprivnik and Streocke Mountains, it was determined that, the community of *Wulfenio - Pinetum mughi* is poorer in florist sense (75 species), with 27 species being common in both communities. These are as follows: *Pinus mugo, Pinus peuce, Picea abies, Sorbus aucuparia, Vaccinum myrtillus, Juniperus sibirica, Lilium albanicum, Ligisticum mutellina, Anthemis montana, Geum bulgaricum, Anthoxanthum odoratum, Achillea lingulata, Geum montanum, Gentiana punctata, Soldanella alpina, Hypericum alpinum, Mysotis silvatica, Cystopteris fragilis, Hieracium murorum, Doronicum columnae, Rumex acetosa, Polygonum viviparum, Geranium silvaticum, Veratrum album, anemone nemorosa, Valeriana montana* and *Trollius europeaus*. The fact that, the highest degree of similarity exists in the floor of high and low bush, and that, the greatest differences are present in the floor of herbaceous flora, induces great interest. Such an expressed florist heterogeny of the two Prokletije communities of twisting pine, apart from the existence of certain number of the same and differential species, just indicates local climatic, edaphic and orographic factors of each Prokletije massif individually, that are quite conditioned by the specifics of their position and genesis.



Slika 1. Spektar florinih elemenata zajednice Pinetum mughi - Geum bulgaricum
Figure 1. Chorological spectrum of the community Pinetum mughi - Geum bulgaricum



Slika 2. Spektar životnih formi zajednice Pinetum mughi - Geum bulgaricum
Figure 2. Life - forms spectrum of the community Pinetum mughi - Geum bulgaricum

CONCLUSION

Pinetum mughi - Geum bulgaricum ass. new community occupies northeastern slopes of Nedzinat, one of numerous massifs of the Prokletije mountain system. The respective is developed on limestone - dolomite rocks and shallow brown soil with the inclinations from 5 to 75, within the altitude of 2,020 to 2,341 m a/s/l/.

Mountain pine, *Pinus mugo* Turra, dominating in the floor of bush and the endemic *Geum bulgaricum* Pancic, the most present in the floor of herbaceous vegetation, are general creators of the community. The community (108 species), very rich in florist sense, has an endemic character and chemi-crypto-phyte characteristics.

From the sin-taxonomic point, the association of *Pinetum mughi - Geum bulgaricum* belongs to the taxon of *Pinion mugi* Pawl. 1928, to the order of *Vaccinio - Piceetalia* Br. - Bl. 1939, to the class of *Vaccinio Piceetea* B. - Bl. 1939.

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REZIME

PINETUM MUGHI - GEUM BULGARICUM, NOVA ASOCIJACIJA PLANINSKOG BORA (*PINUS MUGO* TURRA) NA PROKLETIJAMA

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Na Nedžinatu , jednom od mnogobrojnih prokletijskih masiva , utvrđeno je prisustvo zajednice *Pinetum mughi - Geum bulgaricum* ass. nova .

Zajednica zauzima severoistočno eksponirne padine penjući se mestimično do glavnog grebena. Ovaj deo masiva izgrađuju krečnjačko - dolomitske stene na kojima se javljaju naslage glacijalnog materijala i plitko smeđe zemljište . Čitav pojas planinskog bora nalazi se pod uticajem prokletijske varijante šumatundralnog tipa ekoklime .

U zajednici je registrovano 108 vrsta . Kao dominantne se javljaju planinski bor *Pinus mugo* Turra koji pripada srednje - južnoevropsko planinskom elementu flore i *Geum bulgaricum* Pančić , balkanski endemit , osnovni graditelj sprata zeljaste flore . Pored njih , karakterističnu kombinaciju vrsta čine *Vaccinium myrtillus, Vaccinium uliginosum* i *Helianthemum alpestre.* Analiza areal spektra ukazuje na njen endemičan karakter , a spektra životnih formi na hemikriptofitsko obeležje .

U sintaksonomskom pogledu zajednica *Pinetum mughi - Geum bulgaricum* ass. nova , pripada svezi *Pinion mugi* Pawl. 1928 , reda *Vaccinio - Piceetalia* Br. - Bl. 1939, klase *Vaccinio - Piceetea* Br. - Bl.

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ORIGINAL SCIENTIFIC PAPER

COMPOSITION AND DISTRIBUTON OF LEECHES (ANNELIDA: HIRUDINEA) IN RIVER SITNICA BASIN AND IN RIVER IBAR

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ABSTRACT

The composition and spread of leech fauna in the river net of Sitnica basin that encircles 1/4 or 2.861 km2 of tributaries of Kosovo and Metohija province are insufficiently or sporadically studied. Because of its large ecological diversity in the longitudinal profile, river Sitnica has a characteristic composition and spread of leech fauna. There were identified 9 species from 8 genera and 4 families. The most numerous species were those that prefer eutrophic and polluted ecosystems, *Herpobdella octoculata, Hellobdella stagnalis, Glosiphonia heteroclita,* and less numerously with smaller spread are species Haementeria costata, *Haemopis sanguisuga* and *Hirudo medicinalis*. The species Dina lineata, Herpobdella monostriata and Piscicola geometra were identified on few localities and with only several individuals, mostly in the upper flow of river Sitnica or in the vicinity of inflow of smaller and partially polluted tributaries. In the localities of the middle flow of river Sitnica that are affected by pollution leech fauna is absent. Of 9 identified leech species 8 were identified in other parts of this province, except the species *Piscicola geometra* that was not identified so far. All the identified species are characteristic for stagnant or slow flowing waters.

Key words: Distribution, Hirudinea, Sitnica, Ibar.

INTRODUCTION

Leech fauna of Kosovo and Metohija province is insufficiently investigated. Previous knowledge of this fauna is based on the investigations of Šapkarov, 1975, and relates on the leech collection of the areas from small number of localities of which some are insufficiently investigated. Basin of river Sitnica, the main river of Kosovo valley that drains 1/4 or 2.861 km^2 of the province territory, belong to such areas. Only two localities of this area (Kosovo Polje - river Sitnica and Kosovska Mitrovica - river Ibar) were covered with the previous investigations.

River Sitnica in its longitudinal profile is ecologically different as the consequence of the natural exchange of inflow substrate of many tributaries, and mostly because it receives a huge amount of effluents with various type of pollutants (Plakolli, 1983; Urošević, 1989; Rašani, 1986).

Such state offers a big ecological diversity that affects the composition of *Hirudinea* fauna and spread of some species in the basin of river Sitnica.

MATERIALS AND METHODS

The qualitative and quantitative compositions of Hirudinea fauna were monitored in the basin of river Sitnica during eight seasons, from the summer 1992. to the summer 1994.

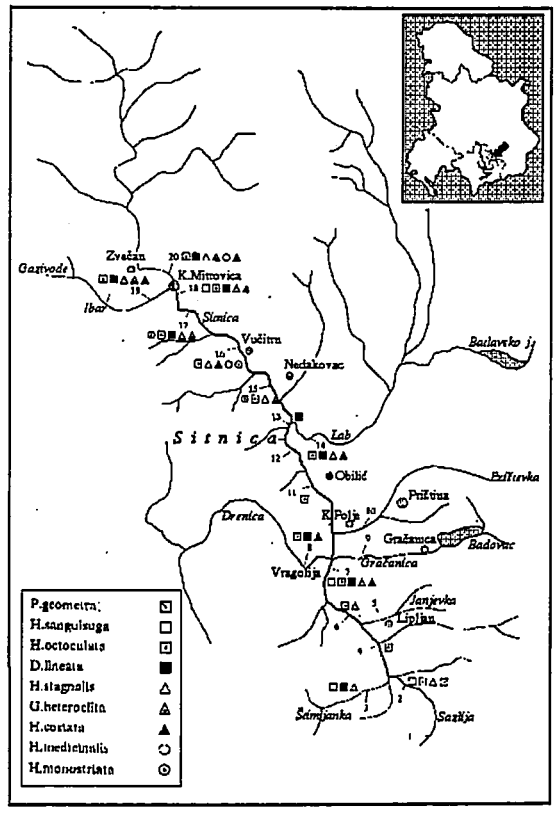

Fig.1. Distribution of leeches on investigated localities

The samples were collected on 20 localities: 13 in river Sitnica, 5 in tributaries and two localities were in river Ibar before and behind the inflow of river Sitnica (Fig.1). The localities were selected in that way to cover all important basin zones, specially those parts where certain changes in the water quality and substrate may have occurred. The samples were picked by 1.200 cm^2 Sorber's quantitative net, with different micro habitats covered on the investigated localities. The number of leeches is presented as the total number of separated individuals.

Determination is performed in the fixed material according to Lukin determinate (1976) from which the systematic division has been taken over.

RESULTS AND DISCUSSION

The leech collection gathered on the investigated localities of river Sitnica basin and river Ibar during two year period consists of 9 species from 8 genera and 4 families (Table 1). The highest number of species belong to *Alboglossiphonidae* and *Herpobdellidae* families, three of each, two belong to *Hirudinidae* family, and one species belong to *Piscicolidae* (or *Ichtyobdellidae*) family. In the river Sitnica leech fauna is presented with eight species, in the river Ibar with six, river Drenica with two and river Lab with four species. In other tributaries the leech fauna is not determined (Fig.1 and Table 2.).

Table 1. Composition if leech fauna on investigated ecosistems

HIRUDINEA EUHIRUDINEA

RHYNCHOBDELLIDA

Fam: Ichtyobdellidae (Piscicolidae)

Rod: Piscicola Blainville, 1818

1. Piscicola geometra Linnaeus, 1758 Fam: Glossiphoniidae Vaillant, 1890 Rod: Haementeria de Filippi, 1849

2. Haementeria costata Fr Muller, 1846 Rod: Alboglossiphonia Johnon, 1816

3. Alboglossiphonia heteroclita Linnaeus, 1758 Rod: Helobdella Blanchard, 1896

4. Helobdella stagnalis Linnaeus, 1758

GNATHOBDELLIDA

Fam: Hirudinidae Whitman, 1886 Rod: Hirudo Linnaeus, 1758

5. Hirudo medicinalis Linnaeus, 1758 Rod: Haemopis Savigny, 1822

6. Haemopis sanguisuga Linnaeus, 1758

PHARYNGOBDELLIDA

Fam: Herpobdellidae Blanchard, 1894 Rod: Herpobdella Agassiz, 1846

7. Herpobdella octoculata Linnaeus, 1758

8. Herpobdella monostriata Gedryc, 1916

Rod: Dina Blanchard, 1892

9. Dina Lineata O. F. Muller, 1774

The distribution of river Sitnica on upper, middle and lower flow (Pllana, 1974) and diversity of ecological conditions reflect on the composition and abundance of leeches. In the upper flow (localities 1,2 and 3) 5 species were identified, in the middle flow (localities 7,11,12 and 13) 4 species and in the lower flow (localities 15,16,17 and 18) 6 species of leeches were identified.

Herpobdella octocullata species inhabits the largest number of the investigated localities (13). Many localities are inhabited by *Hellobdella stagnalis* species (11), *Dina lineata* (9), *Alboglossiphonia heterochila* (7) and others, while *Pisciola geometra* was found in only one locality. Leech fauna was not identified in localities 1,5,9,10 and 12 because of extremely bad ecological conditions (Plakolli, 1983; Urošević, 1989; Živić, 1996).

River Sitnica and river Ibar have 6 common leech species: *H. octoculata, D. lineata, H. stagnalis, A. heteroclita and H. medicinalis.* It was established that first four are the most spread leeches in the water ecosystems of Kosovo and Metohija (Šapkarev, 1975). In the lower flow of river Sitnica and in river Ibar the species were presented with more individuals comparing to upper, and specially to middle flows which have inconvenient ecological conditions, as the consequence of large amount of effluents inflow (Table 2).

The established leech fauna comprises the species that are characteristic for the stagnant waters in which they are more frequent and more abundant (Šapkarev, 1981), so that, according to Bennike (1943) they belong to the lake forms. The presence of such leech forms in the investigated river basin may be explained by the fact that river Sitnica is characterized by slow flow (min. 0.07 cm^3/sec, Pllana, 1974) with numerous meanders and dead arms which are convenient for the development and multiplication of species with such features.

Herpobdella octoculata was identified in most of the investigated localities and was presented with large number of individuals which is, according to Lukin (1976), its characteristic for most of Palearctic regions. This leech is characterized by the possibility to withstand the lack of O_2 and large variations of pH well so that it may live in very polluted waters (Bennike, 1943). According to Kalbe (1966), this leech is often encountered in alpha mezosaprobic zone. Since the larger part of river Sitnica basin is situated in the variations of this saprobic zone (Plakolli, 1983; Urošević, 1989) this leech found the convenient habitat for its distribution and multiplication.

