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Faculty of Mathematics and Natural Science
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Contemporary energy storage sources. Energy saving

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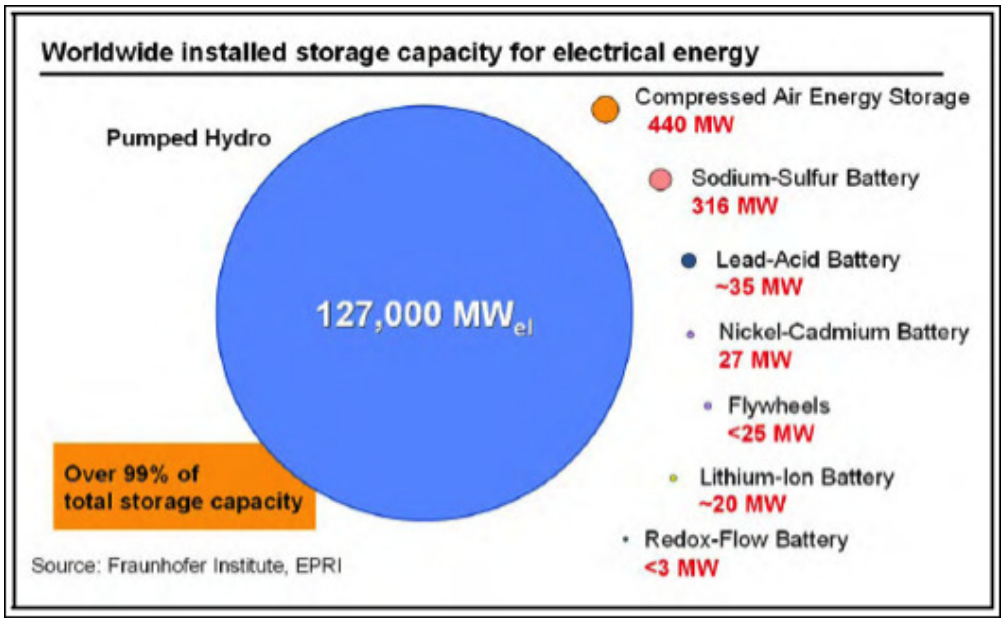
PLENARY REPORT – presentation

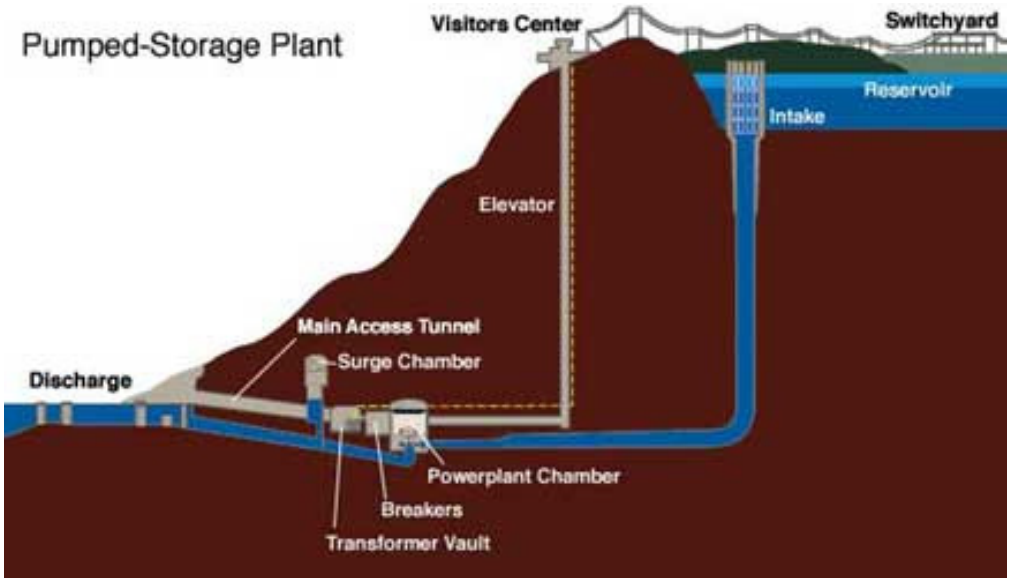
Global installed energy storage capacity

- *While global electric power generating capacity is roughly 4,000 GW, total installed energy storage capacity is less than 128 GW, or 3.2% of generating capacity.*
- *Water (pumped hydro) is practically the only currently existing energy storage facilities – the contribution of the other facilities is so far negligible.*

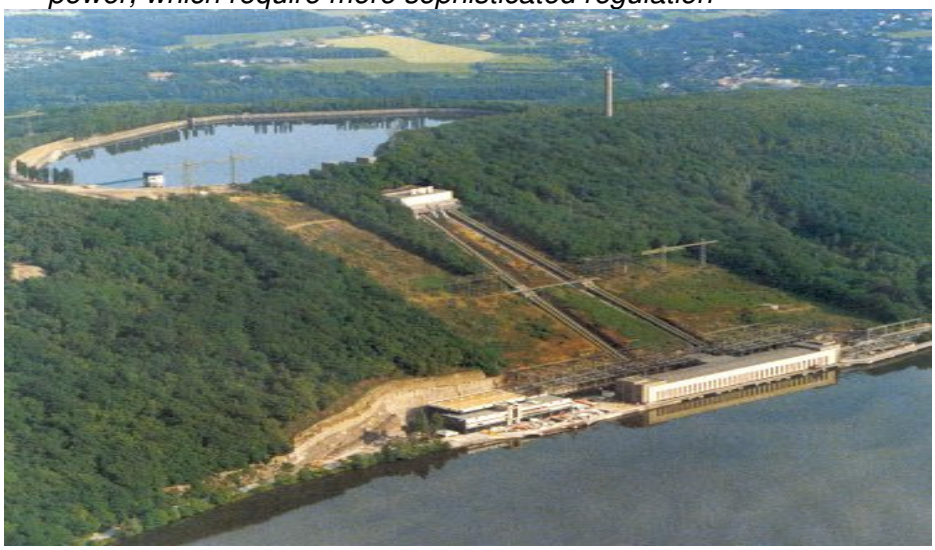


Pumped hydro energy storage

- *Advantage: long life & 50 years, availability, 70%-80% efficiency*
- *Disadvantage: environment concerns, may use only part of its power for greed regulation*



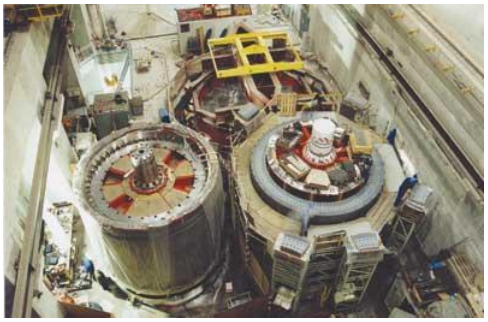
- *Typically, pumped hydro facilities have two reservoirs with water pumped uphill during off-peak times and released during peak times using a generator which can be run ``backwards'' as an electric motor.*
- *While this is good enough for peak shaving it is not good enough to accommodate the fast power changes caused by wind and solar power, which require more sophisticated regulation*



Goldisthal water Pumped-Storage Plant - Germany

- *A typical example of the new generation of pumped hydro is Goldisthal pumped-storage plant*
- *The 1,060-mw Goldisthal pumped-storage plant features two variable-speed (asynchronous) motor-generators.*

Construction on the project began in September 1997, and the plant started commercial operation in October 2004.

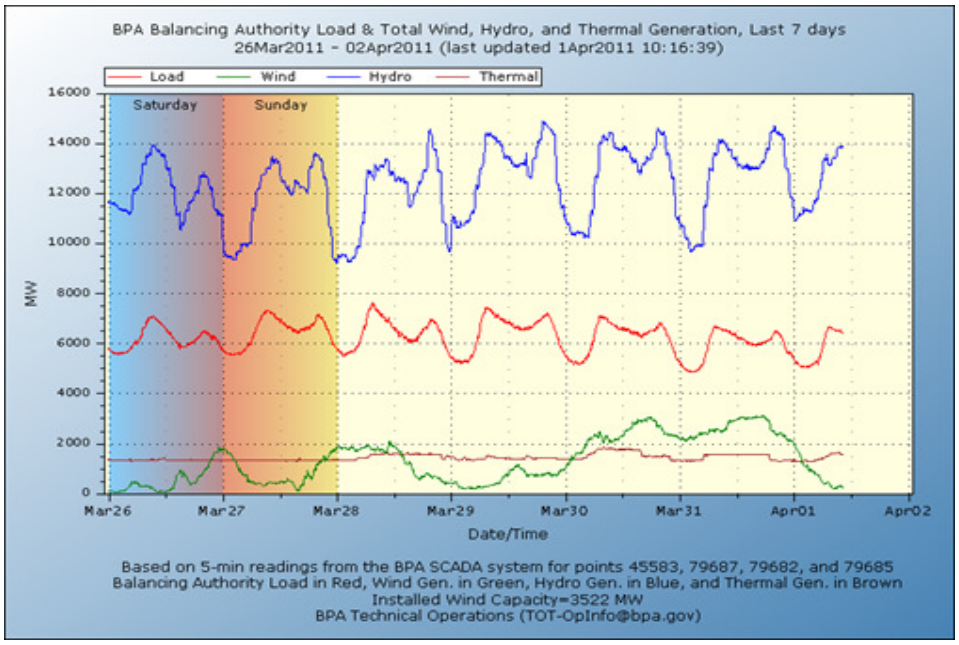


Effect of Solar and Wind power on the electrical grid

- *In spite of their many advantages, the renewal solar and solar energy will require nearly equivalent installed energy storage power to generate a stable energy.*

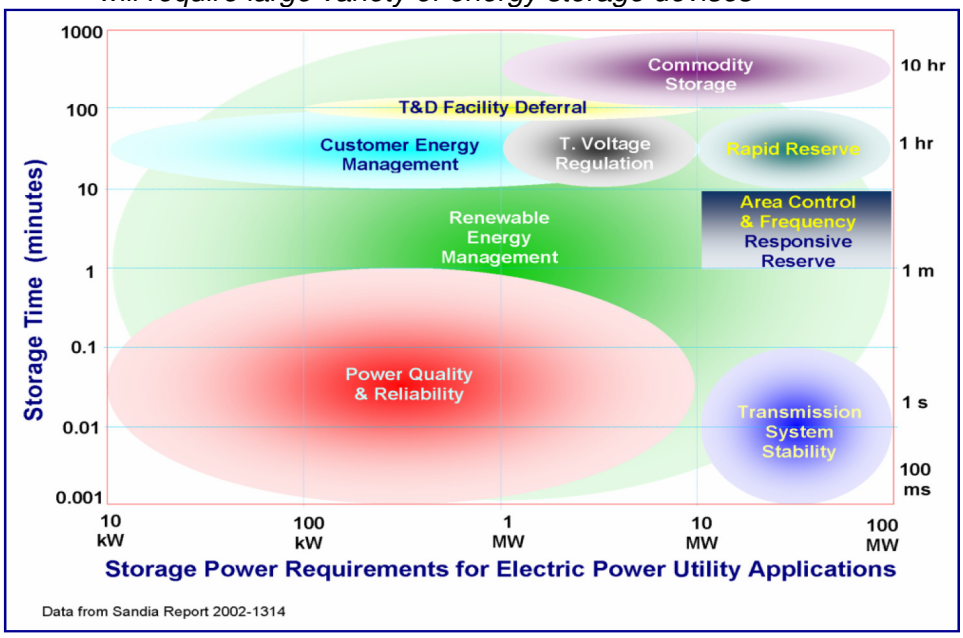
Pumped Hydro & wind energy

- *Seven days BPA (Pacific Northwest) balancing data: Balancing Load (red) & Total wind (green), hydro (blue), thermal (brown)*
- *As displayed, pumped Hydro can use only part of its installed power capacity for regulation and wind power needs energy storage to operate efficiently*



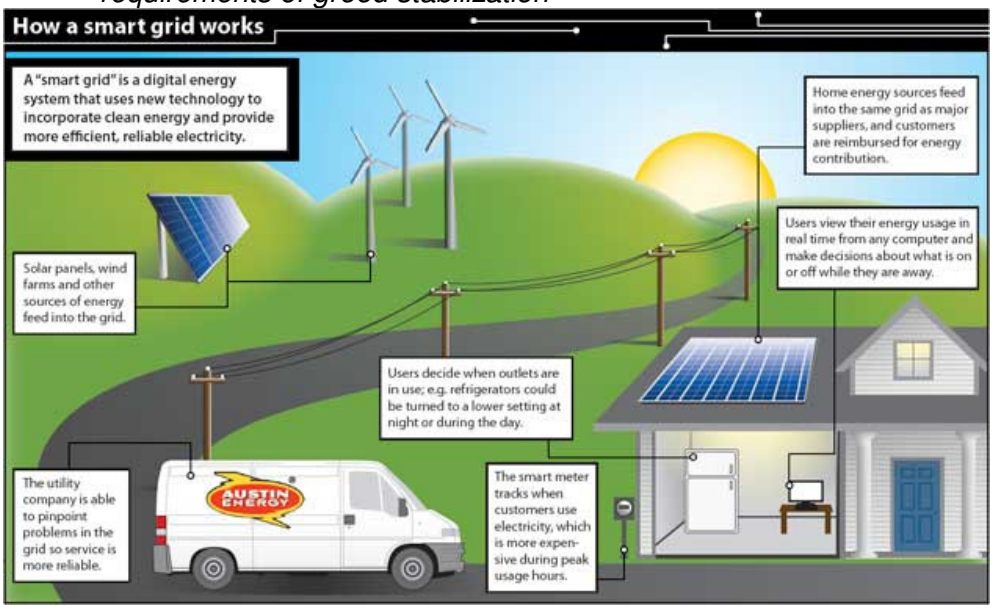
Energy storage requirements and application

- *Energy storage needs for electric greed stabilization and regulation according to 2010 DOE-EPRI publication .*
- *Note that as illustrate below the renewable energy (Wind and Solar) will require large variety of energy storage devises*