Helobdella stagnalis is also frequent and can be found in the most of the investigated localities. It is known as one of the most spread leeches (also a Cosmopolite) characterized by the big euribioticness (Bennike, 1943). It is characteristic and numerous in distrophic lakes and water flows with increased eutrophication (Mann, 1953). In the large part of river Sitnica

Table 2. Total number of fauna Hirudinea.

Localities	1	2	3	4	5*	6	7	8*	9*	10*	11	12	13	14*	15	16	17	18	19*	20	Total number
Species																					
H. sanguisuga		3	4				2											1			10
H. octoculata		1		5		4	20	15			2			24	7	28	32	18	65	10	323
D. lineata			8				3	19					8	1			2	4	15	18	88
H. stagnalis		4	2			9	2							17	28	14	22	7	48	95	248
G. heteroclita														1	4	3	39	4	19	21	91
H. costata							3	3											3	2	11
H. medicinalis																1				2	3
H. monostriata															1	1	2				4
P. geometra		1																			1

basin the increased eutrophication is distinct (Živić, 1997) and this is convenient for maximal development and distribution of this species. It is earlier identified in the river Ibar (Šapkare, 1975) but not in river Sitnica.

Characteristic for small well flowing waters (Pawlowski, 1936); Šapkare, 1975), *Dina lineata* species was identified in oligotrophic habitats (locality 3). However, many habitats indicate that it inhabits, in smaller number, fish ponds, lakes and rivers (Stammer, 1932; Šapkarev, 1963,1964,1975,1981; Soos, 1967; Sket, 1968) which is confirmed by its finding in the localities of river Sitnica basin and river Ibar, which are outside the zones of the impact pollution. The distribution of this species may be directly connected with numerous small tributaries from which it had actively or by drift inhabited those localities of river Sitnica and river Ibar in which it may survive. The wider spread of this species is Palearctic.

Alboglossiphonia heteroclita species mostly lives in stagnant waters, especially in eutrophic lakes and rarely inhabits the flowing waters and if it does it may be found in the lower flow in the habitats with vegetation under the stones (Bennike, 1943). Lower flow of river Sitnica and river Ibar are characterized by such habitats so that its distribution is restricted only on the localities of this part of water flow.

Haementeria costata species can be found in different aquatic ecosystems, as mud ponds, stagnant and flowing waters are, in which it usually follows the turtles, and its distribution depends on turtle presence. It is found in the slime on the locality number 7 of the middle flow of river Sitnica and in the river Ibar. Its general spread is Holarctic.

Haemopis sanguisuga species is mostly found in muddy ecosystems and fish ponds (Wilkialis, 1970), but Pawlowski (1936) had indicated that it may be found in the coastal parts of stagnant and flowing waters and in some polluted waters it may reach high abundance. Its presence was identified in many flowing waters in Kosovo and Metohija. In the river Sitnica it was identified on 4 localities of the upper and lower flow. The general spread is Palearctic.

Herpobdella monostriata is a leech of the clear waters. Šapkarev (1975,1981) has found it in the wells and creeks of East and Southwest Macedonia. In Kosovo and Metohija the same author has found it in certain smaller and clean creeks and rivers. In the river Sitnica it is not numerous and inhabits three localities of the lower flow where it probably came from the smaller tributaries. Its wider spread is restricted on the European part of the ex-USSR, Romania, Hungary and territory of the former SR Jugoslavia.

Hirudo medicinalis is Palearctic species characteristic for the stagnant waters, specially for muddy ponds, eutrophic lakes and fish ponds. Only one individual has been found in river Sitnica, while in river Ibar two individuals has been identified. Small abundance and restricted spread is probably in connection with small distribution of amphibians in the investigated ecosystems.

Pescicola geometra is the only species that has not been identified so far on the territory of Kosovo and Metohija. Only one individual has been identified on the locality number 2 indicated its exceptionality in this biota or its incidental finding. Wider spread of this species is Palearctic.

CONCLUSION

The results of investigating the composition and spread of Hirudinea species in the river Sitnica basin and river Ibar were presented in this work. The investigations were conducted on 20 localities on which 9 leech species were identified and 8 of them were identified in other areas of Kosovo and Metohija province. The registered leeches were grouped in 8 genera and 4 families: *Herpobdellidae* family is presented with 2 genera and 3 species, *Alboglossiphonidae* family with

3 species, *Hirudinidae* family with 2 and Piscicolidae family is presented with 1 species.

Herpobdella octoulata and *Hellobdella stagnalis* species were found in most of the localities (13 and 11), *Dina lineata* in 9, *Alboglossiphonia heteroclita* on 7, *haemopis sangusuga* on 4, *Herpobdella monostriata* on 3, *Hirudo medicinalis* on 2 and *Piscicola geometra* was found on 1 locality.

Leech fauna does not inhabits localities number 1,5,9,10 and 12 which are characterized by the high degree of pollution.

The largest number of leech species (6) with a large number of individuals was identified in the lower flow of river Sitnica, while middle flow was qualitatively and quantitatively extremely poor, as a consequence of inconvenient ecological conditions.

For the river ecosystems Sitnica and Ibar 6 leech species are common.

Registered leeches in the investigated ecosystems are characteristic for stagnant waters. Many of them prefer eutrophic and polluted ecosystems: *H. ocroculata, H. stagnalis, A. heteroclita, H. costata, H. sanguisuga* and *H. medicalis.*

The identified leech fauna is widespread in Jugoslavija and they are registered in the flowing waters of the remaining parts of the Province, except Piscicola geometra which is not identified in this area so far.

The largest number of leeches presents the Palearctic species (6), Holarctic species (1), almost cosmopolite (1) and the spread of one species covers the European part of the former USSR, Hungary, Romania and the are of the former SR Jugoslavija.

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REZIME

SASTAV I RASPROSTRANJENJE PIJAVICA (ANNELIDA, HIRUDINEA) U SLIVU REKE SITNICE I U RECI IBAR

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Rečna mreža sliva reke Sitnice obuhvata 1/4 ili 2861 km^2 površine AP Kosova i Metohije. Ovaj sliv, a posebno r. Sitnica odlikuje raznovrsnost ekoloških uslova u longitudinalnom profilu, kao posledica prirodne promene supstrata, a naročito uliva velikih količina efluenata. Sastav i rasprostranjenje faune pijavica u ovom slivu nedovoljno je ispitan. Našim istraživanjima utvrđeno je 9 vrsta pijavica iz 8 rodova i 4 familije (Slika 1, Tabela1). Od 20 lokaliteta u slivu reke Sitnice i reke Ibra vrste *Herpobdella octoculata* i *Hellobdella stagnalis* su nađene na 13 odnosno 11 lokaliteta, *Dina lineata* na 9, *Alboglossiphonia heteroclita* na 7, *Haemopis sanguisuga* na 4, *Herpobdella monostriata* na 3, *Hirudo medicinalis* na 2 i *Piscicola geometra* na 1 (Tabela 2). Na lokalitetima 1, 5, 9, 10 I 12 na kojima je utvrđen visok stepen zagađenja, fauna pijavica odsustvuje. Najviše vrsta pijavica (6) sa visokom abundancijom utvrđena je na lokalitetima donjeg toka reke Sitnice. U srednjem toku gde je ova reka

najzagađenija pijavice su odsutne ili pojedinačno zastupljene.

Pijavice istraživanih ekosistema su uglavnom karakteristične za stajaće vode. Mnoge od njih preferiraju eutrofne, a podnose i zagađene ekosisteme (*H. ocroculata, H. stagnalis, A. heteroclita, H. costata, H. sanguisuga* i *H. medicinalis*). U reci Sitnici koja se odlikuje sporim tokom sa brojnim meandrama i mrtvajama, izraženom eutrofikacijom i zagađenjem ove vrste su našle pogodna staništa gde dostižu veliku abundanciju.

Ovim istraživanjem su dobijeni podaci o sastavu i rasporostranjenju faune pijavica u delu područja Pokrajine koji dosad nije potpuno ispitan. Registrovane vrste faune pijavica su široko rasprostranjene u Jugoslaviji, a istraživani ekosistemi predstavljaju njihova nova nalazišta. Osim vrste Piscicola geometra ostale vrste su utvrđene i u drugim oblastima Pokrajine. Obzirom da je nađen samo 1 primerak ove vrste može se smatrati da se radi o njenoj izuzetnosti u ovom biotopu ili o slučajnom nalazu.

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HIGH DEGREE OF ENDEMICITY OF LUMBRICIDFAUNA ON THE BALKANS

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ABSTRACT

The subject of the explanation deals to the high degree of the endemicity of the earthwormfauna from the family Lumbricidae. 153 endemic taxa, resp. 130 species and 23 subspecies, are established on the Balkans up to now. According to their distribution, all endemic taxa are divided in to three groups: endemites with very restricted area; endemites wider distributed on the Balkans; and endemites distributed also in some neighbouring Balkanic countries. The greatest number of endemic taxa belongs to genus Dendrobaena (33 taxa) while the genera Proctodrilus, Micreophila, Meroandriella, and Lumbricus just one taxa each.

Key words: Lumbricidae, endemicity, Balkans, distribution.

INTRODUCTION

Nothing had being known concerning the lumbricid fauna of the Balkans almost up to this century. The initial and considerably small in number were the data from 1895 by Rosa. In addition the latter investigations (such as those of Cognetti de Martiis, 1906; Michaelsen, 1906; Szuts, 1918 for example) had fragmented character. The lumbricid fauna on the Balkan Peninsula was greatly investigated in the period between the two World wars, however intensive research of this fauna was undertaken during the last 40 years by greater number of investigators. The last investigations approach almost to the definite list under some Balkan countries, such as Rumania, Macedonia, Slovenia, S.R. Yugoslavia (Pop, 1948 Sapkarev, 1978; Mrsic, 1973; Mrsic and Sapkarev, 1987) at one side and several countries such as Albania, European part of Turkey are very little investigated or Bosnia and Herzegovina, Bulgaria and Greece and insufficiently investigated.

In connection with the mentioned investigations the number of lumbricid taxa was exceptionally great in which great number of taxa were endemites.

LIST OF ENDEMIC TAXA

On the following list are reviewed the genera and their endemic taxa of the family Lumbricidae populated on the Balkans only in some neighbouring mostly.

List of the genera and their endemic species on the Balkans

Genus Proctodrilus Zicsi, 1985
P. opisthoductus Zicsi, 1985

Genus Helodrilus Hoffm., 1845
H. patriarchalis (Rosa, 1892)
H. balcanicus balcanicus (Cern., 1931)
H. balcanicus plavensis (Kar., 1972)
H. kratochvili (Cern., 1937)
H. dublinskae Zicsi and Csuzdi, 1986
H. jadronensis Sapk., 1989
H. serbicus Sapk., 1989
H. dinaricus Mrs., 1991
H. ospensis Mrs., 1991
H. slovenicus Mrs., 1991
H. vagneri Mrs., 1991
H. oculatus Hoffm., 1845

Genus Cernosvitovia Omodeo, 1956
Subgenus Cernosvitovia Omodeo, 1956
C. (C.) rebeli (Rosa, 1897)
C. (C.) bulgarica (Cern., 1934)
C. (C.) biserialis (Cern., 1937)
C. (C.) dobrogenea (Pop, 1938)
C. (C.) schweigeri (Zicsi, 1973)
Subgenus Zicsiona Mrs. and Sapk., 1987
C. (Z.) getica (Pop, 1947)
C. (Z.) dudichi (Zicsi and Sapk., 1982)
C. (Z.) crnicae Kar., 1987
C. (Z.) silicata Mrs. and Sapk., 1987

Genus Italobalcaniona Mrs. and Sapk., 1988
I. opisthocystis (Rosa, 1895)
I. opisthocystis krainensis (Sapk., 1987)
I. demirkapiae (Kar., 1969)
I. stankovici (Sapk., 1971)
I. zicsii (Sapk., 1975)
I. macedonica (Sapk., 1977)
I. pyrenaicoides (Sapk., 1977)
I. knazevensis (Sapk., 1979)
I. treskavicensis Mrs., 1991

Genus Serbiona Mrs. and Sapk., 1978
S. robusta robusta (Rosa, 1895)
S. robusta serbica (Kar., 1988)
S. mehadiensis mehadiensis (Rosa, 1895)
S. mehadiensis boscaiui (Pop, 1948)
S. mehadiensis oreophila (Pop, 1978)
S. mehadiensis voivodinensis (Sapk., 1988)
S. dofleini dofleini (Ude, 1922)
S. dofleini udei (Sapk., 1991)
S. tuleskovi (Cern., 1934)
S. kosowensis kosowensis (Kar., 1968)
S. kosowensis montenegrina (Sapk., 1975)
S. strumicae (Sapk., 1973)
S. paratuleskovi (Sapk., 1975)
S. serbica (Sapk., 1977)
S. yugoslavica (Sapk., 1977)
S. zarandensis (Pop, 1978)
S. speciosa (Mrs. and Sapk., 1987)
S. mayeri Mrs., 1990
S. carneluttii Mrs., 1990
S. matjasici Mrs., 1990
S. panonnica (Cognetti, 1906)