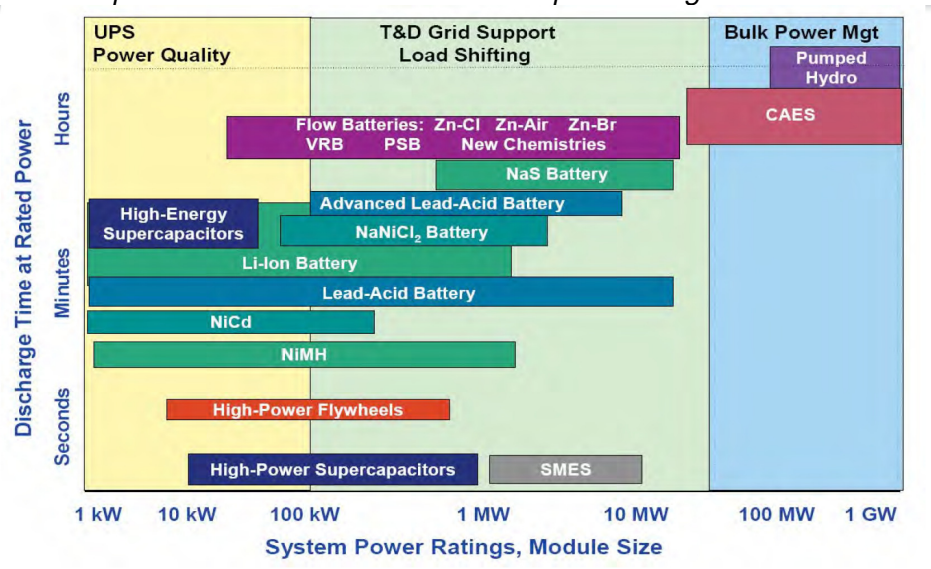
Smart greed basics

- *The smart greed application most likely will increase the requirements of greed stabilization*



Energy storage options according to DOE - EPRI 2010 review

- *Various energy storage technology options in terms of system power rating along the X-axis and duration of discharge time at rated power on the Y-axis. These comparisons are very general, many of the options have broader duration and power ranges than shown.*



Potential market of energy storage application

- *The estimated size of the potential market for 15 key energy storage applications on the horizontal axis and then shows the maximum price per kWh of storage capacity an end-user would be willing to pay on the vertical axis.*

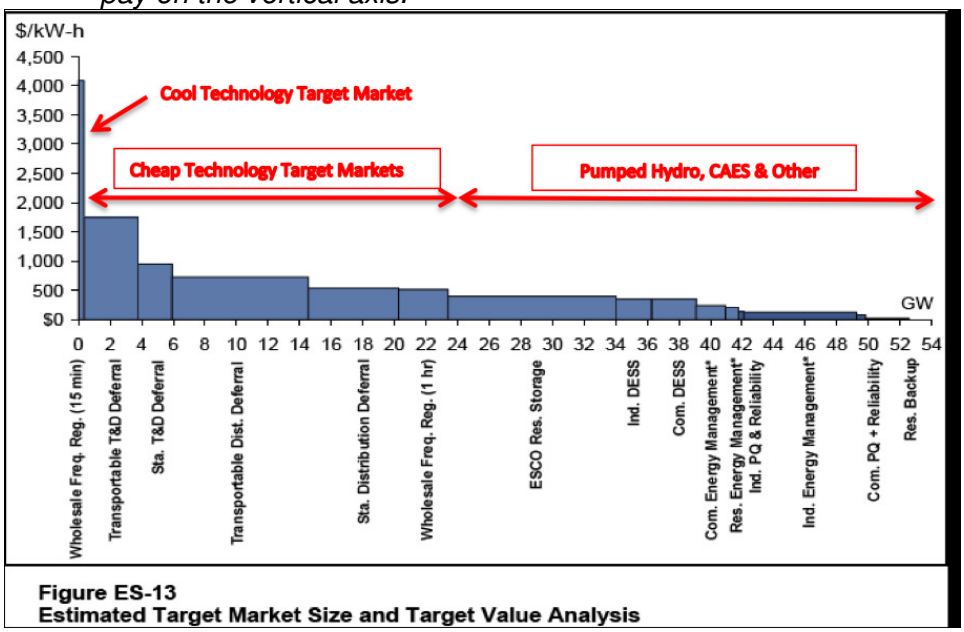
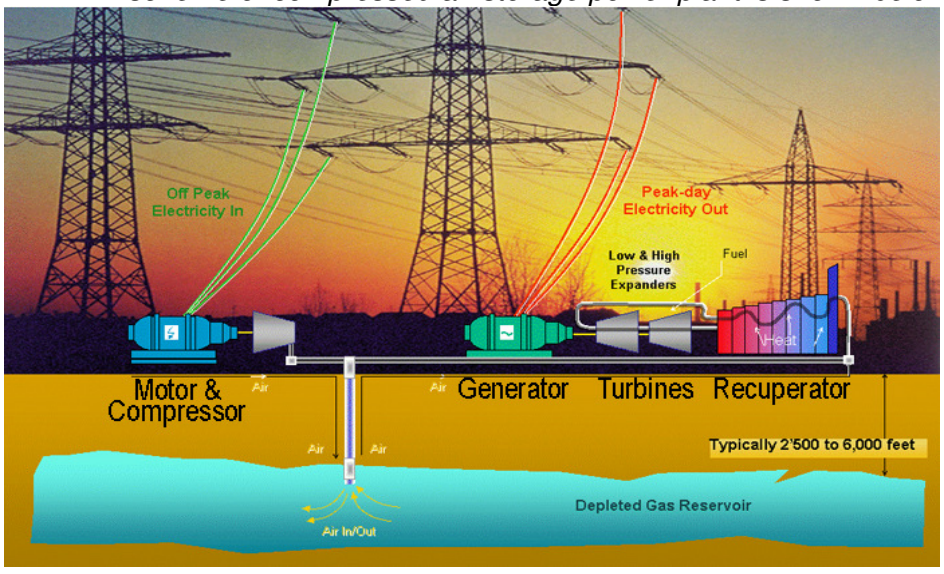


Figure ES-13
Estimated Target Market Size and Target Value Analysis

Pumped hydro alternative: Compressed air storage power plant

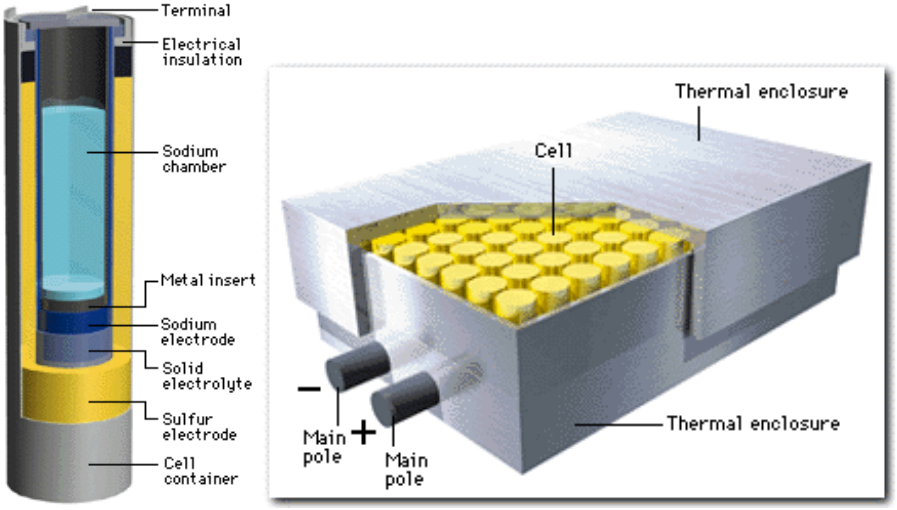
- *A scheme of compressed air storage power plant is shown below*



- *Alabama Electric Cooperative 110 MW McIntosh compressed air storage power plant*
- *Compressed air advantages: Long life & 50 years, 70-80 efficiency, more environment friendly than pumped hydro.*
- *Disadvantages: safety concerns*

Na-S energy storage battery

- *Sodium-sulfur cell (left) and sodium-sulfur battery module (right)*
- *Sodium-sulfure cell include Na negative electrode, S positive electrode and ceramic solid electrolyte. Operating temperature about 320oC*



- *General futures of Ns-S battery: cycle life +4,000 cycles, calendar life +15 years, C/3 charge-discharge rate.*

- *Below 2 MW Sodium-sulfur battery operating in IN, USA*

Advanced Lead acid batteries

- *Advanced lead acid batteries are also testing for electric greed regulation*
  - *Advantage, low cost, 90% round trip efficiency,*
  - *Disadvantage: God cycle life only at low DOD, calendar life not defined*
- *Below is 45T &1.5 MW/1MWh, Xtreme's advanced lead acid battery*

Flywheels energy storage devises

- *Beacon's flywheel rotor spins between 8,000 and 16,000 rpm and have charge/discharge efficiency 85 percent and expected life 20 years.*
- *At 16,000 rpm, a single Smart Energy 25 flywheel can deliver 25 kilowatt-hours (kWh) of extractable energy at a 100 kW power level for 15 minutes.*

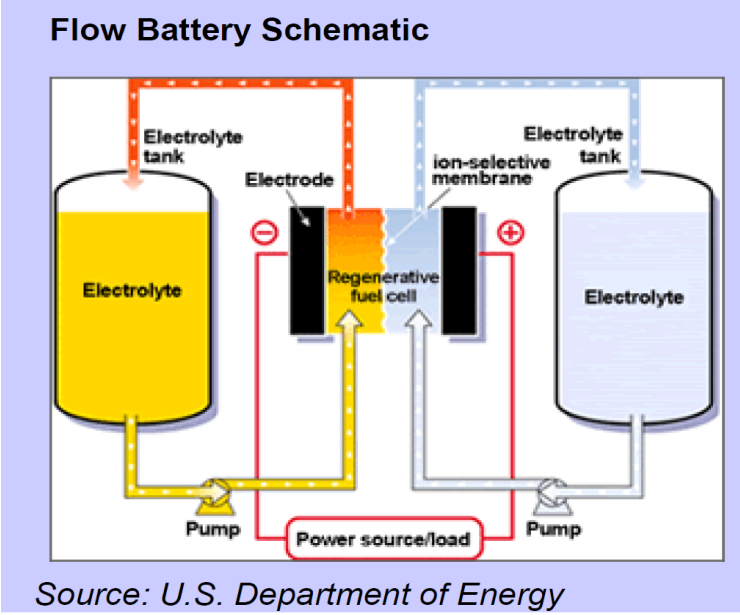
Flywheels energy storage devises

- *Beacon's 10 MW flywheel plant project. The plant consists of 100 Smart Energy 25 flywheels housed below ground in concrete*

cylinders (blue covers seen above), along with 10 steel containers (1 per MW) placed on concrete pads. The containers house electronics and communications equipment.

Vanadium redox flow battery

- *The VRB is a flow battery that uses liquid vanadium-based electrolytes, stored in external tanks that flow into a regenerative power cell, producing electric power electrochemically. A key advantage of the VRB is that more energy can be stored by simply increasing the size of the electrolyte tanks. The power is a function of the regenerative fuel cell and relatively lower.*
- *Disadvantage: low charge/discharge rate, low efficiency of about 50%*

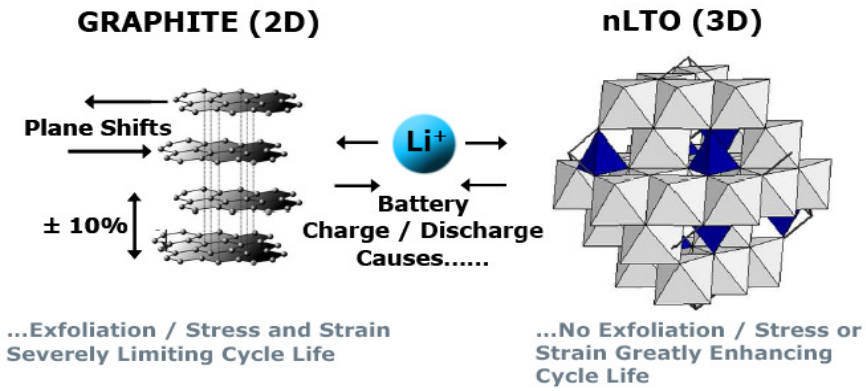


Source: U.S. Department of Energy

Altairnano nano-$Li_4T_5O_{12}$ lithium ion cell basics

- *Altairnano have developed large lithium ion battery using nano lithium titanate negative electrode instead graphite.*
- *The nano particles are integrated in large aggregates*
- *Cell with nano-$Li_4T_5O_{12}$ have very fast charge/discharge rate, response in msec. and improved safety and extremely long cycle and calendar life*

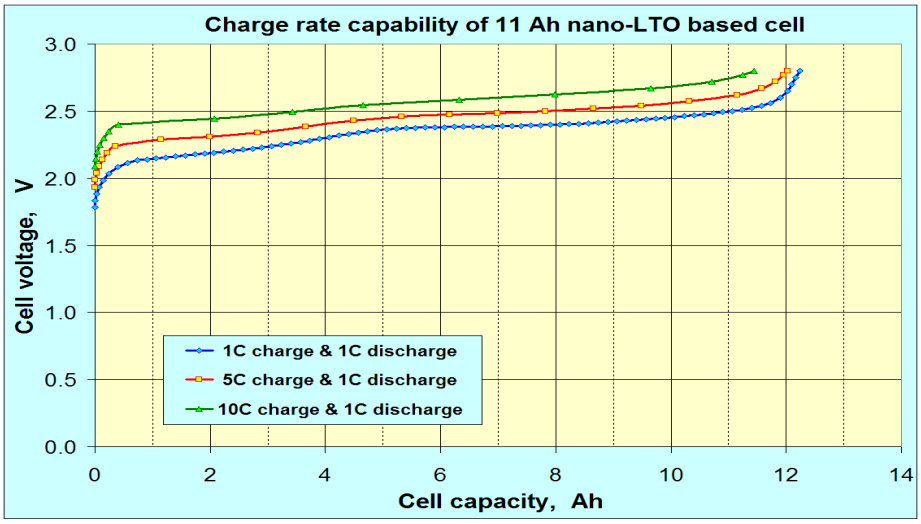
In typical lithium ion batteries, graphite undergoes life limiting stress.