Genus Allolobophora Eisen, 1874
A. carphatica Cognetti, 1927
A. vardarensis Sapk., 1971
A. chlorotica kosovensis Sapk., 1977

Genus Microeophila Omodeo, 1955
M. nematogena (Rosa, 1903)
M. cryptocystis (Cern., 1935)

Genus Alpodinaridella Mrs., 1987
Subgenus Dinaridella Mrs., 1987
A. (D.) biokovica (Mrs., 1985)
Subgenus Alpodinaridella Mrs., 1987
A. (A.) gestroi (Cog., 1905)
A. (A.) lozniciana (Mrs., 1987)

Genus Karpatodinariona Mrs. and Sapk., 1988
K. sturanyi dacidoides (Bouche, 1973)
K. altimontana (Mrs., 1982)

Genus Aporectodea Oerley, 1885
Subgenus Aporectodea Bouche, 1972
A. (A.) rosea balcanica (Cern., 1942)
A. (A.) jassyensis phoebea (Cogn., 1913)
A. (A.) macvensis (Sapk., 1975)
A. (A.) bohiniana Mrs., 1987
A. (A.) papokiana Mrs., 1987
A. (A.) pannoniella Mrs., 1987
A. (A.) smaragdionoides Sapk., 1989
A. (A.) kozjekensis Mrs., 1991
A. (A.) cemernicensis Mrs., 1991

Subgenus Meloandriella Mrs., 1987
M. dinarica Mrs., 1987

Genus Octodrilus Omodeo, 1956
O. gradinesqi (Pop, 1938)
O. exacystis (Rosa, 1896)
O. mima (Rosa, 1896)
O. tergestinus (Mch., 1910)
O. rucneri (Plisko and Zicsi, 1970)
O. slovenucus (Kar., 1972)
O. meroandricus Mrs., 1985
O. crainensis Mrs., 1987
O. illyricus Mrs., 1987
O. kvarnerus Mrs., 1988
O. zirianus Mrs., 1987
O. robustus Pop, 1973
O. compromisus Zicsi and Pop, 1984
O. oesophagus Mrs., 1991
O. velebiticus Mrs., 1991
O. istrianus Mrs., 1991
O. pseudolisaensis Mrs., 1991
O. pseudozirianus Mrs., 1991
O. frivalskyi (Oerley, 1885)

Genus Octodriloides Zicsi, 1986
O. janetscheki (Zicsi, 1970)
O. kovacevici (Zicsi, 1970)
O. camnensis (Bald., 1919)
O. transillvanicus Zicsi and Pop, 1984
O. marinceki Mrs., 1987
O. zupancici Mrs., 1987
O. bolei Mrs., 1987
O. poklonensis Mrs., 1991
O. dinaricus Mrs., 1991
O. nasarensis Mrs., 1991
O. bosniensis Mrs., 1991

Genus Lumbricus Linn., 1758
L. improvisus Zicsi, 1963

Genus Eisenia Malm., 1877
E. oltenica (Pop, 1938)
E. spelaea athenica Cern., 1938
E. grandis ebneri (Mich., 1914)
E. grandis storkani Cern., 1934
E. kattoulasi Zicsi and Mich., 1981

Genus Eiseniella Mich., 1900
E. ochridana ochridana Cern., 1931
E. ochridana profunda Cern., 1931
E. peleensis Tzel., 1943

Genus Spermophorodrilus Bouche, 1975
S. antiquus antiquus (Cern., 1938)
S. antiquus nichalisi (Car., 1972)
S. antiquus boutchei (Zicsi and Mich., 1981)

Genus Fitzingeria Zicsi, 1978
F. annectens (Rosa, 1895)
F. platyura montana (Cern., 1935
F. viminiana Mrs., 1986

F. loebeli Zicsi, 1985

Genus Dendrobaena Eisen, 1873
D. aegea (Cogn., 1913)
D. ariadne Mich., 1928
D. brabei (Cern., 1934)
D. rhodopensis (Cern., 1937)
D. balcanica (Cern., 1937)
D. olympica (Cern., 1938)
D. olympica peristerica Sapk., 1996
D. clujensis Pop, 1938
D. antiqua tuberculata Tzel., 1943
D. kozuvensis (Sapk., 1971)
D. sketi Kar., 1972
D. michalisi Kar., 1972
D. panteleonis balagnensis Bouche, 1972
D. zicsii Kar., 1973
D. serbica Kar., 1973
D. mahnerti Zicsi, 1974
D. bokakotorensis Sapk., 1975
D. ochridana Sapk., 1987
D. pseudohortensis Sapk., 1977
D. sasensis Sapk., 1983
D. jastrebensis Mrs. and Sapk., 1987
D. velkovrhi Mrs., 1988
D. papokiana Mrs., 1988
D. durmitorensis Mrs., 1988
D. bosniaca Mrs., 1988
D. montenegrina Mrs., 1988
D. jahorensis Mrs., 1991
D. macedonica Mrs., 1991
D. vranicensis Mrs., 1991
D. grmecensis Mrs., 1991
D. slovenica Mrs., 1991
D. alpina popi Sapk., 1971
D. alpina mavrovensis Sapk., 1971

From this list it can be seen that the total number of registered endemic lumbricids up to now is 153 taxa (130 species and 23 subspecies). From this number the most numerous is the genus Dendrobaena (33 taxa), followed by the genera Serbiona (21) and Octodrilus (20). With much small number of taxa (12-9) are genera Helodrilus (12), Aporrectodea (10), Octodriloides (11), Cernosvitovia (9), Italobalkaniona (9) and all other genera are with very small number of taxa (1-5).

DISTRIBUTION OF THE BALKANIC ENDEMITES

The distribution of the relatively great number of endemic species of the lumbricid fauna on the Balkans is different for different lumbricid species.

In connection with their distribution all endemic taxa can be divided into three categories:

- endemites with very restricted area;
- endemites wither distributed on the Balkans;
- endemites distributed also in some neighbouring countries of the Balkans.

In the first category belong the endemites which are distributed in a small area, only in one of the countries on the Balkans. Such endemites are the most numerous.

They are:

Helodrilus patriarchalis
H. balcanicus plavensis
H. kratochvili
H. dublinskae
H. jadronensis
H. serbicus
H. dinaricus
H. ospensis
H. slovenucus
H. vagneri
Cernosvitovia bulgarica
C. schweigeri
C. dudichi
C. crnicae
C. silicata
Italobalkaniona opisthocystis
I. krainensis
I. demirkapiae
I. stankovici
I. zicsii
I. macedonica
I. pyrenaocoides
I. nazevensis
I. treskavicensis
Serbiona robusta robusta
S. robusta serbica
S. mehadiensis boscaiui
S. mehadiensis oreophila
S. mehadiensis voivodinensis
S. dofleini udei
S. tuleskovi
S. kosowensis kosowensis
S. kosowensis montenegrina
S. strumicae
S. paratuleskovi
S. serbica
S. yugoslavica
S. zarandensis
S. speciosa
S. mayeri
S. carneluttii
S. matjasici
S. pannonica
Allolobophora vardarensis
A. chlorotica kosovensis
Alpodinaridella biokovica
Karpatodinariona sturanii datsidoides
Aporrectodea macvensis
A. bohiniana
A. papokiana

A. pannoniella
A. smaragdionides
A. kozjekensis
A. cemernicensis
A. predalpina
Meroandriella dinarica
Octodrilus gradineskui
O. meroandricus
O. illiricus
O. kvarnerus
O. savinensis
O. zirianus
O. robustus
O. compromisus
O. velebiticus
O. istrianus
O. pseudolisaensis
O. pseudozirianus
O. frivalskyi
Octodriloides kovacevici
O. janetscheki
O. transsilvanicus
O. marinceki
O. zupancici
O. poklonensis
O. dinaricus
O. nasarensis
O. bosniensis
Eisenia spelaea
E. grandis ebneri
E. grandis storkani
E. katoulassi
Eiseniella peleensis
E. ochridana ochridana
E. ochridana profunda
Spermophorodrilus antiquus
S. antiquus michalisi
S. antiquus bouchei
Fitzingeria annectens
F. viminiana
Dendrobaena aegea
D. ariadne
D. rhodopensis
D. balcanica
D. olympica peristerica
D. cluensis
D. antiqua tuberculata
D. kozuvensis
D. sketi
D. michalisi
D. panteleonis balagnensis
D. zicsii
D. serbica
D. mahnerti
D. ochridana
D. pseudohortensis
D. sasensis
D. jastrebensis
D. velkovrhi
D. papokiana
D. durmitorensis
D. bosniaca
D. montenegrina
D. macedonica
D. jahorensis
D. vranicensis
D. slovenica
D. alpina popi
D. alpina mavrovensis

Figure 1. The countries on the Balkans.
1. Slovenia, 2. Croatia, 3. Bosnia and Herzegovina, 4, S.R. Yugoslavia ,5. Rumania, 6. Bulgaria, 7. European part of Turkey, 8. Macedonia, 9. Albania, 10. Greece

In the second category belong something smaller number of endemites which are distributed on the Balkans but at least two or more countries. They are:

Halodrilus balcanicus balcanicus
Cernosvitovia rebeli
C. dobrogenea
C. getica
Serbiona dofleini dofleini
Allolobophora carpathica
Alpodinaridella lozniciana
Karpatodinariona altimontana
Aporrectodea rosea balcanica
A. jassyensis phoebea
Octodrilus slovenicus
Eisenia oltenica
Dendrobaena olympica
D. bokakotorensis
D. grmecensis

In the third category belongs the smallest number of endemites which are distributed in one or more countries on the Balkans and in one or more neighbouring countries of the Balkans. They are:

Proctodrilus opisthoductus
Helodrilus oculatus
Italobalkaniona opisthocystis opisthocystis
Serbiona mehadiensis mehadiensis
Microeophila nematogena
Alpodinaridella gestrui
Octodrilus gradineskui
O. mima
O. tergestinus
O. rucneri
Octodriloides cannensis
Lumbricus improvisus
Fitzingeria platyura montana
Dendrobaena hrabei

In connection with the distribution of endemic species on the Balkans, there is a great interest since the greatest number of them from some genera such is Cernosvitovia, Italobalkaniona, Serbiona, Octodrilus and Dendrobaena are distributed to restricted area on the Balkans, and only a small number of them can be find outside of the Balkans, i.e. in neighbouring territories of the Balkan Peninsula.

So, for example the species of the genus Cernosvitovia (9 species all together) are restricted mainly to the territories of western Bulgaria and eastern Serbia. The endemites of Serbia belong to the subgenus Zicsiona while the endemites of Bulgaria - to the subgenus Cernosvitovia. Only three endemites, outside Bulgaria, are registered: C. rebeli in Greece and Albania, C. dobrogenea and C. getica in Romania, and C. schweigeri was discovered in European part of Turkey.

Genus Italobalkaniona possesses 9 endemite species, of which 5 species are exceptionally registered only in Macedonia, while 3 species exceptionally in Serbia. Only the species I. opisthocystis, except in Romania, was registered in Hungary.

Genus Serbiona with 21 endemic taxa is distributed mainly in Serbia (12) and partly in Romania (6). Only the species S. dofleini and S. strumicae are found in Macedonia, but S. mehadiensis, except in Romania, was registered in Bulgaria and Hungary.

20 endemic species of the genus Octodrilus mainly are distributed in the region of the Balkans where are located Slovenia and Croatia. It is very interesting that 5 species of them: O. gradineskui. O. robustus, O. compromisus and O. frivalskyi were founded exceptionally in Romania. Only 3 species, except on the Balkans, are registred in north Italy, resp. in Austria or in Hungary. It is the same case with the endemites (11) of the genus Octodriloides.

Finally, the genus Dendrobaena possesses on the Balkans the greatest number of endemites (33 taxa) mainly distributed in Greece, Macedonia and Yugoslavia.

The previous presentation have suggested the possibility that the mentioned regions could be considered as centres of formation of the endemic species from the mentioned genera.

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REZIME

VISOKI STEPEN ENDEMIČNOSTI LUMBRICIDNE FAUNE BALKANA

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U radu je dat prikaz endemičnih lumbricida i istaknut je veoma visoki stepen endemizma balkanske faune kišnih glista. Na osnovu dosadašnjih istraživanja, ustanovljeno je da na Balkanskom poluostrvu živi ukupno 15 endemičnih taksona, odnosno, 130 vrsta i 23 podvrsta. Najveći broj endemita pripada rodu Dendrobaena (34 taksona), a najmanji broj rodovima Lumbricus, Proctodrilus, Microeophila i Meroandriella, po jedan predstavnik.