Altairnano nano-$Li_4T_5O_{12}$ lithium ion cell performance

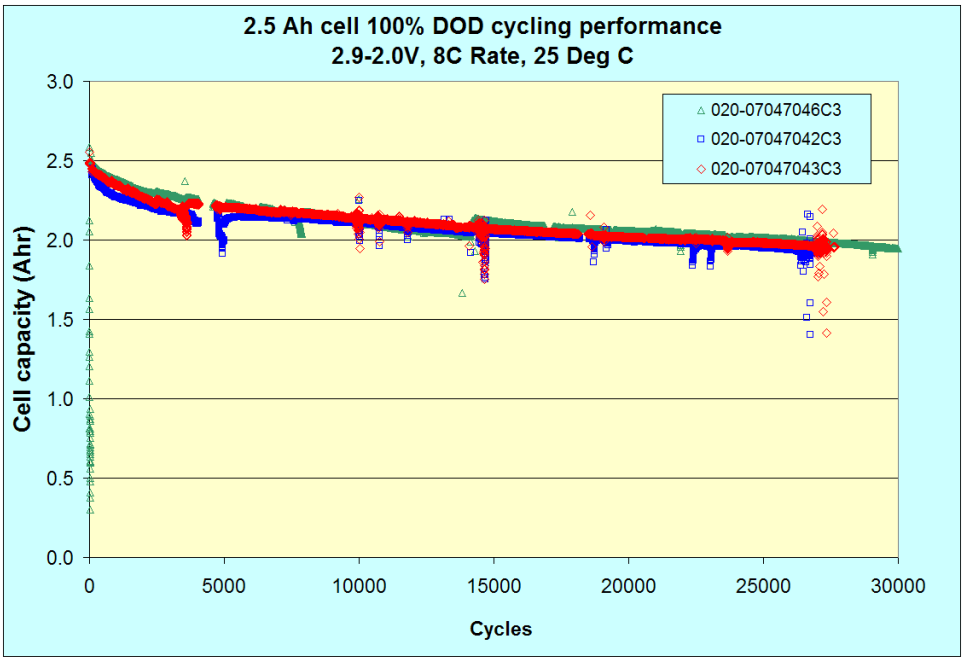
11 & 50 Ah energy storage cells charge rate capability

- *More than 90% capacity retention at 10C (6 min charge time) observed.*



Altairnano 2.5 Ah high power cell cycling performance

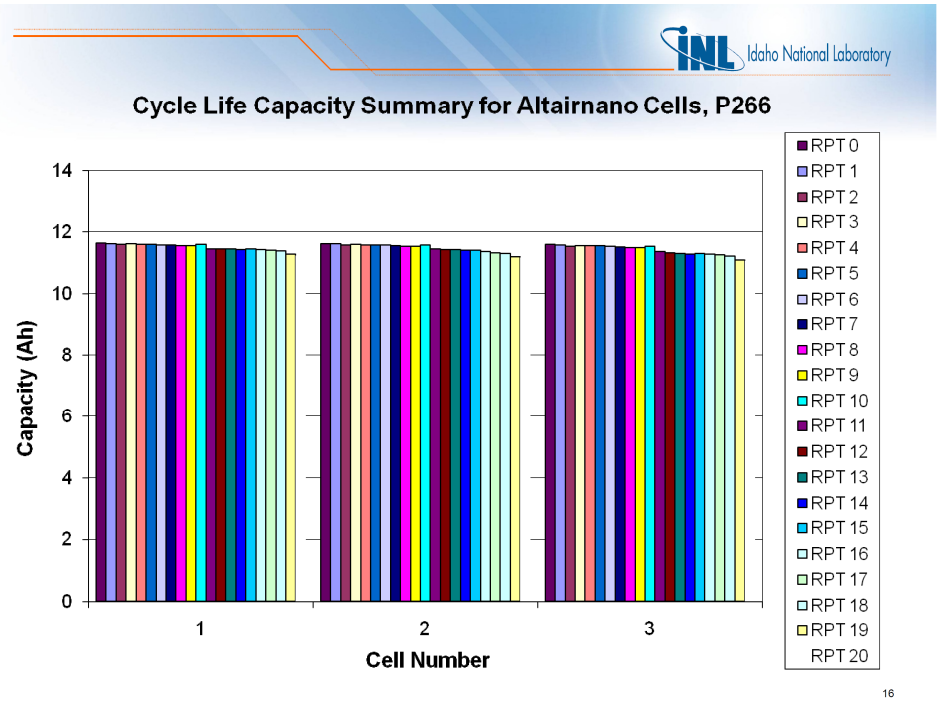
- *27,000 full 100% DOD cycles at 8C charge/discharge rate & 25oC observed*
  - *8C charge/discharge rate correspond to 7.5 min charge & 7.5 min discharge*



Altairnano 11 Ah Cells Third party test

INL & DOE test results of 11 Ah cells for PHEV-10 application

- *According to INL test data the 11 Ah cells have performed the required 5000 charge depleting cycles with only 4% capacity fade and 11% power fade.*
  - ✓ *After the 5000 charge depleting cycles the cell power is still 2.5 times larger than required.*



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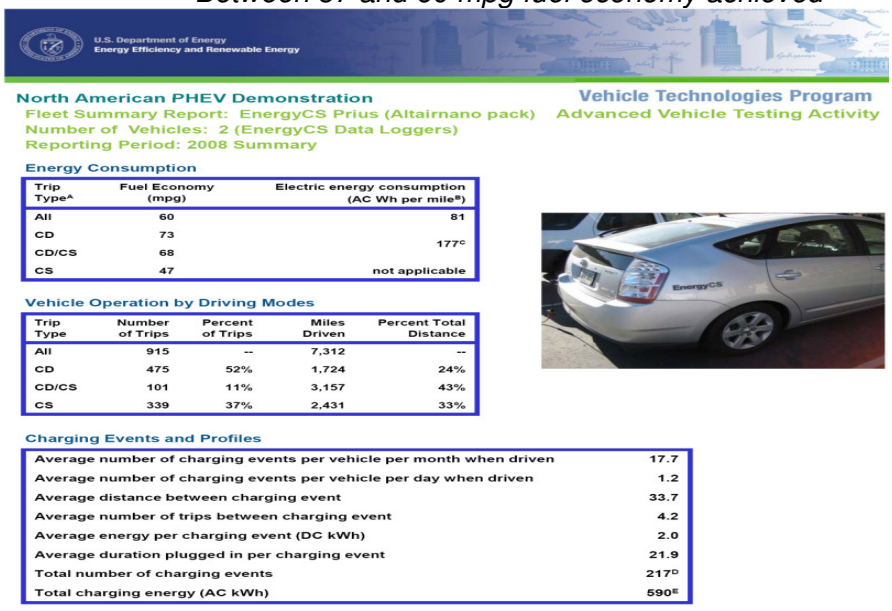
Altairnano PHEV Battery Demonstration

- *2008 and 2009 DOE performance reports of **2 EnergyCS Prius PHEV cars** using an Altairnano battery*
  - ✓ *Between 57 and 60 mpg fuel economy achieved*



- ***Proterra EcoRide™ 35' Hybrid & Battery-Electric Transit Bus*** *uses an Altairnano battery pack*

In April 2009, independent verification at the Altoona Test Track resulted in 17.5 to 29.5 MPG diesel fuel equivalent.

Altairnano Lithium ion batteries Stationary Power Application 1MW/250kWh Altairnano Energy Storage Systems (ALTI-ESS)

- *The Altairnano Energy Storage System (ALTI-ESS) consists of two major components, the Altairnano Power Module (ALTI-PM) and the Power Control System (PCS).*

Conclusions

- *The development of renewable energy system for electricity production is impede because of needs to be stabilized with nearly equivalent installed power of energy storage devices.*
- *The development of more electrical energy storage facilities will be extremely important for electricity generation in the future.*
- *Using hydro pumping, combined with a long life & fast charge/discharge rate, highly efficient cotemporary power energy storage as Altairnano lithium ion battery, currently is seems to be the best solution for fast penetration rate of wind and solar energy systems.*

One proof of analytic representation of distributions of several variables

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Abstract. *In this article we present one proof for the analytic representation of distributions of several variables. For simplicity we give the detailed proof for two variables.*

1. INTRODUCTION

The base functions in the analytic representation of distributions of several variables are the Cauchy and the Poisson kernels

$$K(z-t)=\frac{1}{(2\pi i)^n}\prod_{j=1}^{n}\frac{1}{t_j-z_j} \text{ where } z_j=x_j+iy_j \ , \ \operatorname{Im} z_j\neq 0$$
$$j=1,2,...,n$$

$$P(z,t)=\operatorname{sgn} y\frac{y_1...y_n}{\pi^n}\prod_{j=1}^{n}\frac{1}{\left|t_j-z_j\right|^2} \ , \ y=(y_1,...,y_n) \ ,$$

$$\operatorname{sgn} y=\operatorname{sgn} y_1...\operatorname{sgn} y_n$$

Let $f(t_1,...,t_n)$ be a bounded measurable function on R^n. Then the function

$$f^*(z)=\operatorname{sgn} y\frac{y_1...y_n}{\pi^n}\int_{R^n}f(t)\prod_{j=1}^{n}\frac{1}{\left|t_j-z_j\right|^2}dt_1...dt_n$$

is n-harmonic function if $\operatorname{Im} z_j\neq 0$, $j=1,2,...,n$ and

$$\sup_z\left|f^*(z)\right|\leq\sup_t\left|f(t)\right|$$

We use the spaces $O_{\alpha_1,...,\alpha_n}$ and the dual spaces $O'_{\alpha_1,...,\alpha_n}$

This spaces are given in (1)

If $T \in O'_{0,...,0}$ then

$$T^*(z) =< T, P(t,z) > .$$

It is clear that the Cauchy kernel belongs to the space $O_{-1,...,-1}$ for $\operatorname{Im} z_j \neq 0$, $j = 1,2,...,n$, hence the function

$$\hat{T}(z) =< T, \frac{1}{(2\pi i)^n} \prod_{j=1}^{n} \frac{1}{t_j - z_j} >$$

exists if $T \in O'_{-1,...,-1}$

Also the function $T^*(z)$ we may present in the following way

$$T^*(z) = \hat{T}(z_1,...,z_n) + ... + (-1)^n \hat{T}\left(\bar{z}_1,...,\bar{z}_n\right)$$

where the sign is determined with the numbers of conjugate complex numbers.

The numbers of adding in the above decomposition is

$$\binom{n}{0} + ... + \binom{n}{n} = (1+1)^n = 2^n$$

For the proof of the analytic representation we consider the space $O_{\alpha_1,...,\alpha_n}$ where $\alpha_1 = ... = \alpha_n = -1$

Let T be a distribution of the space O'_{α}, and let we consider the function

$$\hat{T}(z) = \frac{1}{(2\pi i)^n} < T, \frac{1}{(t_1 - z_1)...(t_n - z_n)} > \qquad (1)$$

where $t = (t_1,...,t_n)$, $z = (z_1,...,z_n)$ $z_j = x_j + iy_j$, $\operatorname{Im} z_j \neq 0$.

As in the one-dimensional case is proved that the function $\hat{T}(z)$ is analytic of each complex variables z_j, and by the Harthogs theorem implies that the function $\hat{T}(z)$ is analytic function of $n-$complex variables in the region $\operatorname{Im} z_j \neq 0$, $j = 1,...,n$ in C^n.

Now for simplicity we give the proof in two-dimensional case.

Theorem1. Suppose that $T \in O'_{-1,-1}$, then the function

$$\hat{T}(z) = \frac{1}{(2\pi i)^2} < T, \frac{1}{(t_1 - z_1)(t_2 - z_2)} >$$

is analytic representation for the distribution T.

Proof. In the four octants in the space C^2 we consider the following functions

$$\begin{aligned} &\hat{T}(x_1 + i\varepsilon_1, x_2 + i\varepsilon_2) && \hat{T}(x_1 - i\varepsilon_1, x_2 + i\varepsilon_2) \\ &\hat{T}(x_1 + i\varepsilon_1, x_2 - i\varepsilon_2) && \hat{T}(x_1 - i\varepsilon_1, x_2 - i\varepsilon_2) \end{aligned} \tag{2}$$

where $\varepsilon_1, \varepsilon_2 > 0$.

Since the four functions are continuous they determine regular distributions to the space $D'(R^2)$.

First we consider the distribution $\hat{T}(x_1 + i\varepsilon_1, x_2 + i\varepsilon_2)$. Let $\phi \in D$, then we have

$$< \hat{T}(x_1 + i\varepsilon_1, x_2 + i\varepsilon_2), \phi(x_1, x_2) >= \iint_{R^2} \hat{T}(x_1 + i\varepsilon_1, x_2 + i\varepsilon_2)\phi(x_1, x_2)dx_1 dx_2 .$$

Since the integral is Riemann we may approach to the Riemann sum i.e.

$$\iint_{R^2} \hat{T}(x_1 + i\varepsilon_1, x_2 + i\varepsilon_2)\phi(x_1, x_2)dx_1 dx_2 =$$

$$= \lim_{n,k\to\infty} \sum_{i,j=1}^{n,k} \hat{T}(x_i + i\varepsilon_1, x_j + i\varepsilon_2)\phi(x_i, x_j)\Delta x_i \Delta x_j =$$

$$= \lim_{n,k\to\infty} \sum_{i,j=1}^{n,k} \frac{1}{(2\pi i)^2} < T, \frac{\phi(x_i, x_j)\Delta x_i \Delta x_j}{(t_1 - x_i - i\varepsilon_1)(t_2 - x_j - i\varepsilon_2)} >=$$

$$= \frac{1}{(2\pi i)^2} \lim_{n,k\to\infty} < T, \sum_{i,j=1}^{n,k} \frac{\phi(x_i, x_j)\Delta x_i \Delta x_j}{(t_1 - x_i - i\varepsilon_1)(t_2 - x_j - i\varepsilon_2)} >$$

(since T is linear)

Now we consider the functions

$$\psi_{n,k}(t_1,t_2)=\sum_{i,j=1}^{n,k}\frac{\phi(x_i,x_j)\Delta x_i\Delta x_j}{(t_1-x_i-i\varepsilon_1)(t_2-x_j-i\varepsilon_2)} \tag{3}$$

When n and k are change throughout the set of nonnegative integers, for fixed $\varepsilon_1,\varepsilon_2>0$ we have the countable set of functions for which we will prove that is uniformly bounded and equicontinuous on every compact set of R^2

Since ϕ has compact support there exits $L>0$ such that $\operatorname{supp}\phi\subset[-L,L]\times[-L,L]$, and we give

$$\left|\psi_{n,k}(t_1,t_2)\right|\le\sum_{i,j=1}^{n,k}\frac{\left|\phi(x_i,x_j)\right|\Delta x_i\Delta x_j}{\left|t_1-x_i-i\varepsilon_1\right|\cdot\left|t_2-x_j-i\varepsilon_2\right|}\le\frac{M\,4L^2}{\varepsilon_1\varepsilon_2}$$

where $M=\sup_{x_1,x_2}\left|\phi(x_1,x_2)\right|$

From above we proved that the functions are uniformly bounded.
Now we will prove that the functions are equicontinuous

$$\left|\psi_{n,k}(t_1',t_2')-\psi_{n,k}(t_1,t_2)\right|\le$$

$$\le\sum_{i,j}^{n,k}\left|\phi(x_i,x_j)\right|\Delta x_i\Delta x_j\left|\frac{1}{(t_1'-x_i-i\varepsilon_1)(t_2'-x_j-i\varepsilon_2)}-\frac{1}{(t_1-x_i-i\varepsilon_1)(t_2-x_j-i\varepsilon_2)}\right|\le$$

$$\le\frac{4L^2M}{\varepsilon_1^2\varepsilon_2^2}\left[\left|t_1'-t_1\right|\left|t_2\right|+\left|t_1'\right|\left|t_2'-t_2\right|+\varepsilon_1\left|t_2'-t_2\right|+\varepsilon_2\left|t_1'-t_1\right|+L\left|t_2'-t_2\right|+L\left|t_1'-t_1\right|\right].$$

From this estimate implies that the functions are equicontinuous on given compact set.

For fixed t_1,t_2 the Riemann sums converges to the integral

$$\iint_{R^2}\frac{\phi(x_1,x_2)dx_1dx_2}{(t_1-x_1-i\varepsilon_1)(t_2-x_2-i\varepsilon_2)}\ \text{as}\ n,k\to\infty$$

and by Arzela –Ascoli theorem implies that the convergence is uniform on every compact set.

Similarly we give that the functions $\left(D^{\alpha}\psi_{n,k}\right)$ converges uniformly on any compact set.

Since $\psi_{n,k}$ belongs to the space $O_{-1,-1}$, it follows that the functions $\psi_{n,k}$ converges to the functions $\psi_{\varepsilon_1,\varepsilon_2}$ in the sense of $O_{-1,-1}$, where

$$\psi_{\varepsilon_1,\varepsilon_2}(t_1,t_2)=\iint_{R^2}\frac{\phi(x_1,x_2)dx_1dx_2}{(t_1-x_1-i\varepsilon_1)(t_2-x_2-i\varepsilon_2)} \tag{4}$$

It is obviously that the functions $\psi_{\varepsilon_1,\varepsilon_2}$ for $\varepsilon_1,\varepsilon_2>0$ belongs to the space $O_{-1,-1}$.

Now we consider the functions $\psi_{\varepsilon_1,\varepsilon_2}$, if we set $u=t_1-x_1$, $v=t_2-x_2$ then we have

$$\psi_{\varepsilon_1,\varepsilon_2}(t_1,t_2)=\iint_{R^2}\frac{\phi(t_1-u,t_2-v)dudv}{(u-i\varepsilon_1)(v-i\varepsilon_2)}$$

The functions $\psi_{\varepsilon_1,\varepsilon_2}$ are convolutions of the regular distributions $\frac{1}{(u-i\varepsilon_1)(v-i\varepsilon_2)}$ and the function $\phi(x_1,x_2)$. This functions belongs to the space E (space of infinity differentiable functions on R^2).

Now we will show that the functions $\psi_{\varepsilon_1,\varepsilon_2}$ converges in the space $O_{-1,-1}$ as $\varepsilon_1,\varepsilon_2\to 0$. We consider the integral

$$\iint_{R^2}\frac{\phi(t_1-u,t_2-v)}{(u-i\varepsilon_1)(v-i\varepsilon_2)}dudv=\iint_{|u|\le 1,|v|\le 1}\frac{\phi(t_1-u,t_2-v)-\phi(t_1,t_2)}{(u-i\varepsilon_1)(v-i\varepsilon_2)}dudv+$$

$$=\phi(t_1,t_2)\iint_{|u|\le 1,|v|\le 1}\frac{1}{(u-i\varepsilon_1)(v-i\varepsilon_2)}dudv+\int_{|u|>1}\int_{|v|>1}\frac{\phi(t_1-u,t_2-v)}{(u-i\varepsilon_1)(v-i\varepsilon_2)}dudv.$$

By the mean value theorem for the functions of several variables we have that the first integral converges as $\varepsilon_1,\varepsilon_2\to 0$.

We know that the convergence of separately integrals implies convergence of double integral thus the integral

$$\iint\limits_{|u|\le 1,|v|\le 1} \frac{dudv}{(u-i\varepsilon_1)(v-i\varepsilon_2)} = \int\limits_{-1}^{1} \frac{du}{u-i\varepsilon_1} \int\limits_{-1}^{1} \frac{dv}{v-i\varepsilon_2},$$

converge.

The convergence of the last integral is obviously.

On the other hand

$$\lim_{\varepsilon_1\to 0}\lim_{\varepsilon_2\to 0} \iint\limits_{R^2} \frac{\phi(t_1-u,t_2-v)dudv}{(u-i\varepsilon_1)(v-i\varepsilon_2)} =$$

$$= \lim_{\varepsilon_1\to 0} \int\limits_{-\infty}^{\infty} \frac{du}{u-i\varepsilon_1}\left[i\pi\delta_v\phi(t_1-u,t_2-v) + vp\frac{1}{v}\phi(t_1-u,t_2-v)\right] =$$

$$= (i\pi)^2(\delta_u\otimes\delta_v)\phi(t_1-u,t_2-v) + i\pi vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v) +$$

$$+ i\pi\delta_u\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v) + vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v).$$

From above we proved that the functions $\psi_{\varepsilon_1,\varepsilon_2}(t_1,t_2)$ converges to the function

$$\psi(t_1,t_2) = (i\pi)^2(\delta_u\otimes\delta_v)\phi(t_1-u,t_2-v) + i\pi vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v) +$$
$$+ i\pi\delta_u\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v) + vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v) \qquad (5)$$

as $\varepsilon_1,\varepsilon_2\to 0$, where we know that vp denote the Cauchy principal value and $\otimes$ denote the tensor product.

We proved that the regular distribution $\frac{1}{(u-i\varepsilon_1)(v-i\varepsilon_2)}$ weakly converges to the distribution

$$(i\pi)^2(\delta_u\otimes\delta_v) + i\pi vp\frac{1}{u}\otimes\delta_v + i\pi\delta_u\otimes vp\frac{1}{v} + vp\frac{1}{u}\otimes vp\frac{1}{v}.$$

But since weak convergence implies strong convergence of distributions it follows that the functions $\psi_{\varepsilon_1,\varepsilon_2}$ converges to the function (5) in the space $O_{-1,-1}$.

Thus for the regular distribution $\hat{T}(x_1+i\varepsilon_1, x_2+i\varepsilon_2)$ holds the following relation

$$\lim_{\varepsilon_1,\varepsilon_2\to 0}\iint_{R^2}\hat{T}(x_1+i\varepsilon_1, x_2+i\varepsilon_2)\phi(x_1,x_2)dx_1dx_2 =$$

$$=<T,\frac{1}{4}(\delta_u\otimes\delta_v)\phi(t_1-u,t_2-v))>+<T,\frac{1}{4\pi i}vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)>+$$

$$+<T,\frac{1}{4\pi i}\delta_u\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)>+<T,\frac{1}{(2\pi i)^2}vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)> \quad (6)$$

Similarly

$$\lim_{\varepsilon_1,\varepsilon_2\to 0}\iint_{R^2}\hat{T}(x_1-i\varepsilon_1, x_2-i\varepsilon_2)\phi(x_1,x_2)dx_1dx_2 =$$

$$=<T,\frac{1}{4}(\delta_u\otimes\delta_v)\phi(t_1-u,t_2-v))>+<T,-\frac{1}{4\pi i}vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)>+$$

$$+<T,-\frac{1}{4\pi i}\delta_u\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)>+<T,\frac{1}{(2\pi i)^2}vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)> \quad (7)$$

$$\lim_{\varepsilon_1,\varepsilon_2\to 0}\iint_{R^2}-\hat{T}(x_1-i\varepsilon_1, x_2+i\varepsilon_2)\phi(x_1,x_2)dx_1dx_2 =$$

$$=<T,\frac{1}{4}(\delta_u\otimes\delta_v)\phi(t_1-u,t_2-v))>+<T,\frac{1}{4\pi i}vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)>+$$

$$+<T,-\frac{1}{4\pi i}vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)>+<T,-\frac{1}{(2\pi i)^2}vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)> \quad (8)$$

$$\lim_{\varepsilon_1,\varepsilon_2\to 0}\iint_{R^2}\hat{T}(x_1+i\varepsilon_1, x_2-i\varepsilon_2)\phi(x_1,x_2)dx_1dx_2 =$$

$$=< T,\frac{1}{4}(\delta_u \otimes \delta_v)\phi(t_1-u,t_2-v))> + < T,-\frac{1}{4\pi i} vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)> +$$

$$+ < T,\frac{1}{4\pi i} vp\frac{1}{u}\otimes\delta_v\phi(t_1-u,t_2-v)> + < T,-\frac{1}{(2\pi i)^2} vp\frac{1}{u}\otimes vp\frac{1}{v}\phi(t_1-u,t_2-v)>$$

(9)

Finally, from (6), (7), (8), and (9) we have

$$\lim_{\varepsilon_1,\varepsilon_2\to 0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\hat{T}(x_1+i\varepsilon_1,x_2+i\varepsilon_2)-\hat{T}(x_1-i\varepsilon_1,x_2+i\varepsilon_2)\right]\phi(x_1,x_2)dx_1dx_2 +$$

$$+\lim_{\varepsilon_1,\varepsilon_2\to 0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\hat{T}(x_1+i\varepsilon_1,x_2-i\varepsilon_2)-\hat{T}(x_1-i\varepsilon_1,x_2-i\varepsilon_2)\right]\phi(x_1,x_2)dx_1dx_2 =< T,\phi >$$

Thus the functions

$$f_1(z_1,z_2)=\frac{1}{(2\pi i)^2}< T,\frac{1}{(t_1-z_1)(t_2-z_2)}> \text{ for } \operatorname{Im} z_1>0,\operatorname{Im} z_2>0$$

$$f_2(z_1,z_2)=-\frac{1}{(2\pi i)^2}< T,\frac{1}{(t_1-z_1)(t_2-z_2)}> \text{ for } \operatorname{Im} z_1<0,\operatorname{Im} z_2>0$$

$$f_3(z_1,z_2)=-\frac{1}{(2\pi i)^2}< T,\frac{1}{(t_1-z_1)(t_2-z_2)}> \text{ for } \operatorname{Im} z_1>0,\operatorname{Im} z_2<0$$

$$f_4(z_1,z_2)=\frac{1}{(2\pi i)^2}< T,\frac{1}{(t_1-z_1)(t_2-z_2)}> \text{ for } \operatorname{Im} z_1<0,\operatorname{Im} z_2<0$$

are analytic representation of the distribution T.

Example: Let we consider the Dirac two dimensional distribution. We know that this has the Cauchy representation

$$\hat{\delta}(z_1,z_2)=\frac{1}{(2\pi i)^2}<\delta,\frac{1}{(t_1-z_1)(t_2-z_2)}>=\frac{1}{(2\pi i)^2}\frac{1}{z_1z_2}$$

More precisely the functions

$$f_1(z_1,z_2)=\frac{1}{(2\pi i)^2}\frac{1}{z_1z_2} \quad \text{for } \operatorname{Im} z_1>0,\operatorname{Im} z_2>0$$

$$f_2(z_1,z_2)=-\frac{1}{(2\pi i)^2}\frac{1}{z_1 z_2} \quad \text{for } \operatorname{Im} z_1>0, \operatorname{Im} z_2<0$$

$$f_3(z_1,z_2)=-\frac{1}{(2\pi i)^2}\frac{1}{z_1 z_2} \quad \text{for } \operatorname{Im} z_1<0, \operatorname{Im} z_2>0$$

$$f_4(z_1,z_2)=\frac{1}{(2\pi i)^2}\frac{1}{z_1 z_2} \quad \text{for } \operatorname{Im} z_1<0, \operatorname{Im} z_2<0$$

The singular points for the function belong to the union of two dimensional regions i.e.

$$\{(z_1,z_2): z_1=0\}\cup\{(z_1,z_2): z_2=0\}.$$

On the other hand the support of the Dirac distribution is the point $(0,0)$. Thus the set of singular points not is equal to the support of δ, which is equal in one dimensional case. But this fact for several dimensions representations is not connected with the

choice of determined representation.

Analytic functions of n-complex variables $n>1$ have not singular points. The following assertion is true:

If the function $f(z)$ is analytic out of the bounded set A and $n>1$ then the function $f(z)$ may be analytic continued on the set A.

Consequently, if the distribution has compact support, it is impossible that the support contains singular points for the function which is analytic continuation one to other two in 2^n-octants of the space C^n and which functions give the analytic representation for the distribution T.

Remark. In the proof are given also several boundary values relations of distributions which are also of interest.

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On a Mathematical Model Describing the Immunological Response to Virus

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Abstract*: A mathematical model of immune response to viral infection is proposed and analyzed. The model is developed in the framework of the kinetic theory of active particles. It is formulated as a bilinear system of integro-differential equations of Boltzmann type. Results of numerical experiments are presented.*

Keywords: *Numerical modelling, kinetic theory of active particles, integro-differential equations, nonlinear dynamics, virus, humoral immunity.*

1. INTRODUCTION

In this paper we develop and analyze numerically a recently proposed model of humoral immune response to viral infection [2]. The model is formulated as a system of partial integro-differential equations. It is developed within the framework of the kinetic theory of active particles [1].