Takodje, prikazana je distribucija endemita na Balkanu i u vezi sa tim endemična lumbricidna fauna podeljena je u tri kategorije:

- endemiti sa veoma ograničenim arealom rasprostranjenja;
- endemiti sa širom distribucijom na Balkanu i

- endemiti rasprostranjeni na pojedinim susednim teritorijama Balkana.

Najzad je konstantovano da se rodovi sa većim brojem endemičnih predstavnika, uglavnom, nalaze na odredjenim teritorijama Poluostrva. U vezi sa tim, postoji mogućnost da su ti regioni verovatno centri formiranja tih endemičnih taksona.

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ORIGINAL SCIENTIFIC PAPER

CONTRIBUTION TO THE STUDY OF SNOUT BEETLES FAUNA (CURCULIONIDAE, COLEOPTERA) IN THE PELISTER MOUNTAIN

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ABSTRACT

The study presents taxonomic and ecological investigations conducted from made in the course of 1990 to 1992, on the Pelister Mountain (Baba Mountain).

Nine sites on different altitudes in the area between the Rotinska River (1067 m above the sea level) and the Big Lake (2226 m above the sea level), was chosen as sampling sites.

During the investigations were stated 35 species of 8 Subfamilies among which 25 are new for the Fauna of Macedonia.

The greatest number of species are harmful for the woody plant's.

Key words: Fauna, taxonomy, Curculionidae, Macedonia

INTRODUCTION

Initial data of fauna of the Snout Beetles (Curculionidae, Coleoptera) on the Pelister Mountain are connected with the name of V. Apfelbeck, who lists several endemic types of the genus Otiorhynchus (Apfelbeck, 1918, 1929).

Pelister Mountain is a part of the Baba Mountain which steeply increases in altitude from 600 m (Pelagonija Valley) to 2600 m above the sea-level (the peak of Pelister itself).

The species from the Family Curculionidae are extremely fitofag Insects and their living cycle is closely connected to determined feeding plant's.

The richness (abundance) of the Flora on Pelister as a result of the climate, geological, and hydrological conditions have contributed for Pelister to become a floristic treasure defined through 21 plant's communities (R. Rizovski, 1992).

All that is a pre-condition for the presence of various types of Snout Beetles on the Pelister Mountain.

MATERIALS AND METHODS

Collectioning of enthomologic material in the region of Pelister Mountain was made over 9 locations:

1. Rotinska Reka, 1067 m altitude
2. Niže Pole, 1083 m altitude
3. Golema Livada, 1100 m altitude
4. Jorgov Kamen, 1450 m altitude
5. Široka, 1650 m altitude
6. Kopanki, 1700 m altitude
7. Crveni Steni, 1800 m altitude
8. Palisnopje, 1800 m altitude
9. Golemo Ezero, 2226 m altitude

Therein were used standard methods for collectioning of this Family of Insects.

Method of mowing (catcher) - collecting of species living in the grassy plant's;

Method of a parasol - collecting of species prom bushes and branches;

Method of the individual collecting - from determined feeding plant's.

After the collecting, the material was conserved in ethyl-acetate, labeled and laboratory elaborated.

Determination of the material was made according to the tables of a P. Angelov (1976, 1978, 1980 and 1981), V. Apfelbeck (1916), M. Bajtenov (1974), A. Hoffman (1950, 1954, 1958), E Reitter (1916) and A. Winkler (1932).

For confirmation of the feeding plant's besides the statements of the authors there were used literature data: P. Angelov (1976, 1978, 1980 and 1981), I. Bureš & A. Lazarov (1956), B. Mihajlova (1978) and S. Živojinović (1950).

During the examination of the materials there were used specimen of the collection of D-r Hieke deposited at the Natural-History Museum of Macedonia.

Besides the figures about the place and the time for collectioning of the species there are given data in the literature about the biology and the spreadiness of each species.

The sequence of species is given in the catalogue of Winkler, 1932.

RESULTS AND DISCUSSION

The authors expose their results from the research of the species from the family Curculionidae (Coleoptera), made in the course of 1990-1992 on the Pelister Mountain.

Those are initial continuous researches over this group of insects known as large harmful insects, due to which they have great economic significance.

As a result of heterogenic florists composition on Pelister Mountain which is a pre-condition for the presence of these fitofags species, there is collected very rich faunistic material.

At determination of their taxonomic status, there is stated a presence of 35 species from 8 subfamilies.

25 species from them are for the fauna of Macedonia, whitch however extends the possibility for the presence of new species in the science.

Systematic part

Family Curculionidae

Subfam. Apioninae

* *Apion violaceum* Kirby, 1808

One ♂ specimen, collected on Baba Mountain at 1300 m altitude (May 22,1980, leg. Hieke)

Palearktic species with biological cycle is connected to the species of genus *Rumex*.

The area of distribution covers the Middle and South Europe and Algeria.

* *Apion cruentatum* Walton, 1844

On the Kopanki locality, (May 24,1980, Hieke), was collected one ♂ specimen. Frequently met on damp terrain, with development tyed up for the species of Rumex acetosa.

General distribution: Europe and Minor Asia.

* *Apion nigritarse* Kirby, 1808

Widely distributed species collected at Kopanki locality (May 23,1980, leg. Hieke).

Well-known as harmful, with development tyed up for several species of clover (*Trifolium* sp.).

General distribution: Siberia, Middle and Asia Minor, Europe up to North Africa.

* *Apion viciae* Paykull, 1798

Collected one ♀ specimen at Kopanki locality, (May 22,1980, leg. Hieke).

Widely distributed palearctic species with development closely tyed up for the plant's of the genera: *Vicia* and *Lathyrus*.

General distribution: Europe, Siberia, Syria and Algeria.

Subfam. Otiorrynchinae

* *Phyllobius pyri* (Linnaeus, 1758)

4 ♂ and 8 ♀ specimens collected in the course of May and June 1991, at the localities: Kopanki, Golema Livada and Niže Pole. Known as harmful for deciduous trees (Birch and Beech), while in Bulgaria is registered as harmful for fruit trees (Angelov, 1976).

Cosmopolitan species distributed in Europe, Siberia, Iran.

Phyllobius canus Gyllenhal, 1834

9 ♀ specimens collected over the leaves of *Acer campestris* and donkey thorn (*Cirsium* sp.) in the course of July 1991-1992 on the following locations: Crveni Steni and Široka.

General distribution: of species covers the Balkan Peninsula, Asia Minor and Caucasus.

Phyllobius maculicornis Germar, 1924

On the localities Golema Livada and Niže Pole, collected 2 ♂ and 13 ♀ specimens in the course of June 1991. The species is frequently met in deciduous forests in Europe and Siberia.

Phyllobius argentatus (Linnaeus, 1758)

Cosmopolitan species and harmful for the leaves of forest trees: beech tree (*Fagus* sp.) and oak tree (*Querqus* sp.). With a method of branches shaking, collected are 3 ♂ and 6 ♀ specimens in the locality Golema Livada in June 1991.

Area distribution covers Japan, Siberia, Europe.

Phyllobius lateralis Reiche, 1857

This species is treated as aberration of *Phyllobius betulae* (F.)

On Pelister, collected only one specimen (May 22,1980, leg. Hieke).

According to Angelov, (1976) frequent species in Bulgaria. In Macedonia found on Bistra locality (10.06.1977, leg. Mihajlova).

General distribution: Greece, Bulgaria and SR Yugoslavia.

* *Phyllobius longipilis* (Boheman, 1843)

From the localities Kopanki, Jorgov Kamen and Golema Livada collected are 2 ♂ and 1 ♀ specimens (June 13,1991, leg. Krpač).

The species is known as harmful.

This is the first founding for Macedonia

General distribution: Middle and South Italy, Balkan Peninsula.

* *Phyllobius pilicornis* Desbrochers, 1873

Only 1 ♂ specimen collected on donkey thorn (Cirsium sp.) (July 10,1991, leg. Krpač) on the locality Široka.

(*) new species for the Fauna of Macedonia

Frequently met in Bulgaria (Angelov, 1976) in deciduous trees forests known as harmful for walnut tree (*Juglans* sp.).

Its distribution covers Southeast parts of Middle Europe, Hungary, and Southeast Europe.

* *Phyllobius pinicola* Kiesenwelter, 1875

The species is new for the Fauna of Macedonia.

24 ♂ and 38 ♀ specimens collected in the course of June and July 1991 at the localities: Jorgov Kamen, Rotinska Reka, Široka, Golemo Ezero, Palisnopje and Golema Livada. Frequently met on pin-shaped leaves zones of the Mountains, whereas is collected from the leaves of the Molika tree (Pinus peuce) and fir tree (Abies alba).

Apfelbeck (1915) gives figures about this species that it is distributed all over from Bosnia to Greece mainly in evergreen forests.

General distribution covers the Balkan Peninsula (South Balkan).

Subfam. Brachyderinae

* *Polydrosus pilosus* Gredler, 1866

In the course of May and June 1991, collected were 3 specimens of this species (2 ♂ and 1 ♀) from the leaves of beech tree (Fagus sp.) on the localities: Jorgov Kamen, Široka and Niže Pole. The species is met in fresh and cool area of deciduous forests in Europe and Western Siberia.

Polifag which is met on the birch tree (*Betula* sp.), fir tree (*Abies* sp.), willow (*Salix* sp.), beech tree (*Fagus* sp.) poplar tree (*Populus* sp.) (*Dieckmann*, 1980).

Polydrosus tibialis Gullenhal, 1834

3 ♀ specimens of this species are collected on Pelister localities: Jorgov Kamen and Golema Livada (June 13,1991, leg. Krpač) on the leaves of Beech tree (Fagus sp.).

This species is frequently met in the plains (from 200 to 700 m altitude), on grassy plant's, but also on the leaves of some fruit trees, cherry tree (*Cerasus*) and apple tree (*Malus*) (Angelov, 1976).

General distribution covers Middle, South and Southeast Europe and Asia Minor.

Polydrosus mollis (Stroem, 1768)

By methods of shaking branches, there were collected 10 specimens of this species (2 ♂ and 8 ♀) on the leaves of beech tree (Fagus sp.) in the localities: Niže pole and Rotinska Reka.

The species is polifag which is fed with the leaves of broadleaf's plant's: oak tree (*Querqus* sp.), beech tree (*Fagus* sp.), (*Corylus* sp.), linden tree (*Tilia* sp.) etc.

Distributed over Europe (except Spain and Greece), Anatolia, Caucasus, North Kazakhstan and Siberia.

* *Scytropus mustela* (Herbst, 1797)

New species for the Fauna in Macedonia, which in the course of June and July 1991/1992 was collected on several localities on Pelister: (Kopanki, Jorgov Kamen, Široka, Golema Livada, Palisnopje and Crveni Steni). There were collected 21 ♂ and 8 ♀ specimens of this species.

Known as harmful for the Molika tree (*Pinus peuce*) and the Common maple (*Acer campestre*).

Monofag, with exclusively tyed up getting with the pine tree.. According to the previous foundlings it is met in the zone of pine trees forests on the Mountains of Middle Europe and the Northern parts of the Balkan Peninsula.

In Bulgaria it lives on the Osogovo and Rhodope Mountains (Angelov, 1978).

Its founding on the locality Pelister might be considered as the most south point in the area of distribution.

Subfam. Cleoninae

* *Larinus brevis* Herbst, 1795

Only 1 ♀ specimen collected (June 27,1992, leg. Krpač) on the plant *Verbascum* sp. On the locality Niže Pole by method of mowing. According to the literature figures as a typical plant - host for this new species appear the species from the genus *Carlina*.

The species is new for the Fauna of Macedonia and has a widely spread area of distribution: Middle and South Europe and Asia Minor.

* *Larinus sturnus* (Schaller, 1783)

Large population of this species (25 ♂ and 26 ♀) collected from the leaves of genera *Cirsium, Cardus* and *Centaurea* on the localities: Niže Pole, Široka, Palisnopje, Jorgov Kamen, Golemo Ezero and Crveni Steni, in the course of July 1990/1991/1992.

The area of distribution covers Persia, Turkmenistan, across Middle and South Europe, and according to Angelov (1978) met throughout the entire Palearktiks region.

Larinus jaceae (Fabricius, 1775)

The species is frequent and until the present determined on numerous localities in Macedonia.

On Pelister (Niže Pole) collected only 1 ♀ specimen (July 27,1992, leg. Krpač) from the leaves of the plant Verbascum sp., which, however is not his characteristically plant - host.

Adult attacks the leaves of genera: *Cardus, Cirsius* and *Centaurea* which, at the same time are his characteristically plant's - hosts.

General distribution: Turkmenistan, Russia, Middle and South Europe.

* *Larinus turbinatus* Gyllenhal, 1836

3 specimens (1 ♂ and 2 ♀) of this species are collected (June - July 1991-1992, leg. Krpač) from the

leaves of the plant's from the genera Cirsium and Cardius on the localities Široka and Niže Pole. Those are typical plant's for which is tyed up the development of the adult.