The kinetic models describe the dynamics of the statistical distributions over the microscopic inner state of the populations of interacting individuals. The internal state variable u describes their biological activity or ability to express their main functions. The distribution density of the population labelled by the index i at time t is denoted by:

$f_i(t,u), f_i : [0,\infty)\times[0,1] \to R^+.$

The concentrations of the individuals belonging to population i are denoted by:

$$(1)\quad n_i(t) = \int_0^1 f_i(t,u)du, n_i : [0,\infty) \to R^+.$$

The present model describes the so-called humoral immunity, which is one of the most important parts of the adaptive immunity. The humoral response of an organism is performed mainly by antibodies (ABs) (immunoglobulins) which are produced by B lymphocytes. The antibodies are able to destroy free virus particles which invade the host body. The viruses can enter the susceptible cells and use their metabolic machinery in

order to produce new virus particles that may leave the infected cells. The viral particles can destroy some of the host cells.

Another important part of the adaptive immunity is called cellular (or cell-mediated) immunity. It is performed mainly by T cells, divided into the subpopulations of T helper cells and cytotoxic T lymphocytes (CTLs). The role of the T helper cells is to activate other immune cells while CTLs are able to destroy infected cells of the host organism [4].

2. DESCRIPTION OF THE MATHEMATICAL MODEL

We present a generalized model of the kinetic model describing the humoral response to virus proposed in [2]. The model is the following bilinear system of Boltzmann type integro-differential equations:

$$(2)\quad \frac{dn_1}{dt}(t) = S_1(t) - d_{13}n_1(t)\int_0^1 vf_3(t,v)dv - d_{11}n_1(t),$$

$$(3)\quad \frac{\partial f_2}{\partial t}(t,u) = p_{13}^{(2)}(1-u)n_1(t)\int_0^1 vf_3(t,v)dv - d_{22}f_2(t,u) + c_{22}(2\int_0^u (u-v)f_2(t,v)dv - (1-u)^2 f_2(t,u)),$$

$$(4)\quad \frac{\partial f_3}{\partial t}(t,u) = p_{22}^{(3)}\int_0^1 vf_2(t,v)dv - d_{34}f_3(t,u) - \int_0^1 vf_4(t,v)dv - d_{33}f_3(t,u),$$

$$(5)\quad \frac{\partial f_4}{\partial t}(t,u) = S_4(t) + p_{34}^{(4)}(1-u)\int_0^1 f_3(t,v)dv\int_0^1 f_4(t,v)dv - d_{44}f_4(t,u),$$

where all parameters are assumed to be nonnegative and $p_{13}^{(2)} = 2d_{13}$. The model describes the interactions between the following four populations:

- susceptible uninfected cells denoted by the label 1;
- infected cells denoted by the label 2;
- free virus particles denoted by the label 3;
- antibodies denoted by the label 4.

The activation state of populations denoted by $i \in \{2,3,4\}$ is assumed to be a variable $u \in [0,1]$.

The activation state of the population of infected cells is assumed to describe the destruction rate of the infected cell by virus as well as the reproduction rate of virus particles inside the infected cells. The cells that are infected by cytopathic (i.e. very aggressive) virus possess higher

activation states (i.e. values of u close to 1). Also, more active infected cells are assumed to produce higher amount of new viruses.

The activation state of the population of virus particles denotes the capability of the virus to infect susceptible cells. The higher the ability of a free virus particle to enter a host cell is, the higher its activation state is.

Further, we assume that the activation state of the population of antibodies expresses their ability to destroy virus particles and to lower their activation states.

In the present model, we suppose for simplicity that the distribution function of the population labelled by $i = 1$ of uninfected cells is independent of their activation states, i.e.

$$f_1(t,u) = n_1(t), \forall u \in [0,1], t \geq 0.$$

Equation (2) of the modelling system describes the evolution of the concentration $n_1(t)$ of the uninfected cells. The following processes are taken into account:

- the proliferation of uninfected cells described by the function $S_1(t)$;
- the natural death of the uninfected cells described by the loss term corresponding to the parameter d_{11};
- the infection of uninfected cells by virus particles described by the term corresponding to the parameter d_{13}.

Equation (3) describes the temporary dynamics of the distribution density $f_2(t,u)$ of the infected cells. We suppose that the activation state of the newly infected cells is low and thus introduce the factor *(1 – u)* in the gain term corresponding to the parameter $p_{13}^{(2)}$. Further, the destruction of infected cells by virus particles is described by the loss term corresponding to the parameter d_{22}. Finally, the possible increase in the activation state of the infected cells due to the replication of the virus inside the infected cells is described by the conservative term corresponding to the parameter c_{22}. The relationship $p_{13}^{(2)} = 2d_{13}$ assures that the terms describing the concentration of the infected cells (the corresponding loss term in Eq. (2) and gain term in Eq. (3)) give equal amount of cells.

Equation (4) describes the temporary dynamics of the distribution density $f_3(t,u)$ of the free virus particles. The following processes are taken into account:

- the reproduction of viral particles described by the gain term corresponding to the parameter $p_{22}^{(3)}$;
- the natural death of the virus particles described by the loss term corresponding to the parameter d_{33};

- the destruction of viral particles by antibodies described by the loss term corresponding to the parameter d_{34}.

Equation (5) describes the temporary dynamics of the distribution density $f_4(t,u)$ of the population of antibodies. The following processes are taken into account:

- the production of ABs described by the gain term corresponding to the parameter $p_{34}^{(4)}$ (here it is assumed that the activity of the newly produced ABs is low);
- the influx of antibodies, e.g. due to medical treatment, described by the function $S_4(t)$;
- the natural death of ABs described by the loss term corresponding to the parameter d_{44}.

3. NUMERICAL RESULTS AND DISCUSSIONS

The modelling system (2)-(5) composed of partial differential equations has been discretized, more precisely, the state of activity *u* was discretized over a suitable set of uniform grid-points. The values of integrals were approximated by the composite Simpson formula. The resulting system of ordinary differential equations was solved by the code ode15s from the Matlab ODE suite [3]. The temporary dynamics of the concentration $n_1(t)$ of uninfected cells is presented in Fig. 1.The concentrations $n_i(t)$ of populations $i \in \{2,3\}$ of infected cells and free virus particles were computed from the obtained approximate solutions for $f_i(t,u)$ by using Eq. (1). The results for the infected cells are presented in Fig. (2).

System (2)-(5) has to be supplemented by initial conditions. We have performed numerical experiments with the following initial values and values of parameters:

$$n_1(0) = 1, f_2(0,u) = 0, f_3(0,u) = f_4(0,u) = 0.1, \forall u \in [0,1],$$

$$S_1(t) = 100, \forall t \geq 0,$$

$$d_{11} = d_{33} = d_{34} = d_{44} = p_{22}^{(3)} = p_{34}^{(4)} = 100, d_{13} = 115, d_{22} = 55, c_{22} = 15.$$

We present the results of our numerical simulations for three different choices of the function $S_4(t)$ as constants, namely:

$$S_4(t) = 0; S_4(t) = 1; S_4(t) = 10, \forall t \geq 0.$$

This choice of the function $S_4(t)$ allows us to investigate the ability of additional source of antibodies to destroy the viral particles and to clear the infection in cases when without such an influx of ABs the humoral response

is not successful. The numerical experiments show, that when there is no influx of antibodies ($S_4(t)=0$) or it is not very high ($S_4(t)=1$), the humoral immune response is not able to clean the aggressive viral infection. On the other side, in cases when there is higher influx of ABs (e.g., $S_4(t)=10$), the humoral response is successful in the fight against the infection. These cases are illustrated in Figs. (1)-(2).

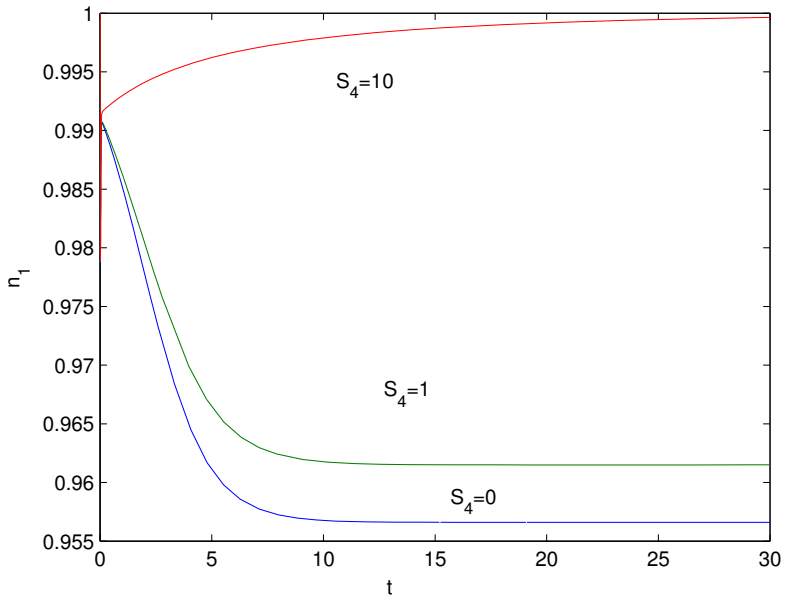

Fig. 1: Dynamics of the uninfected cells for values $S_4(t)=0$, $S_4(t)=1$ and $S_4(t)=10$.

4. CONCLUSIONS

In the present paper we analysed numerically the role of additional influx of antibodies in the competition between virus infection and humoral immunity. This role is important and therefore the medical treatment approach using such an influx can be successful for cleaning various viral infections.

Our future work will address the further development and analysis of the proposed mathematical model as well as its comparison with other modelling approaches.

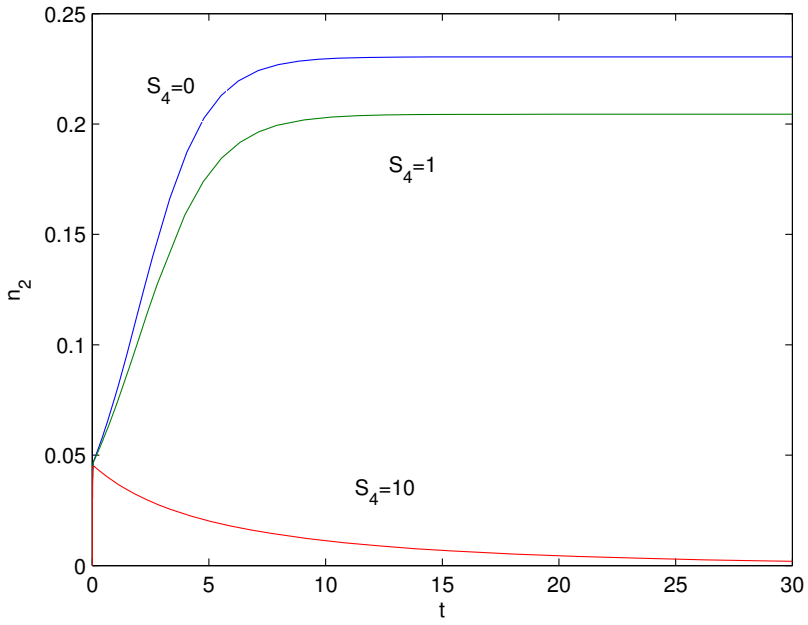

Fig. 2: Dynamics of the infected cells for values $S_4(t) = 0$, $S_4(t) = 1$ and $S_4(t) = 10$.

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FEW RESULTS ON WEAK ORBITS UNDER SEQUENCES OF OPERATORS

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Abstract: *In this paper we give a brief survey of the results about the behavior of the weak orbits under sequences of bounded linear operators acting on an infinite-dimensional complex Banach spaces. These results, along with some additional assumptions, imply that the direct product of the underlying space with its dual space, endowed with the product topology, contains a dense set of pairs each having a weak orbit tending to infinity under every operator in a given sequence of operators.*

Keywords: *Banach spaces, bounded linear operators, weak orbits.*

1 INTRODUCTION

Let X denote a complex, infinite-dimensional Banach space, $B(X)$ the algebra of all bounded linear operators on X and X^* the dual space of X. For a vector $x \in X$ and a bounded linear functional $x^* \in X^*$, $\langle x, x^* \rangle$ will denote the number $x^*(x)$.

A *weak orbit* of the pair $(x, x^*) \in X \times X^*$ under the operator $T \in B(X)$ is the sequence of complex numbers

$$\{\langle T^n x, x^* \rangle : n = 0,1,2,\ldots\}. \qquad (1.1)$$

By the inequalities

$$|\langle T^n x, x^* \rangle| \leq \| T^n x \| \cdot \| x^* \|, \; n = 0,1,2,\ldots,$$

many of the questions related with the existence of bounded weak orbits, weak orbits converging to 0 and the structure of the sets of all pairs $(x, x^*) \in X \times X^*$ with these type of weak orbits are merely corollaries of the corresponding results on the "ordinary" orbits, i.e. sequences of form

$$\{T^n x : n = 0,1,2,\ldots\}, x \in X. \qquad (1.2)$$

The results in [6], [7], [8] and [9] show that for a single operator $T \in B(X)$ the same conditions under which the space X contains vectors with orbits under T tending strongly to infinity also imply that the product $X \times X^*$ contains pairs with weak orbits under T tending to infinity. Moreover, the set of all vectors $x \in X$ with $\| T^n x \| \to \infty$ as $n \to \infty$ and the set of all pairs $(x, x^*) \in X \times X^*$ with $| \langle T^n x, x^* \rangle | \to \infty$ as $n \to \infty$ actually have the same topological properties.

Working with sequences of operators, each with an approximate point spectrum containing points that are not eigenvalues, in [3] and [4] we've obtained the following results based on the corresponding results for a single operator in [2].