Distributed in Turkmenistan and Caucasus till Middle and South Europe.

* *Larinus minutus* Gyllenhal, 1836

Only 1 specimen of this species collected (May 22, 1980, leg. Hieke)) on 1300 m altitude on the Baba Mountain.

As characteristic plant - host are assumed the plant's from the genus *Centaurea,* and its general distribution covers the Balkan Peninsula, Crimea and Caucasus.

* *Rhinocylus conicus* (Frölich, 1792)

14 specimens from this species are collected (July, 1991, leg. Krpač) from different localities from the Pelister Mountain.

Polifag, on the plant's of genera *Cirsium, Cardius* and *Centaurea.* Most frequently it is met on the plant *Cardius nitans.* It has a broad area of distribution: Middle and South Europe, North Africa, Asia Minor, Caucasus till Middle Asia.

Subfam. Curculioninae

* *Sibinia subelliptica* Desbrochers, 1873

Only 1 ♀ specimen collected on the locality Široka (July 19, 1990, leg. Krpač). The species is monofag. The development is they'd up for the plant's from genus *Dianthus.*

Distributed mainly over the dry terrain's on the altitude up to 1000 m.

Spread across Middle and South Europe, Anatolia till Algeria.

Anthonomus rubi (Ferbst, 1795)

Palearktiks species with widely spread area of distribution.

1 ♂ and 1 ♀ specimen collected on the locality Golema Livada (June 13, 1991, leg. Krpač). Most frequently attacks the leaves of the plant's from genera *Fragaria, Rubus, Rosa* and *Geum* (Angelov, 1980).

* *Curculio villosus* Fabricius, 1781

1 ♀ specimen collected on the locality Kopanki (May 21,1980, leg. Hieke), in the zone of oak tree forests. Its larvae are developed in the gals of the wasp *Biorhiza terminalis* (Hymenoptera, Cynipidae) and the general distribution covers the entire Europe (excluding the Northern parts) and North Africa.

Subfam. Hylobiinae

* *Hylobius abietis* (Linneus, 1758)

The species is known as harmful for the conifer tree forests. On Pelister (locality Široka and Golema Livada) collected were 3 specimens (1 ♂ and 2 ♀) (June, 1991, leg. Krpač) in the zone of the conifer tree forest of the Molika tree *(Pinus peuce).*

Area of distribution: Europe, Siberia and Japan.

* *Plinthus squalidus* s. sp. *parreyssi* Boheman, 1824

5 specimens (3 ♂ and 2 ♀) collected under the stone on the localities: Kopanki, Niže Pole and Široka in the course of June and July 1991. According (Freude et all., 1983), the species is tyed up for the Mountain massive of Southeast Alps, the Balkan Peninsula, Minor Asia and Italy, and according Winkler's catalogue (1832) it is met on the Alps, Carpathian Mountains, the region of Transylvanian Alps and Corsica.

Subfam. Ceutorhynchinae

* *Rhinoncus pericarpius* (Linneus, 1758)

7 specimens of this species collected on Pelister in the course of May 1980 (leg. Hieke).

Development and feeding of the species is tyed up with the species of the genus *Rumex.* The area of distribution of this species is Paleatktik but it is also transferred in to the North America

Subfam. Mecininae

Gymnaetron asellus (Gravenhorst, 1807)

It is a species with a widely spread area of distribution (Middle and South Europe, Asia Minor, Caucasus, Syria) 1 ♀ specimen collected on the locality Široka (July 19, 1990, leg. Krpač), from the leaves of the plant *Verbascum* sp.

* *Gymnaetron tetrum* (Fabricius, 1792)

Widely distributed species, with a development connected to various species of the genus *Verbascum* sp. The larvae are developed in to the trunk of the same plant, whereas forms spindle - eshaped or oval gall, in which continues the development the stadium of a cocoon. 13 specimens of this species (6 ♂ and 7 ♀) collected on 6 localities of Pelister (Rotinska Reka, Crveni Steni, Palisnopje, Niže Pole and Široka) (July 1991-1992, leg. Krpač).

The area of distribution covers Middle and South Europe, Mediterranean, Caucasus, Siberia and transferred into the North America.

Cionus hortulanus (Geoffroy, 1785)

3 ♂ and 3 ♀ specimens collected on the terrain's of Niže Pole and Široka (June-July, 1991-1992, leg. Krpač) from the leaves of the plant *Verbascum* sp. With which it feeds. Also met on the plant *Scrophularia* sp. General distribution on of the species is Europe. It is frequent in Macedonia and until now it is determined in the surrounding of Skopje, on the Galičica Mountain, Derven - Prilep area (Mihajlova, 1978).

* *Cionus gebleri* Gyllenhal, 1838

New species for the fauna of Macedonia. On Pelister determined 1 ♀ specimen on the locality Široka (July 19, 1990, leg. Krpač) on the leaves of the plant *Verbascum* sp. Rare in Bulgaria (Angelov, 1980). Met in Slovakia, Austria, Italy, Hungary, Greece, Rumania, South Russia, Asia Minor, Turkmenistan and Siberia.

* *Cionus thapsi* (Fabricius, 1792)

On the locality Rotinaska Reka collected was only 1 specimen of this species (July 10, 1991, leg. Krpač). It is a new species for the fauna of Macedonia. Its larvae is developed in to the flowers and unripe fruits of the plant *Verbascum* sp. The area of distribution covers Middle and South Europe, West and Middle Asia.

* *Cionus nigritarsis* Reitter, 1904

In the course of 1990 - 1991 collected 3 ♀ specimens from the leaves of the plant *Verbascum* sp. On the locality Široka. It is a new species for the fauna of Macedonia. Its area of distribution covers the zone from Caucasus to the Pyrenees on the West and to the North till the Southern part of Scandinavia.

* *Cionus hypsibatus* Wingelmüller, 1914

High - mountaineers species met on altitude up to 2500 m. On Pelister (Rotinska Reka, Široka) collected were 2 ♂ and 1 ♀ specimens (July, 1991-1992, leg Krpač) from the leaves of the plant *Verbascum* sp. It is a new species for the Macedonia enthomofauna, with general distribution covering Bulgaria.

CONCLUSION

Investigation over the Fauna of Snout Beetles, performed on Pelister Mountain, in the period 1990-1992, give the presence of a 35 species from 8 Subfamilies. Among them 25 species are new for the Fauna of Macedonia: *Apion violaceum, Apion cruentatum, Apion nigritarse, Apion viciae, Phyllobius pyri, Phyllobius longipilis, Phyllobius pilicornis, Phyllobius pinicola, Polydrosus pilosus, Scytropus mustela, Larinus brevis, Larinus sturnus, Larinus turbinatus, Larinus minutus, Rhinocylus conicus, Sibinia subelliptica, Curculio villosus, Hylobius abietis, Plinthus squalidus s. sp. parreyssi, Rhinoncus pericarpius, Gymnaetron tetrum, Cionus gebleri, Cionus thapsi, Cionus nigritarsis* and *Cionus hypsibatus*, which represents 71,4% new species out of the total stated, which however extends the possibility for the presence of a new species in the science.

Largest number is noted with the species from the Subfam.: Otiorhynchinae (8), Mecininae (7) and Cleoninae (6).

With the assistance of the floristic analysis was stated that the greatest number of species are harmful for the woody plant's.

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REZIME

PRILOG POZNAVAWU FAUNE SURLAŠA (CURCULIONIDAE, COLEOPTERA) PLANINE PELISTER

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Prilog sadrži rezultate istraživanja faune surlaša (Curculionidae, Coleoptera) na planini Pelister, tokom 1990-1992 godine.

Taksonomskom obradom utvrđeno je prisustvo 35 vrsta, svrstanih u 8 podfamilija.

Među njima 25 vrste su nove za faunu Makedonije: *Apion violaceum, Apion cruentatum, Apion nigritarse, Apion viciae, Phyllobius pyri, Phyllobius longipilis, Phyllobius pilicornis, Phyllobius pinicola, Polydrosus pilosus, Scytropus mustela, Larinus brevis, Larinus sturnus, Larinus turbinatus, Larinus minutus, Rhinocylus conicus, Sibinia subelliptica, Curculio villosus, Hylobius abietis, Plinthus squalidus s. sp. parreyssi, Rhinoncus pericarpius, Gymnaetron tetrum, Cionus gebleri, Cionus thapsi, Cionus nigritarsis* i *Cionus hypsibatus.*

Većinom su štetočine određenih biljaka, što je potvrđeno florističkom analizom.

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ORIGINAL SCIENTIFIC PAPER

INFLUENCE OF CATTLE BREED ON ECONOMICAL EFFECT OF MEAT PRODUCTION

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ABSTRACT

We have investigated the influence of the two different genotypes of male slaughter calves (Domestic spotted cattle and F1 bastards between Domestic spotted breed x Busha cattle) on the following traits: obtained growth (y), food consumption for the growth unit (x) per a month of feeding, average productivity (A.P.) presented as the relation between the total growth and consumpted feed-units, marginal productivity (M.P.) presented as the relation between the increased growth and the increased consumption of feed-units, as well as growth elasticity for the realizeed production, i.e. the relation between percental growth increase and percental increase of feed-units consumption in the feeding period.

According to the feeding results F1 bastards had a lower daily growth by 11.24% and higher food consumption per growth unit (7.041 : 5.975) comparing with Domestic spotted breed calves. The average productivity had a more favourable tendency in Domestic spotted breed calves than in F1 bastards. The correlation coefficient food:growth in the feeding period was 0.733 in F1 bastards, and 0.569 in Domestic spotted calves. The optimum points of food consumption and realized growth in F1 bastards were 7.61 FU and 1.15 kg of growth, and in Domestic spotted calves 6.51 FU and 1.28 kg of growth respectively.

The reached economical feeding effect was the result of genetic properties of the investigated genotypes besause the feeding process was done in the same conditions, and the non-genetical variance can, conditionally, be ignored.

The economical feeding effect was favourable in both studied genotypes, but it was significantly better in Domestic spotted breed calves.

Key words: Domestic spotted cattle, bastards, growth, conversion, economy.

INTRODUCTION

Beef meat is a specially important food for inhabitants of Kosovo and Metohia, because it represents 43% of the total produced meat supplies. However, despite the fact that kind of meat is prevalent in this territory, the total produced amount is insufficient regarding demands.

Low production of beef meat is, above all, a consequence of bad cattle breed composition in this area, where Busha breed takes part of over 50%. Having in mind that Busha breed (because of its low exterier dimensions and mass, late-maturity and bad food conversion) is a bad starting material for production of large amounts of quality beef meat, producers atempt to do a change of breed composition using hibridization of Busha breed with thoroughbred breeds.

The basic goal of the investigation was a comparative study, in the same conditions, of the influence of two different cattle breeds genetic potential on the economical effect of beef meat production.

MATERIAL AND METHTODS

The investigation of calf feeding economical efects has been carried out in the area of Istok community.

For the investigation we supplied, from the local cattle market, 39 calves; twenty of them were Domestic spotted ones in the Simmentaler type, and 19 heads were bastards between Domestic spotted cattle and Busha cattle.

We have chosen only heads suitable for feeding.

In the feeding period heads were in the bound growing system, and grouped according to aproximate mass. Daily meal was established according to the average head mass and group feeding was applied but, because the total food consumption was registered, we found out the data concerning food consumption, i.e. feed-units consumption per kg of growth.

The first measurement of feeding heads was carried out at the 30-th day of feeding, and then measurements were carried out each 30 days and at the end of feeding, so we could observe the growth.

Measurements were carried out after morning feeding.

Table 1. Average daily consumption of feed-units and average daily growth per head

Month	x		dx	y		dy	y/x (AP)	dy/dx (MP)	E=(dy/y) / (dx/x)
	Feed-units			Growth			Average	Marginal	Elasticity of
	kg	%		kg	%		productivity	productivity	productivity
Domestic spotted breed									
1	5.00	100.0	-	0.982	100.0	-	0.196	-	-
2	6.51	130.2	1.51	1.278	130.1	0.296	0.196	0.196	1.000
3	6.67	133.4	0.16	1.282	130.6	0.004	0.192	0.025	0.130
4	7.30	146.0	0.63	1.284	130.7	0.002	0.176	0.003	0.009
5	7.65	153.0	0.35	1.275	129.8	-0.009	0.167	-0.025	-0.155
6	9.03	180.6	1.38	1.291	131.5	0.016	0.143	0.011	0.078
7	9.20	184.0	0.17	1.210	123.2	-0.065	0.132	-0.382	-0.043
Bastards (Domestic spotted breed x Busha breed)									
1	5.46	100.0	-	0.813	100.0	-	0.148	-	-
2	6.82	124.9	1.36	1.096	134.8	0.283	0.161	0.208	1.296
3	6.94	127.1	0.12	1.112	136.8	0.016	0.160	0.133	0.823
4	7.69	140.8	0.75	1.147	141.1	0.035	0.149	0.046	0.309
5	8.11	148.5	0.42	1.189	146.2	0.042	0.146	0.010	0.686
6	9.12	167.0	1.01	1.176	144.6	-0.013	0.129	-0.012	-0.100
7	9.58	175.4	0.46	1.099	135.2	-0.077	0.115	-0.167	-1.458

The data were processed using correspondable matematical and statistical methods.

Significance of the correlation coefficient r_{xy} was calculated by t-test.

The investigation was carried out in 1995. Feeding lasted 213 days.

RESULTS AND DISCUSSION

Genetic potential in meat production often represents a limiting factor for meat production, i.e. economical effect of feeding.

Genetic abilitiy for food conversion to growth, presented by month of feeding and the investigated breeds, is given in table 1.

This table, except the average daily consumption of feed-units and the realised average daily growth per month, containes absolute and relative values of these two parameters, marginal effect of feeding, relation of feed-units conversion and realised growth and, finally, elasticity coefficient of production physical extent.

With the aim to establish dependence degree of food conversion to growth we calculated, on the basis of the obtained data, the following parameters: tendency of feed-units consumption (x) and the obtained growth (y) per feeding month, average productivity (AP), marginal productivity (MP), and growth elasticity for the obtained production.

Average productivity is the relation between the total growth and spent feed-units. Marginal productivity is the relation between the increased growth and the increased consumption of feed-units.

Elasticity is the relation between percental growth increase and percental increase of feed-units during the feeding period.

This table shows some processes and tendencies which could not be characterized as properties of the investigated heads breed.

It is obvious that genetic potential was not exploited completely, because heads had different reaction to feeding conditions and, on the other hand, heads had not the same age and body mass.

The average productivity had more favourable tendency (0.1673) in Domestic spotted breed heads comparing with F1 bastards between Domestic spotted and Busha breeds, where the average coefficient was 0.142. Value of elasticity coefficient in Domestic spotted breed heads was specially expressed at the second additional point, and in bastards that was at the second and third point. In the investigated heads of both breeds at the additional points 5 and 7 i.e. 6 and 7 respectively, elasticity coefficient was low and was below zero, which can be related with presence of other limiting factors in the feeding process, that limited further food increase and determined upper rentability limit of food conversion to growth.

It is clear that there are similarities concerning parameters tendency in both breed groups, but not with the same intensity, and we can ignore quality differences of the economical result. That result is caused by different consumption of feed-units per growth unit and different expenses of feeder heads buying.

Consumption of feed-units per kg of growth, listed by breed and feeding stage, is given in table 2.

Table 2. Consumption of feed-units per kg of growth

Parameters	Breed	
	Domestic spotted	Bastards (D. spot x Busha
I stage of feeding	5.130	6.363
II stage of feeding	6.558	7.483
Mean of the whole feeding	5.975	7.041

Calves spent meanly 6.473 feed-units (FU) per kg of growth during feeding period, but, as is obvious, there were highly significant differences between the investigated breeds and feeding stages.

In the given feeding and lodging conditions, in which the investigation was conducted, the maximum growth of Domestic spotted breed calves was reached during the fourth month of feeding, and that is presented in chart 1. At the point when limiting production reaches zero, the maximum growth is reached. One might question how much food have to be spent per a head. The answer depends on relation between meat price and cattle food price. The solution is in the second stage of the function in which is:

$$E<1 \text{ and } E>0$$

If one wish to reach the maximum growth, food consumption ought to be increased till 7.30 FU per feeding day, because that amount of food gives the maximum growth of live mass.

In F1 bastards between Domestic spotted breed x Busha breed food consumption ought to be increased till 8.03 FU per feeding day, when the maximum growth of live mass is reached (chart 2).

CONCLUSION

During the feeding period, bastard calves showed a lower daily growth than Domestic spotted breed calves by 11.24%, which ilustrates validity of the investigated genotypes for the production process, i.e. feeding.

FU consumption for a kg of growth was lower in the Domestic spotted breed calves (5.975) in regard to the bastards (7.041). This makes an economy by saving of feed-units in comparision with bastards.

Chart 1. Tendency of the total, limiting, and average growth of the Domestic spotted breed calves

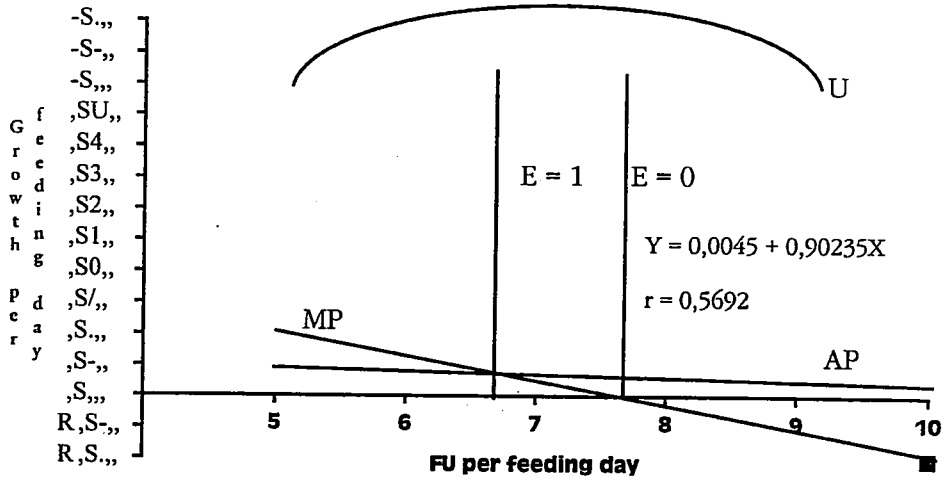

Chart 2. Tendency of the total, limiting, and average grovth of the bastard calves

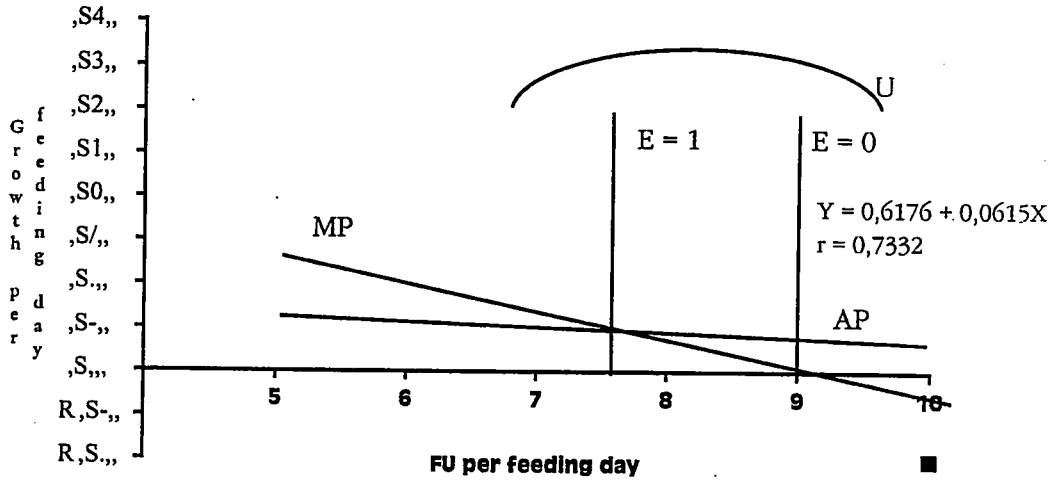

Table 3. Economical and financial results of calf feeding

	PARAMETERS	Dinars per feeder calf	
		Dom. spotted breed	Bastards
I	Expenses	1,817.40	1,746.49
1	Material	1,754.25	1,683.34
a)	Basic	1,631.45	1,553.53
	heads for feeding	760.20	653.85
	food and base material	871.25	899.68
b)	Supplementary	41.60	48.61
	medicines	31.10	37.36
	other	10.50	11.25
c)	Services	81.20	81.20
	tractors	28.20	28.20
	trucks	20.00	20.00
	interests	33.00	33.00
2	Amortization	34.05	34.05
3	Salaries of workers	29.10	29.10
II	Incomes		
	(live mass - purchase price)	2,515.80	2,105.48
III	Reached profit	698.40	358.99
IV	Taxes and fees	62.60	32.16
V	Accumulation	635.80	326.83
VI	Production cost		
	(1 kg of live mass)	4.04	4.40
	Market price	5.60	5.30

The total financial result of calf feeding was positive. There were differences in favour of the Domestic spotted breed calves.

All the above mentioned showed that the genetic potential of food conversion per kg of growth was significantly higher in the Domestic spotted breed heads, which influenced better economy of the breed.

The average productivity showed more favourable tendency in Domestic spotted breed calves, but it had a similar tendency in bastard calves.

The correlation coefficient food:growth, during the whole feeding, was 0.7332 in F1 bastards Domestic spotted breed x Busha breed, and 0.5692 in Domestic spotted breed.

The optimum points of food consumption and realized growth in F1 bastards were 7.61 FU and 1.147 kg of growth, and in Domestic spotted calves 6.51 FU and 1.278 kg of growth respectively.

The reached economical result of feeding was caused by genetic potential and feeding conditions.

On the basis of the above presented we might conclude that genetic potential of calves, in the present feeding conditions, determines economy, and one ought to be careful when chooses heads of a breed for feeding.

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REZIME

UTICAJ RASE GOVEDA NA EKONOMSKE EFEKTE U PROIZVODNJI MESA

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Ispitivan je uticaj dva različita genotipa junadi (domaće šarene rase i melezi F1 domaće šarene X buša rase) na: ostvareni prirast (y), utrošak hrane za jedinicu prirasta (x) po mesecima trajanja tova, prosečan produktivitet (P.P.), predstavljen odnosom ukupnog prirasta i utrošenih hranljivih jedinica, marginalni prirast (M.P.), koji predstavlja odnos povećanog prirasta i povećanog ulaganja hranljivih jedinica, kao i elasticitet prirasta za ostvarenu proizvodnju, tj. odnos procentualnog povećanja prirasta i procentualnog povećanja hranljivih jedinica u periodu tova.

Rezultati tova ukazuju da su melezi F1 ostvarili manji dnevni prirast za 11,24% i veći utrošak hrane po jedinici prirasta (7,041 : 5,975) od junadi domaće šarene rase. Prosečan produktivitet ima povoljniju tendenciju kod junadi domaće šarene rase od meleza F1 generacije. Koeficijent korelacije hrna:prirast u toku trajanja tova kod meleza F1 iznosio je 0,733, a kod domaće šarene 0,569. Optimalna tačka utroška hrane i realizovanog prirasta kod meleza F1 je 7,61 HJ i 1,15 kg prirasta, a kod domaće šarene rase 6,51 HJ i 1,28 kg prirasta.

Postignuti ekonomski efekti tova su rezultat genetske predispozicije ispitivanih genotipova pošto se tov odvijao u istim uslovima, pa se negenetska varijansa može, uslovno, zanemariti.

Ekonomski efekti tova za oba posmatrana genotipa su povoljni, stim što su znatno povoljniji za rasu gomaće šareno goveče.

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BOOK REVIEWS - PRIKAZI

Pulević V., Vincek D. i Bušković V.,

CRNOGORSKE PLANINE - PUTOPISI I ZAPISI. Izdavač: "Obod", "Unireks", "ZoNo-publik", Cetinje., 1997.

ISBN 86-305-0276-2

Krajem septembra biblioteka "Crnogorsko nasledje" obogaćena je još jednom značajnom knjigom koja nosi naziv "Crnogorske planine - putopisi i zapisi". Osnovni koncept, obim, bogatstvo i raznovrsnost sadržaja čine je jedinstvenom te vrste kod nas.

Napor priredjivača, dr Vukića Pulevića, Danijela Vinceka i Vasilija Buškovića, pokazao se izvanredno korisnim. Ovi vrsni zaljubljenici i poznavaoci prirode Crne Gore smogli su snage i založili svoju energiju i čeličnu volju da dosadašnju gradju o crnogorskim planinama sakupe i na primjeren način, u ovoj knjizi, predstave čitaocima.

Ova vrijedna knjiga na 605 stranica, pored predgovora, ima tri dijela: prvi, izabrane putopise, drugi, bibliografija o crnogorskim planinama, i treći, bilješke o autorima.