Theorem 1.1 [3, Theorem 2.1] *Let H be a Hilbert space and $(T_i)_{i \geq 1}$ be a sequence in $B(H)$ with $\sigma_{ap}(T_i) \setminus \sigma_p(T_i) \neq \emptyset$, for all $i \geq 1$. Then for any sequence $(\lambda_i)_{i \geq 1}$ satisfying $\lambda_i \in \sigma_{ap}(T_i) \setminus \sigma_p(T_i)$, $i \geq 1$ and any family of strictly decreasing sequences of positive numbers $\{(a_{i,j})_{j \geq 1} : i = 1, 2, \ldots\}$ with $a_{i,j} \to 0$ as $j \to \infty$, for all $i \geq 1$ and $\sum_{i \geq 1} a_{i,1}^2 < \infty$, in every open ball in H with radius $2(\sum_{i \geq 1} a_{i,1}^2)^{1/2}$ there is $z \in H$ so that:*

$\| T_i^n z \| \geq a_{i,n} |\lambda_i|^n$, for all $i \geq 1$ and $n \geq 1$.

Corollary 1.2 [3, Corollary 3.1] *If $(T_i)_{i \geq 1}$ is a sequence of operators in $B(H)$ such that for every $i \geq 1$ the set $\sigma_{ap}(T_i) \setminus \sigma_p(T_i)$ has a nonempty intersection with $\{\lambda \in \mathbb{C} : |\lambda| > 1 + \beta\}$ for some $\beta > 0$, then there is a dense set of vectors $z \in H$ with $\| T_i^n z \| \to \infty$ as $n \to \infty$, for every $i \geq 1$.*

By the following Theorem, the Corollary 1.2 remains true for operators on reflexive Banach spaces.

Theorem 1.3 [4, Theorem 6] *Let X be a reflexive Banach space and $(T_i)_{i \geq 1}$ a sequence of operators in $B(X)$ satisfying: $\sigma_{ap}(T_i) \setminus \sigma_p(T_i) \neq \emptyset$, for all $i \geq 1$. Then for any sequence $(\lambda_i)_{i \geq 1}$ with $\lambda_i \in \sigma_{ap}(T_i) \setminus \sigma_p(T_i)$, $i \geq 1$ and any family of sequences of positive numbers*

$\{(a_{i,j})_{j\geq 1} : i = 1,2,\ldots\}$ *with* $\sum_{i,j\geq 1} a_{i,j} < \infty$, *in every open ball in* X *with radius* $2(\sum_{i,j\geq 1} a_{i,j})$ *there is* $z \in X$ *so that*

$$\| T_i^n z \| \geq \frac{1}{2} a_{i,n} |\lambda_i|^n, \text{ for all } i \geq 1 \text{ and } n \geq 1.$$

The next Theorem, which follows directly from [6, Theorem~V.37.14], allowed us to improve the result in Corollary 1.2.

Theorem 1.4 [5, Theorem 8] *Let* X *and* Y *be Banach spaces and let* $\{T_{i,j} : i, j \in \mathbb{N}\}$ *be a family of operators in* $B(X,Y)$. *Then for every family of sequences of positive numbers* $\{(a_{i,j})_{j\geq 1} : i = 1,2,\ldots\}$ *with* $\sum_{i,j\geq 1} a_{i,j} < \infty$ *in every open ball in* X *with radius greater than* $\sum_{i,j\geq 1} a_{i,j}$ *there is a vector* $x \in X$ *satisfying*

$$\| T_{i,j} x \| \geq a_{i,j} \| T_{i,j} \| \text{ for all } i, j \geq 1.$$

Corollary 1.5 [5, Corollary 9] *If* $(T_i)_{i\geq 1}$ *is a sequence of operators in* $B(X)$ *for which there is* $\beta > 0$ *such that* $r(T_i) > 1 + \beta$, *for all* $i \geq 1$, *then there is a dense set* $D \subset X$ *so that* $\| T_i^n z \| \to \infty$ *as* $n \to \infty$, *for every* $z \in D$ *and* $i \geq 1$.

Theorem 1.4 has another corollary similar to [6, Corollary V.37.16].

Corollary 1.6 [5, Corollary 10] *If* $(T_i)_{i\geq 1}$ *is a sequence of operators in* $B(X)$ *such that* $\sum_{n=1}^{\infty} \| T_i^n \|^{-1} < \infty$, *for all* $i \geq 1$, *then there is a dense set* $D \subset X$ *such that* $\| T_i^n z \| \to \infty$ *as* $n \to \infty$, *for every* $z \in D$ *and* $i \geq 1$.

A similar argument as in Remark 2.8 bellow shows that by the last result, along with the Spectral Mapping Theorem, the conclusion in Corollary 1.5 will remain true for any sequence of operators $(T_i)_{i\geq 1}$ in $B(X)$ such that $r(T_i) > 1$, for all $i \geq 1$ ([5, Corollary 11]).

2 WEAK ORBITS TENDING TO INFINITY

The corresponding results of Theorem 1.1 and Theorem 1.3 are based on the following modified version of [1, Theorem 1].

Proposition 2.1 *Let X be a Banach space, $\{x_{i,j}^* : i \geq 1, j \geq 1\}$ a family of unit functionals in X^* and $\{a_{i,j} : i \geq 1, j \geq 1\}$ a family of non-negative numbers satisfying $\sum_{i,j} a_{i,j} < 1$. Then for every $y \in X$ there is $x \in X$ such that $\|x - y\| \leq 1$ and*

$|\langle x, x_{i,j}^* \rangle| > a_{i,j}$, for all $i \geq 1$ and $j \geq 1$.

In the Hilbert space settings, by the Riesz's theorem for representation of a bounded linear functional, we can identify H^* with H via the isometry $x \mapsto x^*$ if, and only if, $x^*(y) = \langle y \mid x \rangle$, for all $y \in H$. Hence, for the Hilbert space operators we have the next analogues of Theorem 1.1 and Corollary 1.2.

Theorem 2.2 *Let H be a Hilbert space and $(T_i)_{i \geq 1}$ a sequence of operators in $B(H)$ with $\sigma_{\mathrm{ap}}(T_i) \setminus \sigma_{\mathrm{p}}(T_i) \neq \varnothing$, for all $i \geq 1$. If $\lambda_i \in \sigma_{ap}(T_i) \setminus \sigma_{\mathrm{p}}(T_i)$, $i \geq 1$, then for every family of sequences of positive numbers $\{(a_{i,j})_{j \geq 1} : i = 1, 2, \ldots\}$ satisfying $s = \sum_{i \geq 1} a_{i,1}^{2/3} < \infty$ and $a_{i,j} / a_{i,j+1} > 2\sqrt{2}$, for all $i \geq 1$ and $j \geq 1$, there is $n_0 \in \mathbb{N}$ (depending only on s) such that in any two open balls U and V in H with radii $2\sqrt{s}$ there are vectors $u \in U$ and $v \in V$ such that*

$\left|\langle T_i^n u \mid v \rangle\right| \geq \frac{1}{2} a_{i,n} |\lambda_i|^n$, for all $i \geq 1$ and $n \geq n_0$.

Corollary 2.3 *Let H be a Hilbert space and $(T_i)_{i \geq 1}$ a sequence in $B(H)$ for which there is $\beta > 0$ so that $(\sigma_{\mathrm{ap}}(T_i) \setminus \sigma_{\mathrm{p}}(T_i)) \cap \{\lambda \in \mathbb{C} : |\lambda| > 2\sqrt{2} + \beta\} \neq \varnothing$, for all $i \geq 1$. Then there is a dense set of pairs $(x, y) \in H \times H$ such that $|\langle T_i^n x \mid y \rangle| \mapsto \infty$ as $n \to \infty$, for all $i \geq 1$.*

The next theorem is the analogue of Theorem 1.3.

Theorem 2.4 *Let X be a reflexive Banach space and $(T_i)_{i \geq 1}$ a sequence of operators in $B(X)$ with $\sigma_{\mathrm{ap}}(T_i) \setminus \sigma_{\mathrm{p}}(T_i) \neq \varnothing$, for all $i \geq 1$. If*

$\lambda_i \in \sigma_{ap}(T_i) \setminus \sigma_p(T_i)$, $i \geq 1$, and $\{(a_{i,j})_{j\geq 1} : i = 1,2,\ldots\}$ is a family of sequences of positive numbers satisfying $\sum_{i,j\geq 1} a_{i,j}^{1/2} < \infty$, then in any two open balls $B \subset X$ and $B^* \subset X^*$ with radii $2\sum_{i\geq 1} a_{i,j}^{1/2} < \infty$ there are $z \in B$ and $z^* \in B^*$ such that

$$\left|\left\langle T_i^n z, z^* \right\rangle\right| \geq \frac{1}{2} a_{i,n} |\lambda_i|^n, \text{ for all } i \geq 1 \text{ and } n \geq 1.$$

Corollary 2.5 *Let X be a reflexive Banach space and $(T_i)_{i\geq 1}$ a sequence in $B(X)$ with $(\sigma_{ap}(T_i) \setminus \sigma_p(T_i)) \cap \{\lambda \in \mathbb{C} : |\lambda| > 1+\beta\} \neq \emptyset$, for all $i \geq 1$ and some $\beta > 0$. Then there is a dense set of points $(x, x^*) \in X \times X^*$ such that $|\langle T_i^n x, x^* \rangle| \to \infty$ as $n \to \infty$, for all $i \geq 1$.*

In [6], V. Müller gave the next two results on weak orbits.

Theorem 2.6 [6, Theorem V.39.5] *Let X and Y be Banach spaces and let $(T_n)_{n\geq 1}$ be a sequence of operators in $B(X,Y)$. Let $(a_n)_{n\geq 1}$ be a sequence of positive numbers satisfying $\sum_{n\geq 1} a_n^{1/2} < \infty$. Then in any two open balls $B \subset X$ and $B^* \subset Y^*$ with radii strictly larger than $\sum_{n\geq 1} a_n^{1/2}$ there are $x \in B$ and $y^* \in B^*$ such that*

$$|\langle T_n x, y^* \rangle| \geq a_n \| T_n \|, \text{for all} n \geq 1.$$

Corollary 2.7 [6, Corollary V.39.6] *Let X and Y be Banach spaces and let $(T_n)_{n\geq 1}$ be a sequence of operators in $B(X,Y)$ satisfying $\sum_{n\geq 1} \| T_n \|^{-1/2} < \infty$. Then there is a dense set of pairs $(x, y^*) \in X \times Y^*$ such that $|\langle T_n x, y^* \rangle| \to \infty$ as $n \to \infty$.*

Remark 2.8 Corollary 2.7, along with the Spectral Mapping Theorem, implies that for every $T \in B(X)$ with spectral radius $r(T) > 1$ there is a dense set of pairs $(x, x^*) \in X \times X^*$ satisfying $|\langle T^n x, x^* \rangle| \to \infty$ as $n \to \infty$. Namely, if $r(T) > 1$, then the spectrum $\sigma(T)$ contains a point λ such that $|\lambda| > 1$. Clearly, $|\lambda|^{1/2} > 1$ and hence $\sum_{n\geq 1} |\lambda|^{-n/2} < \infty$. On the other hand, by The Spectral Mapping Theorem $\lambda^n \in \sigma(T^n)$, for every

$n \in \mathbb{N}$, and hence $|\lambda|^n \le r(T^n) \le \| T^n \|$. This would imply that $\sum_{n=1}^{\infty} \| T^n \|^{-1/2} \le \sum_{n=1}^{\infty} |\lambda|^{-n/2} < \infty$. Now we only need to apply Corollary 2.7 for $Y = X$ and the sequence $(T^n)_{n\ge1}$.

Having this in mind and the fact that the conclusion in Corollary 1.5 remains true for a sequence of operators $(T_i)_{i\ge1}$ each with a spectral radius greater than 1, it is naturally to ask the following question.

Question 2.9 *If $(T_i)_{i\ge1}$ is sequence of operators in $B(X)$ such that $r(T_i) > 1$ for every $i \ge 1$, will there be a dense set of pairs $(x, x^*) \in X \times X^*$ each having a weak orbit tending to infinity under T_i, for all $i \ge 1$?*

To answer this question, the first step is to modify Theorem 2.6.
Let $f : \mathbb{N}\times\mathbb{N} \to \mathbb{N}$ be the invertible mapping defined with

$$f(i, j) = \frac{(i + j - 2)(i + j - 1)}{2} + j, (i, j) \in \mathbb{N}\times\mathbb{N},$$

and $g : \mathbb{N} \to \mathbb{N}\times\mathbb{N}$ is its inverse mapping. Then, by Theorem 2.6 applied on the sequences $(S_n)_{n\ge1}$ and $(b_n)_{n\ge1}$ defined with $S_n = T_{g(n)}$ and $b_n = a_{g(n)}$, $n \ge 1$ we have:

Theorem 2.10 *Let X and Y be Banach spaces and let $\{T_{i,j} : i, j \in \mathbb{N}\}$ be a family of operators in $B(X,Y)$. Let $\{(a_{i,j})_{j\ge1} : i = 1, 2, \ldots\}$ be a family of sequences of positive numbers satisfying $\sum_{i,j\ge1} a_{i,j}^{1/2} < \infty$. Then in any two open balls $B \subset X$ and $B^* \subset Y^*$ with radii strictly larger than $\sum_{i,j\ge1} a_{i,j}^{1/2}$ there are $x \in B$ and $y^* \in B^*$ such that*

$|\langle T_{i,j}x, y^*\rangle| \ge a_{i,j} \| T_{i,j} \|$, for all $i, j \ge 1$.

At this point we can only give the corresponding result of Corollary 1.5.

Corollary 2.11 *If $(T_i)_{i\ge1}$ is a sequence in $B(X)$ for which there is $\beta > 0$ such that $r(T_i) > 1 + \beta$, for all $i \ge 1$, then there is a dense set of pairs $(x, x^*) \in X \times X^*$ such that $|\langle T_i^n x, x^*\rangle| \to \infty$ as $n \to \infty$, for all $i \ge 1$.*

Lemma 2.12 ([6, Lemma V.37.15]) *Let* $\varepsilon > 0$ *and* $(a_n)_{n\geq 1}$ *be a sequence of positive numbers satisfying* $\sum_{n\geq 1} a_n < \varepsilon$. *Then there is a sequence of positive numbers* $(b_n)_{n\geq 1}$ *such that* $b_n \to \infty$ *as* $n \to \infty$ *and* $\sum_{n\geq 1} a_n b_n < \varepsilon$.

Applying Theorem 2.10 and Lemma 2.12 in a similar way as in the original proof of Corollary 2.7, we have:

Corollary 2.13 *Let* $(T_i)_{i\geq 1}$ *be a sequence in* $B(X)$ *with* $\sum_{n\geq 1} \| T_i^n \|^{-1/2} < \infty$, *for every* $i \geq 1$. *Then there is a dense set of pairs* $(x, x^*) \in X \times X^*$ *such that* $|\langle T_i^n x, x^* \rangle| \to \infty$ *as* $n \to \infty$, *for every* $i \geq 1$.

Since $\sum_{n=1}^{\infty} \| T^n \|^{-1/2} < \infty$ for every operator T with spectral radius $r(T) > 1$ (see Remark 2.8), from Corollary 2.13 directly follows:

Corollary 2.14 *Let* $(T_i)_{i\geq 1}$ *be a sequence of operators* $B(X)$ *such that* $r(T_i) > 1$, *for all* $i \geq 1$. *Then there is a dense set of pairs* $(x, x^*) \in X \times X^*$ *such that* $|\langle T_i^n x, x^* \rangle| \to \infty$ *as* $n \to \infty$, *for every* $i \geq 1$.

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Design and development a children’s speech database

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Abstract*: The report presents the process of planning, designing and the development of a database of spoken children’s speech whose native language is Bulgarian. The proposed model is designed for children between the age of 4 and 6 without speech disorders, and reflects their specific capabilities. At this age most children cannot read, there is no sustained concentration, they are emotional, etc. The aim is to unite all the media information accompanying the recording and processing of spoken speech, thereby to facilitate the work of researchers in the field of speech recognition. This database will be used for the development of systems for children’s speech recognition, children's speech synthesis systems, games which allow voice control, etc. As a result of the proposed model a prototype system for speech recognition is presented.*

Keywords: *Children’s speech recognition, Speech Corpora, Children’s speech recognition system.*

1. INTRODUCTION

The design and realization of the speech database is an integral part of systems for speech recognition. Their quality and scope greatly affect the activities of recognized devices [12]. Therefore, each acoustic-phonetic database must contain in itself all the phonetic richness of language studies. In our case the target group is children at the age of 4 to 6 (kindergarten and preschool group) whose native language is Bulgarian. Often they still cannot read and write, and a few of them know the numbers.

In practice, the collection of spoken speech of such speakers has proved a difficult task and additional resources had to be used. For example, the word to be pronounced is read, and then the child repeats it [4]. Often the selected words appear to be too complicated and the children have difficulty with their reproduction. In addition, young children easily lose concentration and distract, which further hampers the collection of data. Therefore, the purpose of this article is to collect a database that allows recording of additional helpful information related to supporting the process of filling a speech database of spoken speech.

For the development of the model methods that include selecting appropriate texts for spelling will be used, as well as visualization of these texts with images, moving images or sound files, labelling the recordings of each speaker and the organization of data in an easy and accessible form. Since such a research on children's recognition of speech in Bulgarian has not been done yet, the initial filling of the base will consist of only single words.

Such a database of recorded children's speech is a key condition for the application, starting from the pure commercialization as entertainment, education and other social and economically important areas. The resulting database will help many professionals, researchers and speech therapists involved with the study of children's speech.

2. ANALYSIS OF THE PROBLEM

According to [2] spoken speech databases are developed for two main goals - the first is to conduct fundamental research on the acoustic, phonetic, lexical, semantic, syntactic expressions of a language, and the second is to establish the differences between speakers, such as gender, age, environment, channels of data, etc.

In the development of systems related to the processing and speech recognition what is essential is the organization, flexibility and the size of the database. Also, the extent of actual coverage of the structure (syntax, word order, grammar, etc.) used in language and its phonetic features is important [9]. The first factor related to the design of the database determines the response time during the speech recognition and the linguistic factor controls the specificity of the speech.

It is also well known that children's speech contains a set of specific parameters [14], which turn them into a group of users with specific system requirements for automatic speech recognition. Frequent speech disorders are another specific problem to be solved [5]. At present the main trend in the data collection of spoken speech (speech data) of children at the age of 4 to 6 is the collecting and analyzing the acoustic and linguistic characteristics.

Most databases containing a record of children's spoken speech are targeted at children between the age of 6 and 18 (or their subset). This is because with this group the collection of speech is more easily manageable and thus feasible. They are primarily focused on acoustic modeling and analysis of American English as the corpora CID [14], KIDS [6], CU Kids' Audio Speech Corpus [8]. The most famous European corpus is PF-STAR, which contains spoken speech in British English, Italian, German and Swedish [3]. Example of the Russian spoken corpus

of children's speech is ChildRu [15]. Research and comparative characteristics of the existing corpora is done in [11]

Currently there are very few databases of spoken Bulgarian. One is developed with the project "Computer recognition of connected speech in a large dictionary of Bulgarian language" [16]. The read speech consists of general economic, legal and administrative texts, and the speakers are men and women aged over 20. The other database is BG-SRDat presented in [17]. It contains male speech (men at the age over 27) delivered Through a noisy analog telephone channels.

At the time of the survey and writing this article no children's spoken database in Bulgarian was found.

3. PREPARATION FO DEVELOPING THE DATABASE OF SPOKEN SPEECH

There are three main aspects that must be followed when designing a database of spoken speech - the type of dictionary, the number of sessions conducted with a speaker and technical aspects of recording [Lamel et al., 1986].

3.1. Dictionary

According to [7] to achieve satisfactory results in the recognition process with a recognition system, the training must be done by the same target group, whose speech will be recognized. Therefore, records must be oriented towards young children (aged 4 to 6) which provides quick and convenient recording, with an appropriate balance between sex and age. Typically, the dictionary covers the full range of phonemes of the language. Here we face difficulties in young children because they use vocabulary different from that of adults. Therefore we will use suggestions from [1] frequency dictionary. The speakers used have to cover all sections of the existing speech-specific features at this age.

3.2. The number of sessions

Under session we will understand all entries made by a speaker in a given period of time (e.g. per 1 day). This defines the length of the records and the number of sessions for each child who participated in the study. Records must be as short as possible. Each record contains a speech by one speaker.

3.3. . Technical aspects

They contain a representation of the environment, technical equipment (sound card, microphone type etc.) and algorithms for cleaning up the noise. Speech must be collected in a realistic way.

In our case records will be made at home, because from a psychological perspective, it is found that children at this age feel most relaxed and can more easily communicate with the conductor of the experiment. Each record will contain only one spoken word

4. MODEL OF CHILDREN'S SPOKEN SPEECH DATABASE

Most speech recognition systems don't allow the use of interactive elements during the recording of spoken language, such as moving objects, changing the image, listening to different sounds. This system is an attempt to remedy this shortcoming.

A relational diagram of the proposed database is presented in Fig. 1. The three main points on which emphasis falls are: the corpus (table" Words"), speaker (table "Speaker") and conducted recordings (table "Records").

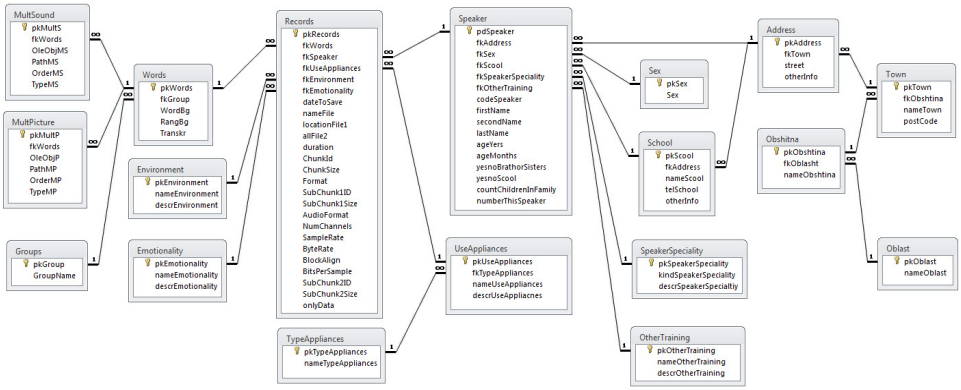

Fig. 1: Relational database diagram for children's speech

Let us now turn our attention to the information stored for each speaker, children whose speech will be collected. It consists of: full name, gender, age (years and months), date of birth, current address, number of children in family, number of the child in order of birth, attending a kindergarten, and if yes what kindergarten, whether attending any additional courses (speech therapist, singing lessons, music lessons), deviations from normal development and diseases.

The information collected about the records is the place of recording, recording equipment, emotional state of the speaker (the child) during the recording and the characteristics of the file. The recorded files are of low compression and extension wav. The original files can contain external noise, the voice of the mother or the tutor of the experiment, the child’s laughing or crying, etc. Therefore, after its recording, filtering to eliminate the additional interference will be made.

5. EXPERIMENT

The experimental part consists of developing a prototype model of the proposed speech database (Fig. 2). There is a main form of which through the menu bar, the other modules are available. The software makes it easy to add new words to the database, there is an automatic phonetic transcription consistent with the International Phonetic Alphabet and application of illustrations and sound files to them. There is also an opportunity to work with electronic papers of the speakers.

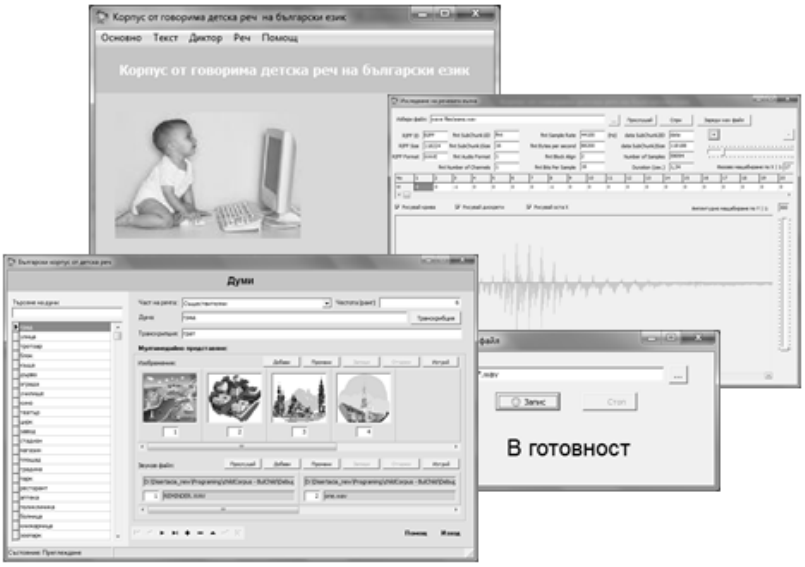

Fig. 2: View of the prototype system for identification children's speech in Bulgarian

Before proceeding to make records, first, we must organize the "Word’s collection" for different sessions. They are organized thematically ("Seasons", "Family," "Numbers", etc.) and a small set of words (about 10-15 of them), since the young child cannot spend a long time (more

than 30 minutes a day) in front of the computer. Once the collections are ready one can continue with recording. From the main menu the form "Record" is started and the speaker is selected, the words collection, and in a dialog mode the words and the accompanying media files (pictures and sounds) are displayed. If the child copes with the first image and pronounces the necessary word correctly, the next picture follows and so on to the end.

All received files are uncompressed file format *. wav. The initial data are available in a simple file sampling rate 16 kHz, in a file channel. Sampling frequency (sample rate) shows the number of sample for one minute. Currently, signal filtering is done at the hardware level.

The file name is formed as a series of the letter b (boy) for a boy or g (girl) for a girl, a unique string (one or more letters), age, underscore, the collection, from which the word is, is marked with a letter and a serial number of the word (Tab.1).

Tab. 1. Example of a possible file name

Attribute	Value	Indication
Sex:	Boy	b
Name:	Ivan Petrov	A
Age:	5 years	5
Word's collection:	Collection B	B
Word order:	Number of the word order 2	2
Indication of the file:		bA5_B2.wav

Because children are highly dependent on the emotions that are directly reflected in speech and the manner of expression, then in the course of each record an opportunity to determine the emotional state of the child is provided. The first results for recognizing emotions in preschool children are presented in [10]. That is why records are made when children are visibly calm.

The presented prototype system was developed with the free development environment, Turbo C++ Explorer. Microsoft Access is used for the development of the database.

6. CONCLUSIONS

This report has completed several tasks. First, the process of developing a database of children's spoken language has been introduced and studied. Second, specific issues related to the recognition of child speech have been analyzed. And third, but no less important, architectural model of the speech database has been proposed. In the experimental

part a prototype system for the children’s recognition in Bulgarian has been presented.

The important advantage of this model is the narrow focus and comprehensive multimedia presentation of individual words in the corpus. In this way children's speech can be recorded with minimal involvement of the tutor.

This database is the beginning of developing a prototype system for automatic speech recognition of children at the age of 4 to 6 whose native language is Bulgarian. In the future the problem of rapid access to the contents of large multimedia databases and to explore the acoustic-phonetic diversity of existing database should be solved. The development of models for segmentation of phonemes from the words of recorded speech and calculate the word error rate is to be elaborated.

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Web Service Based System for Generating Input Data Sets

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Abstract*: This article deals with a three-layer architectural model of a distributed information system based on Web services, which will be used for automatic generation of sets of input data. The information system will be constructed of a client layer, a service layer and of a data layer. The web services as a tool of developing distributed software systems will be presented briefly. A web service and the implementation of its web methods will be described. A way to use the developed web methods in real application will be proposed.*
Keywords: *web services.*

1. INTRODUCTION

When solving optimization problems typically different algorithms are used. The algorithms are compared on the basis of various criteria - performance, efficiency, etc. To do so it is necessary to have the same input data (benchmark) survey on which the algorithms to be applied. Preparation of such sets of input data, if done manually is extremely expensive. It is therefore necessary to use different methods and mechanisms through which input data (most often held in the form of vectors and matrices) to be automated.

It is precisely on this issue that this article focuses on. An approach for building and using a web service that will provide its consumers (applications) web methods to retrieve sets of input data will be proposed. These sets of input data can be generated in an automated way (i.e. their generation requires no user intervention). These data must be current, be obtained for reasonable time, and be able to be requested at a later stage in the same type.