U prvom najobimnijem dijelu knjige priredjivači su uspešno izabrali putopise i zapise o svim planinama Crne Gore, počev od Orjena, Lovćena i Rumije, preko Maganika, Volujka, Durmitora, Ljubišnje, Sinjajevine do Bjelasice, Komova i Prokletija. Autori putopisa i zapisa, iako različitih struka su poznati i priznati poznavaoci prirode od prve polovine XIX vijeka (neki čak i mnogo ranije) do današnjih dana. Imena Antonija Baldačija, Vilhelma Ebela, Marijana Bolice, Ljubomira Nenadovića, Pavla Rovinskog, Kurta Haserta, Branimira Gušića, Branka Kotlajića, Stevana Stankovića, Milisava Lutovca, Jegora Kovaljevskog, Nikole Vasojevića, Radosava Vešovića i Danijela Vinceka samo su dio njih, prisutnih u 58 putopisa i zapisa objavljenih u ovoj knjizi.

U drugom dijelu autori su pripremili 1.230 bibliografskih jedinica koje će zainteresovati čitaoce, upućivati na izvorne radove iz mnogih naučnih oblasti i služiti za stalno produbljivanje znanja o crnogorskim planinama.

Treći dio knjige obuhvata biografske podatke 517 najznačajnijih autora do sada publikovanih radova i priloga iz ove oblasti. Za pojedine autore su priložene i fotografije portreta.

Knjiga predstavlja pravu "Planinsku enciklopediju" Crne Gore, za kojom se osjećala potreba iz mnogih oblasti prirodnih nauka. Nju će uza se imati mnogi ljubitelji prirode prilikom upoznavanja crnogorskih prostora. Zbog navedenih i drugih vrijednosti treba zahvaliti entuzijastima na ovom krupnom poduhvatu, a ovu vrijednu knjigu toplo preporučiti čitaocima.

D.M. Kićović

Zbornik radova

ZAŠTITA ŽIVOTNE SREDINE GRADOVA I PRIGRADSKIH NASELJA. Ekološki pokret Grada Novog Sada, Eko-konferencija '97 - monografija I i II, Novi Sad, 1997.

502.3(082)
124545799

U organizaciji ekološkog pokreta grada Novog Sada, od 24. Do 26. Septembra 1997. godine održana je u Novom Sadu Eko-konferencija '97 - sa medjunarodnim učešćem.

Radovi su grupisani u 6 grupa - sfera: Djelovi životne sredine (vazduh; voda; zemljište i biosfera), Tehničko-tehnološki aspekt zaštite, Sociološki, zdravstveni, kulturni, obrazovni i rekreativni aspekt zaštite, Ekonomski i pravni aspekti zaštite i Projektovanje ekološkog sistema.

Monografija I i II je zbornik radova izloženih na tom skupu. Monografija ima 672 strane teksta, ilustrovanih sa 117 tabela, 36 grafikona, 69 slika, 7 priloga i jednom kartom.

Najobimniji dio monografije obradjuje složenost i visok stepen osjetljivosti aktivnosti na zaštiti i unapredjenju vazduha, vode, zemljišta i biosfere kao osnovnih djelova životne sredine. Kroz 55 referata, koliko je objavljeno, i sadrži čitava I knjiga, obradjeni su, uglavnom, stanje, problemi i mjere zaštite ovih elemenata kako u Novom Sadu sa okolinom, tako i u mnogim gradskim i prigradskim mjestima u našoj zemlji.

U odjeljku "Tehničko-tehnološki aspekti zaštite" izložena su načela opštinske politike uklanjanja čvrstih otpadaka u Bugarskoj i otvaranja novih deponija otpadnih materija i procjene uticaja na životnu sredinu u Slovačkoj. Detaljno su zastupljena i pitanja: rekultivacije degradiranih prostora, recikliranja tehnološkog otpada i spalionica smeća, nafte i naftinih proizvoda kao zagadjivača, intenzivna urbanizacija kao ekodestrukcija u prostoru, komunalna buka i mnoga druga pitanja koja se odnose na neophodnost primjene mnogih tehničko-tehnoloških rješenja u cilju zaštite prirode.

Kod sociološkog, zdravstvenog, kulturnog, obrazovnog, rekreativnog, pravnog i ekonomskog aspekta zaštite životne sredine autori obradjuju: društvene i ekološke aspekte naselja, urbano-demografski razvoj gradskih i prigradskih naselja, problem zaštite i valorizacije prirodnih vrijednosti, stanje i uticaj zagadjenog vazduha na zdravlje ljudi, harmonizaciju nacionalne i ekološke politike Evropske unije, pravni aspekt zaštite životne sredine i dr.

Posljednji odjeljak monografije II nosi naslov "Projektovanje ekološkog sistema". U njemu autori tretiraju aktuelnu problematiku vezanu za: primjenu informacionog sistema u zaštiti životne sredine na teritoriji nekih opština, indikatore stanja životne sredine u urbanim naseljima, automatizovane sisteme kontrole zagadjenosti vazduha, modele tačkastih izvora u teoriji prostorno-vrjemenske raspodjele zagadjenja i dr.

Monografija je nacionalnog značaja i izlazi svake druge godine, kada se i održava Eko-konferencija.

Svih 111 referata imaju rezime na engleskom jeziku i spisak korišćene literature.

D.M. Kićović

Zbornik radova

FIZIČKO-GEOGRAFSKI PROCESI NA KOSOVU I METOHIJI, Posebno izdanje, br. 2, pp. 1 - 148, Glavni i odgovorni urednik prof. dr. Radomir Ilić, Univerzitet u Prištini, Prirodno-matematički fakultet, Odsek za geografiju, Priština, 1997.

911.2: 55(497.115)(082)

Tokom novembra 1997. g. publikovana je druga sveska radova proisteklih iz projekta "Fizičko-geografski procesi na Kosovu i Metohiji". U ovoj svesci su publikovani radovi iz domena klimatologije, hidrologije, hidrobiologije, demografije, turizmologije, zagadjenja i zaštite životne sredine i istorije rudarstva.

Očekivali smo posle publikovanja prve sveske da upravo u ovoj budu saopošteni rezultati naučnih istraživanja po projektnim temama. To je, medjutim, izostalo - medju 12 publikovanih radova jedva da bi se polovina njih mogla svrstati u kategoriju originalnih naučnih radova. Moramo se, zbog izneverenih očekivanja i zbog potrebe da se ovakvo izdanje ne ponovi, kritički osvrnuti na ovu svesku.

Na koricama Zbornika je samostalno prikazana teritorija Kosova i Metohije. Nju je trebalo predstaviti isključivo u okviru granica Republike Srbije. Nijedan publikovani rad nema UDK klasifikaciju, niti oznaku kategorije rada. Naslovi radova sadrže žargon, hemijske simbole, stručne oznake i slično, što je suprotno ustaljenoj praksi i propisima JUS standarda. Merne jedinice iz sistema SI su pisane u pojedinim radovima ćirilicom (?!) a u pojedinim, kako je i propisano, latinicom. Citiranje korišćene literatureje proizvoljno i neujednačeno. I pored preuzimanja činjenica iz literature u pojedinim radovima su te činjenice prezentirane proizvoljno i nekritički. Tako, na pr., Šar-planina (što je opšte prihvaćeni termin u geografskoj literaturi, koji ima svoju predistoriju i dublje značenje) se imenuje kao Šara, što predstavlja uvodjenje žargona u naučnu terminologiju. Ili, navodi se podatak da je dužina Šar-planine 60 km a širina 15 km, a u stvari dužina njenog bila je 83 km a širina 30 km, i t.d. Govoreći o turističkim predispozicijama Šar-planine autori u okviru lovnog turizma navode mogućnost lova na čitav niz retkih, proredjenih i zakonom zaštićenih vrsta, kao na pr. mogućnost lova risa, koji je evidentiran u još samo 10 individua (Ćirović i saradn., 1997), ili tetreba koji je skoro potpuno istrebljen, i t.d. Ovakvo pisanje je apsulutno nedopustivo, bez obzira što je Šar-planina nacionalni park, a što autori ne uzimaju u obzir. Suštinski nedostatak većine publikovanih radova je taj da nije dosledno definisan naučni problem i da nije uspostavljena veza izmedju uzroka i posledice.

Najzad, tehnički nivo pripreme rukopisa je nedopustivo nizak. Kroz celu svesku se susreću brojne štamparske greške koje drastično umanjuju kvalitet radova. Tehnički urednik je morao da autorima dostavi na korekciju probni otisak. Sve ovo daje utisak da je naučni i stručni nivo ove sveske daleko od očekivanog. Zabrinjavajuća je činjenica da su ovakvi tekstovi prihvaćeni od recenzenata, medju kojima su i naši najeminentniji geografi.

Vrednost nekoliko istinski kvalitetnih originalnih naučnih radova, u prvom redu rad prof. dr. Radomira Ilića, je umanjena zbog činjenice da su publikovani u svesci sa ovakvim nedostacima.

P. Jakšić

UROŠEVIĆ Violeta,

PRAKTIKUM IZ SISTEMATIKE NIŽIH BILJAKA
Univerzitet u Prištini, pp. 1-183, Priština

ISBN 86-81029-49-5

Ovaj praktikum, za razliku od postojećih, obuhvata celokupno gradivo iz Sistematike nižih biljaka, pa kao takav biće od velike koristi studentima - biolozima za praćenje praktične nastave i produbljivanje znanja iz pomenutog predmeta.

Sadržaj praktikuma, prezentiran je na 183 strane, obuhvata sva potrebna poglavlja, koja jedan takav praktikum treba da sadrži.

Sistematska podela unutar najglavnijih sistematskih kategorija - algi, gljiva i lišajeva je po najnovijim literaturnim podacima iz oblasti sistematike.

U uvodnom delu autor navodi praktična uputstva o: pravlnom uzimanju uzoraka iz prirodnih staništa, neophodnoj opremi i instrumentima za rad, pripremi svežih i trajnih preparata, hranljivim podlogama za kultivisanje algi i gljiva i dr.

Autor zatim daje prikaz najopštijih karakteristika algi - njihovo morfologije, građe, razmnožavanja i rasprostranjenosti.

Obradjene su sve sistematske grupe algi (tipovi ili klasde): Cyanophyta, Dynophyceae, Chrysophyta, Bacillariophyta, Pheophyta, Rhodophyta, Xanthophyta, Euglenophyta, Chlorophyta i Charophyta.

Posle poglavlja algi obradjena je na isti način grupa gljiva (Mycophyta, Fungi), kao i grupa lišajeva (Lichenophyta).

Za svaku od navedenih sistematskih kategorija autor daje njihove karakteristike, navodeći posebno sa više podataka one rodove i vrste koje studenti obradjuju na praktičnoj nastavi. To su uglavnom vrste koje su najčešće i najrasprostranjenije u prirodi. Istovremeno, navedeni su podaci u kojim vodenim ekosistemima i na kojim staništima se mogu naći pomenuti predstavnici.

Posebno treba istaći veliki broj ilustracija, vrlo uspešnih i preglednih a koje su uz sam tekst, tako da zajedno predstavljaju jednu sadržajnu i vizuelnu celinu. Ovakav način prezentiranja materije osobito je važan za jedan praktikum.

Sadržaj praktikuma je studiozno i opširno obradjen, tako da predstavlja jedan manji udžbenik, što svakako ne umanjuje njegovu vrednost i primenu, na protiv, pomoći će studentima da lakše i uspešnije savladavaju gradivo iz predmeta Sistematike nižih biljaka.

Lj. Petrovska

Tatić B.,

STOTA GODIŠNJICA BOTANIČKE BAŠTE "JEVREMOVAC" UNIVERZITETA U BEOGRADU. Zavod za udžbenike i nastavna sredstva, p.: 1 - 84, Beograd, 1996.

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Za ovom reprezentativnom monografijom se osećala potreba, budući da su mnogi datumi u istoriji ove važne institucije već zaboravljeni. Tako, primera radi, i sada nije jasno koja je stota godišnjica Botaničke bašte: de li je to 1874. kada je Josif Pančić formirao (staru) botaničku baštu, ili 1889. kada je kralj Milan Obrenović priložio kao legat svoju baštu za današnji "Jevremovac" i kada je za upravnika postavljen Stevan Jakšić? U svakom slučaju taj istorijat, koji nam autor monografije iznosi u prvom poglavlju, pokazuje da je borba za Botaničku baštu trajala i da je njeno utemeljenje bilo proces.

"Jevremovac" nema tako dugu istoriju kao Botanički vrt u Padovi ("Instituto ed Oro Botanico"), niti tako bogatu biblioteku ili herbar, ali ima istovetan značaj za razvoj naše botaničke nauke. To značenje je istakao svojevremeno i J. Pančić a potvrda njegovog vizionarstva je činjenica da je "Jevremovac" sa svojih 100 godina vrlo krepka starina, sa mladalačkim srcem. Tu krepkost bašti daje njen biljni fond, o kome dr B. Tatić govori u drugom poglavlju. Medju 300 drvenastih i oko 1000 zeljastih vrsta velkiki broj njih je nov za alohtonu floru Srbije. Vitalnost Bašti daje i njena biblioteka, kojoj je posvećeno naredno poglavlje monografije. Nju čini preko 6000 naslova knjiga, kao i veliki broj svezaka časopisa i pojedinačnih separata. Naravno, "Jevremovac" i sam publikuje časopis Instituta za botaniku i Botaničke bašte od 1928. godine, sa prekidom u predratnom i ratnom periodu. To je jedan od naših najuglednijih časopisa koji dostojno reprezentuje našu botaničku nauku u zemlji i u svetu. Iz popisa institucija sa kojima se vrši razmena vidimo - nažalost - da biblioteka "Jevremovca" nema izdanja Univerziteta u Prištini, to jest PMF-a u Prištini. Tu nemarnost treba što pre ispraviti.

Naredno poglavlje govori o herbaru "Jevremovca", tačnije o mukotrpnim nastojanjima za utemeljenje herbarskog fonda. Ovo je jedan od budućih najvažnijih zadataka Bašte. Primera radi, pomenuti Botanički vrt u Padovi ima herbar sa 20.000 vrsta biljaka i 200.000 primeraka listova. Herbar "Jevremovca" mora imati makar većinu od 7.000 vrsta vaskularne flore Balkana.

U poglavlju Index seminum opisane su neke od najznačajnijih vrsta biljaka: ginko, krivulj, molika, barski taksodijum, tisa i dr.

Najzad, u dva poslednja poglavlja govori se o osoblju botaničke bašte i o njenim narednim zadacima. Na kraju, posle pregleda literature navedeni su

upravnici Botaničke bašte za poslednjih 100 godina. Mišljenja smo da je ova monografija mogla da sadrži još jedno poglavlje u kome bi bila napravljena komparacija "Jevremovca" sa drugim botaničkim baštama na Balkanu. To bi bio najbolji parametar za rangiranje naučnog i stručnog rada realizovanog u proteklih 100 godina.

Medju narednim zadacima Botaničke bašte kao primarni bi smo naveli obogaćivanje biljnog fonda, a u vezi toga treba razmišljati i o novoj lokaciji Bašte. Ako novooformljena botanička bašta planinske flore Crne Gore u Kolašinu može imati 400 biljnih vrsta na 650 m^2 onda "Jevremovac" mora imati makar 1o puta toliko. U jednom periodu izmedju dva svetska rata toliko je vrsta i bilo. Stručnost i mladost sadašnjeg osoblja Botaničke bašte, a verujemo i entuzijazam, garancija su da će tako i biti. Naravno, vrlo važan zadatak je i obogaćivanje bibliotečkog fonda. Čini nam se da je 6.ooo knjiga u biblioteci Bašte ipak mali fond. Primera radi dr M.M. Janković, koji je bio upravnik Bašte od 1973. do 1979., poklonio je Zavodu za zaštitu prirode oko 30.000 bibliografskih jedinica, pa je izvesno da je biblioteka Bašte za 100 godina morala sakupiti više literature.

I na kraju da napravimo i jedno poredjenje: Prirodnjački muzej u Beogradu takodje proslavi stotu godišnjicu, na žalost bez monografije, bez jubilarnog broja časopisa. Ima li izgovora takvom propustu? Otuda autoru dr B. Tatiću čestitka više!

P. Jakšić

LERAUT J. A. Patrice,

LISTE SISTÉMATIQUE ET SYNONYMIQUE DES LÉPIDOPTERES DE FRANCE, BELGIQUE ET CORSE (deuxieme edition). Supplèment à Alexanor, pp. 1-526, Paris., 1997.

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Pre nepunih 17 godina publikovano je prvo izdanje ove kapitalne monografije. U dopunjenom izdanju su predstavljeni rezultati rada na fauni Lepidoptera entomologa Francuske, Belgije i Korzike. U odnosu na prvo izdanje ovo ima 192 stranice više i pokazuje nam da je u medjuvremenu nacionalna fauna obogaćena sa 338 novoutvrdjenih vrsta, medju kojima su neke i novoopisane za nauku. Tako, dakle, fauna Lepidoptera ovih zemalja broji 5.015 utvrdjenih vrsta. Nemožemo a da ovde ne napravimo poredjenje sa poznavanjem naše faune Lepidoptera. Zečević (1996) je dao spisak koji broji 1.334 utvrdjhenih vrsta Lepidoptera u Srbiji. Budući da je naša fauna bogatija od Francuske jasno je koliko je nizak stepen njene istraženosti.

Monografija Lerauta je pisana četvorojezično: francuski, flamanski, nemački i engleski. Osim toga, dat je i rezime na 38 strana, tj. na 38 evropskih jezika, uz prikaz teritorije datih država na karti Evrope. Jugoslavija, Makedonija i Bosna i Hercegovina su predstavljene na 392. strani na srpskom jeziku, ćiriličnim tekstom, u prevodu P. Jakšića. Interesantno je da je stranica predvidjena za Bugarsku ostala prazna, što je iznenadjenje jer u toj zemlji ima više lepidopterologa nego u Jugoslaviji.

Posle Uvoda i izjava zahvalnosti date su fotografije poznatih francuskih lepidopterologa XVIII - XX veka, sa kratkim biografijama. Potom je data osnovna podela reda Lepidoptera na 2 podreda, 30 superfamilija i 72 familije. Podela je bazirana na klasičnim radovima Kristensena (1976, 1986) i de Mineta (1983 - 1991) i drugih autora. Moramo ovde primetiti da se upotrebljena klasifikacija i nomenklatura razlikuju od onih koje upotrebljava Evropsko Lepidopterološko Društvo (SEL), Kudrna (1996) ili Karsholt & Razowski (1996). To samo govori da pitanje filogenije Lepidoptera nije još uvek rešeno i da će težište budućih istraživanja biti usmereno upravo u tom pravcu.

Centralna materija - sistematska lista vrsta, podvrsta i sinonima leptira Francuske, Belgije i Korzike - data je na 175 stranica knjige. To je lista koja može poslužiti kao uzor pri izradi nacionalne faune praktično svake evropske zemlje. Njena upotrebna vrednost je izuzetno velika. Nijedna evropska nacija još nema takvu listu. Kod nas je pokretanjem edicije CATALOGUS FAUNAE JUGOSLAVIAE učinjen pokušaj izrade takvih listi, ali je posle publikovanja svezaka za deo faune projekat zastao. Moramo čestitati autoru na istrajnosti da listu kompletira, kao i stručnosti da reši brojna pitanja nomenklature vezana za stroga pravila ICZN. Uvid u pojedine taksonomske kategorije (familija, rod, vrsta, podvrsta, sinonim i sl.) olakšan je perfektnim slaganjem teksta kombinovano sa pisanjem različitim tipovima slova. Brojna taksonomska i nomenklaturna otvorena pitanja označena su kod pojedinih taksona brojevima i potom su diskutovana u narednom poglavlju (str. 251 - 329). Korišćena literatura je prikazana u narednom poglavlju (str. 331 - 356), a navedene su samo reference publikovane posle 1980. godine, tj. posle publikovanja prvog izdanja. Po našoj slobodnoj proceni navedeno je preko 650 referenci, što znači da je u proteklih 17 godina godišnje u Francuskoj publikovano čedrdesetak lepidopteroloških radova! Uzgred da napomenemo: 650 referenci broji celokupna jugoslovenska lepidopterološka bibliografija od Scopolija (1763) do danas.

Poslednje poglavlje sadrži alfabetski popis navedenih taksona, sa napomenom da su to dva indeksa. U prvom indeksu su više taksonomske kategorije do nivoa vrste. U drugom indeksu su kategorije vrsta, podvrsta i njihovih sinonima.

Imajući u vidu obim i složenost poslova vezanih za izradu ovakvog spiska nacionalne faune možemo postaviti pitanje kada će taj posao biti uradjen kod nas? Najpre je nužno da o potrebi za tim sazri svest, potom da dodje do objedinjavanja institucija i kadrova. Činjenica da mnogo siromašnije nacije od naše imaju svoje nacionalne faune pokazuje da finansije nisu najvažnija prepreka. Najvažnije je da jednom započnemo taj posao, a u ovoj monografiji imamo uzor kako treba raditi.

P. Jakšić

Simpozijum sa medjunarodnim učešćem

"BILJNI I ŽIVOTINJSKI GENETIČKI RESURSI"

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Naučno društvo Srbije, Savezno Ministarstvo za poljoprivredu i Savezni zavod za biljne i životinjske genetičke resurse organizovali su Simpozijum sa medjunarodnim učešćem "Biljni i životinjski genetički resursi", prvi ove vrste u našoj zemlji, održan na Zlatiboru u vremenu od 30. IX - 3. X 1997.

Osnovni cilj Simpozijuma je bio da se dobije tačna i potpuna informacija o stanju genetičkih resursa i definišu pravci razvoja budućeg rada i institucionalnog organizovanja.

S obzirom da SR Jugoslavija predstavlja izuzetno bogat izvor prirodnih autohtonih genetičkih resursa, očuvanje biodiverziteta postaje jedan od osnovnih nacionalnih zadataka kako zbog ekonomskih tako i zbog ekoloških razloga. I pored vrlo razvijene oblasti oplemenjivanja i selekcije postoji mišljenje da genetski resursi nisu dovoljno iskorišćeni. Potrebno je kompletiranje nacionalne kolekcije koju bi pratila dokumentaciona obrada. To je značajno jer je poslednjih 50 godina evidentno smanjenje broja gajenih vrsta u poljoprivredi, a u okviru ekonomski najznačajnijih vrsta, evidentno je sužavanje genetske osnove.

Ukupne površine pod poljoprivrednim kulturama, ukupna proizvodnja, ukupni ekonomski efekti i bitan udeo genotipa u tome, obavezuju sve društvene činioce zemlje na veoma odgovoran odnos prema biljnom genofondu. Zahvaljujući njima mi smo opskrbljeni hranom, nekim lekovima i tekstilom, nekim industrijskim proizvodima i kvalitetom života. Za konstituisanje čvrstog nacionalnog programa upravljanja biljnim genofondom potrebno je, u tehničko-tehnološkom pogledu, izvršiti identifikaciju prirodnih i logičnih faza. Te faze, zasnovane na tehnologiji rada sa genofondom, imaju specifičan sadržaj, različite učesnike u realizaciji, različiti kvalitet finansijskih sredstava za predvidjenje aktivnosti i različite kategorije naučnih istraživanja. Celina programa se može obuhvatiti ovim fazama: 1) Inventarizacija, kolekcionisanje, klasifikacija, karakterizacija, ocenjivanje, čuvanje, dokumentacija i razmena genetičkih resursa

2) Proučavanje genetičke varijabilnosti gajenih i korišćenih biljnih vrsta,3)Sortiranje genetičkig resursa prema genetički poželjnim svojstvima, 4) Proučavanje genetičkih mehanizama kontrole nasledjivanja poželjnih karakteristika, 5) Oplemenjivanje početnog materijala za selekciju - predselekcija, 6) Stvaranje novih genotipova, i 7) Proizvodnja semena.

Na simpozijumu se čulo da iskustva razvijenih zemalja najveće društvene koristi od genofonda (autohtonog i introdukovanog) ostvaruju, ukoliko postoji i funkcioniše efikasan sistem upravljanja genetičkim resursima. Osmišljavanje i uvodjenje u funkciju efikasnog sistema upravljanja genofondom zemlje predstavlja preku potrebu za našu zemlju, jer ga do sada nije imala a nalazi se u velikoj tranziciji.

Do sada su uredjene deskriptorske liste za informacioni sistem za biljne genetičke resurse sa bazama podataka za 58 vrsta (tehnologija rada BBGJ). Sada se čuva 3973 uzoraka semena i 1408 uzoraka u loznim, voćnim vrstama i hmelju (ex situ i in situ).

Organizovani rad na očuvanju životinjskih genetičkih resursa počeo je znatno kasnije od biljnih, i to od 1994. godine. Rad je obuhvatio identifikovanje i inventarisanje postojećih rasa i sojeva koji se gaje kod nas. Ukupno je identifikovano 35 rasa stoke. Prema kriterijumima FAO-a utvrdjene su najvažnije fenotipske i proizvodne karakteristike, kao i brojno stanje. Takodje je izvršen izbor autohtonih rasa i sojeva i predložen program njihovog očuvanja.

Na simpozijumu je prezentovano 105 radova (usmeno i putem postera). Učešće su uzeli stručnjaci iz svih delova naše zemlje kao i gosti iz inostranstva i to iz Češke, Rusije, Madjarske ...

Sa Poljoprivrednog fakulteta iz Prištine na zapažen uspupljanju genofonda povrća na Kosovu i Metohiji (doc. dr. Zorana Ilića), autohtonih voćnih vrsta (prof. dr. Miladina Šoškića) i domaćih sojeva ovaca (prof. dr. Bože Radovića i doc. dr. Jovana Stojkovića).

Z. Ilić