2. WEB SERVICES AS A TOOL FOR DEVELOPMENT OF DISTRIBUTED SOFTWARE SYSTEMS

Currently, the development of server applications running on different operating systems has become a primary goal of developers [1]. Communication between application-application is not a new idea. There are already technologies like DCOM, RPC and others [5, 7] that allow this

type of communication. The main limitation of these technologies is that they only work between two similar systems.

Web services represent a new technology designed to change the way of developing modern information systems. Communicate among different computers using web services is possible thanks to the protocol Simple Object Access Protocol (SOAP). It is built on the standard HTTP (Hypertext Transfer Protocol) protocol. Therefore, the Web server can handle SOAP requests and data packets can pass through firewalls. SOAP defines the XML-based record of making requests to the execution method of an object of the server, passing its parameters, and recording to define the shape of the response [3]. SOAP was originally designed to overcome the weaknesses of using DCOM (Distributed Component Object Model) in web servers. It is presented in the W3C for standardization and is approved [2]. SOAP replaced the calls by using a COM (Common Object Model) among different types of computers. Similarly, the definition of service SOAP format WSDL (Web Services Description Language) replaced IDL (Interface Description Language) standard libraries that are used by COM and COM+. WSDL documents are XML documents providing a definition of metadata for SOAP requests.

3. ARCHITECTURE SCHEME OF THE INFORMATION SYSTEM

In developing information systems based on Web services common functionality between different systems is shared. In other words, different systems use the same web methods that are available from a Web service.

This study was conducted to choose the model of information system that uses multi-layer architecture based on Web services. Other types of architectures of information systems (such as single-layer (monolithic), two-layer (client / server), etc.) restrict the number of layers that can be used. Thus the workload of the entire information system may not be distributed due to the inability of physical separation. We note that the two-layer architecture is only part of the functionality associated with the processing of data to be transferred on the server database.

The proposed architectural model of the system consists of three layers:

• Client layer. This layer includes thin clients (WinForms applications) and standard Web clients (browsers). It is built on client computers (PCs, laptops, etc.).

• Services layer. This layer provides functions as Web services. It is based on servers in the development of business objects, using rules for access to them. Also, queries are processed which form the responses to clients.

• Data layer. This layer actually consists of two sub-layers. One layer of data access which provides the necessary interfaces. The second layer is used for physical storage of the data. This layer offers the opportunity to work with data, such as execution of SQL constructions insert, update, delete and select.

The architectural scheme of information system using Web methods for retrieving sets of input data is presented at Fig 1.

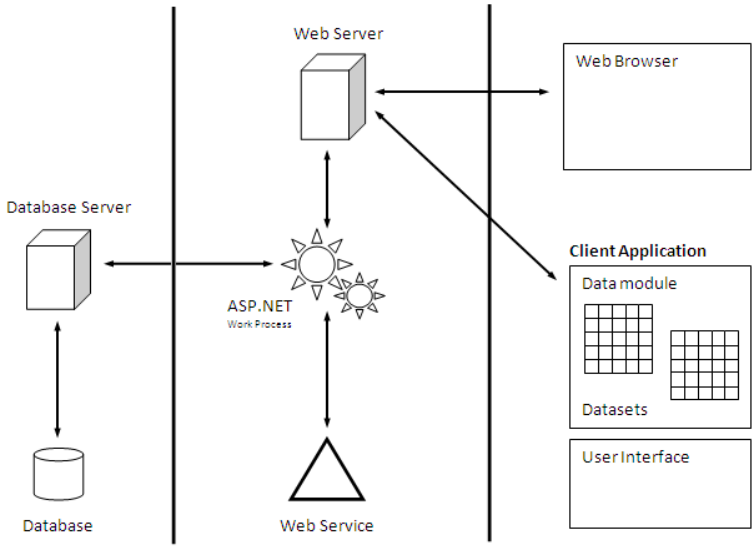

Fig 1: Architectural scheme of the information system.

The applications running in the client layer (Web forms or Win forms based) use SOAP protocol (transported by HTTP protocol) to communicate with the middle layer (i.e. service layer). The relationship between service layer and data layer is implemented by drivers for data access.

4. DEVELOPMENT OF WEB SERVICE FOR GENERATING INPUT DATA SETS

Here, the developed a Web service will be presented briefly. For its implementation the visual environment for design and event-oriented programming - Turbo Delphi for. NET is used. As a technology platform the Microsoft .NET Framework is used.

The web service will be associated with obtaining information from a relational database of existing information systems for automated generating of university timetable [5, 6]. Relational database management system is Microsoft SQL Server 2008.

The developed Web service provides two Web methods that are available to consumers:

1. The method GetSemestersInfoAsXML: String - this is a web method that sends back information in XML format for the semester, faculties, departments, majors and courses. This web method can be used by the Web service consumers to retrieve a list of identification numbers of courses (i.e. primary key values from the table of courses presented by the relational database in [6]). This list may be submitted as a parameter of the second web method.

The pseudo code of the first web method is presented at Fig 2.

```
function GetSemestersInfoAsXML: String;
var sXML: TStrings;
begin
 // created a connection to the database
 Connection := TADOConnection.Create;
//Setting the ConnectionString property and opening the connection
 //Dynamic creation of data sets: dsPeriods, dsFaculties,
 //dsDepartments, dsSpecialities and dsCourses
 // generating the resultant XML stream
 sXML := TStringList.Create;
 sXML.Add('<?xml version="1.0"');
 sXML.Add('<ttr:semesters xmlns:ttr='+
          '"http://timetable.swu.bg/TimetableResearch">');
 for each dsPeriods do begin
  sXML.Add('<ttr:semester name=' + dsPeriods.Name);
  sXML.Add(' id=' + dsPeriods.PrimaryKey + '>');
  for each dsFaculties do begin
   sXML.Add('<ttr:faculty name=' + dsFaculties.Name);
   sXML.Add('id=' + dsFaculties.PrimaryKey + '>');
   for each dsDepartments do begin
    sXML.Add('<ttr:department name=' + Departments.Name);
    sXML.Add('id=' + Departments.PrimaryKey + '>');
    for each dsSpecialities do begin
     sXML.Add('<ttr:speciality name=' + dsSpecialities.Name);
     sXML.Add('id=' + dsSpecialities.PrimaryKey + '>');
     for each dsCourses do begin
      sXML.Add('<ttr:course name=' + dsCourses.Name);
      sXML.Add('id=' + dsCourses.PrimaryKey + '/>');
     end; sXML.Add('</ttr:speciality>');
    end; sXML.Add('</ttr:department>');
   end; sXML.Add('</ttr:faculty>');
  end; sXML.Add('</ttr:semester>');
 end;  sXML.Add('</ttr:semesters>');
 Result := sXML;
end;
```

Fig 2: Pseudo code of a Web method GetSemestersInfoAsXML.

To generate the necessary information object of type TConnection is created through which to contact the database by setting the

ConnectionString property and calling the method Open. For each of the used tables the created object of the type DataSet, which is filled with information from the database. Then an object of type TStringList is created which is stored in XML format generated text. After the prologue of the XML file a namespace is declared, which is related with the developed Web service. The relationships between tables: semester, faculties, departments, majors and courses are one-to-many. Therefore, using nested loops that go any subset of related data, thus forming a hierarchical structure in which they organize their resources. At each step of each loop the corresponding XML node is constructed, adding the name and identification number of each resource. After each loop the corresponding XML block closes. After the outer loop the block of the main root element of the XML file is closed.

2. The method GetTimetableDataSetAsXML (ListOfCodeCourses: String): String - this is a web method on a list of numbers of courses (resulting from the first web method) sends back all relevant information resources within the participating timetable (courses, professors, auditoriums, events, matrices for the distribution of teachers, students and auditoriums in events, etc.).

The pseudo code of the second web method is presented at Fig 3.

```
function GetTimetableDataSet(ListCodeCourses: String): String;
var sXML: TStrings;
begin
 // created a connection to the database
 Connection := TADOConnection.Create;
 //Setting the ConnectionString property and opening the connection
 //Dynamic creation of data sets: dsLecturers, dsRooms, dsStudentsq,
 //dsEvents, dsKursInfo using ListCodeCourses
 // generating the resultant XML stream
 sXML := TStringList.Create;
 sXML.Add('<?xml version="1.0"');
 sXML.Add('<ttr:dataset xmlns:ttr='+
          '"http://timetable.swu.bg/TimetableResearch">');
 // adding a node for teachers
 sXML.Add('<ttr:lecturers count="' + dsLecturers.Count + '">');
 for each dsLecturers do
   sXML.Add('<ttr:lecturer name="' + dsLecturers.Name + '/>');
 sXML.Add('</ttr:lecturers>');
 // adding a node for auditoriums
 sXML.Add('<ttr:auditoriums count="' + dsRooms.Count + '">');
 for each dsRooms do
   sXML.Add('<ttr:auditorium name="' + dsRooms.Name + '/>');
 sXML.Add('</ttr:auditoriums>');
 // adding a node for students
 sXML.Add('<ttr:students count="' + dsStudents.Count + '">');
 for each dsStudents do
   sXML.Add('<ttr:students id="' + dsStudents.Id + '/>');
 sXML.Add('</ttr:students>');
 // adding a node for events
```

```
 sXML.Add('<ttr:events count="' + dsEvents.Count + '">';
 for each dsEvents do begin
  sXML.Add('<ttr:event id="' + /*and other attributes */ + '">');
  for each dsStudents do
   if dsStudents.Pk in dsEvents then /*if student in current event*/
     sXML.Add('<ttr:student id="' + dsStudentId + '"/>');
   sXML.Add('</ttr:event">';
  sXML.Add('</ttr:events">';
 end //for each dsEvents do
 sXML.Add('</ttr:dataset">';
end;
```

Fig. 3: Pseudo code of a Web method GetTimetableDataSetAsXML.

For the web method the connection to the database, dynamic creation of data sets, generating a list of strings and description of the main root element of the second XML file is similar to the first web method. Then alternately nodes for teachers, students and auditoriums are added. In the corresponding sub-nodes the available resources of each type are listed. A special case is the events where for each added event (in common node for the events) nodes for students attending any event are inserted. It is possible for a student node to be added as sub-nodes of more than one event.

Similarly as in the first web method, at the end of each loop the corresponding XML block closes. After the loop of events is closed blocks of the main root element of the XML file.

5. USE OF THE DEVELOPED WEB SERVICE

Each application must perform three steps in order to use a Web service. First - discovery of the service (this is the process of extracting information about a web service), second - generating the proxy class (a class that encapsulates the process of communication between the application and Web service) and third - using the proxy class to call methods web service [7].

We will modify the application that is used to study genetic and mimetic algorithms to solve optimization problems for automated generation of university timetables. The application is developed on Turbo Delphi for Win32 and is presented in [4]. Note that the web service can be used in applications developed with Java, Delphi 6, 7, or client built with. NET (e.g. Visual Studio for. NET).

To the the application under investigation a Web reference is added. The URL address to the WSDL document of the developed Web service is referred to. This WSDL document can be found at:

```
http://194.141.86.222/TimetableResearch/TimetableResearchWebService.asmx?wsdl
```

After adding a Web reference to the application, IDE automatically generates a proxy class that hides the specific means by calling the Web service methods. In other words, the proxy class is a class layer between the HTTP SOAP request to a web server and the code that is written for making this request [7]. In fact, this class works as any other class. Proxy class declares methods that can be called from the application consumed, which in turn invokes methods of a Web service itself.

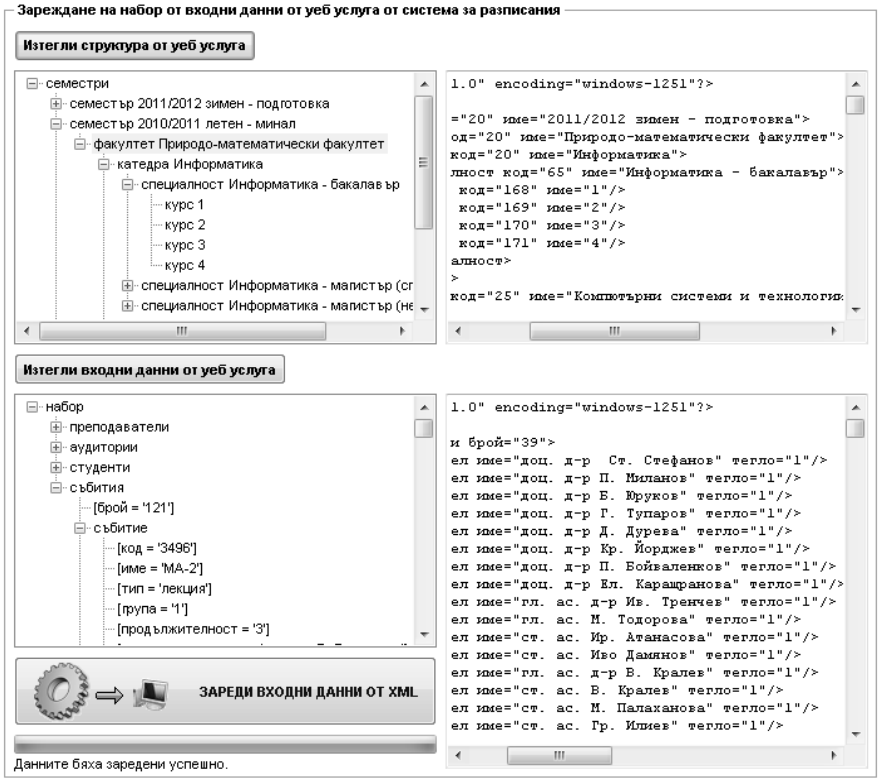

Fig. 4: Sample session using the improved prototype.

An example of the work session with the improved prototype, which is described in [4] is shown at Fig 4. Additional functionality is added that uses the developed and presented in this paper Web service. The first method is used to retrieve information that is organized in a hierarchical form (semester, faculties, departments, majors, courses) regarding courses for which data are available that they have participated in the timetable for the selected semester.

The second web method used to derive data for the participating resources and their interconnections. The range of resources involved is

determined by the given input parameter to the method which is a list of numbers of courses. Once the data have been received in XML format they complet the relevant vectors and matrices (according to the method used in the present prototype [4]).

6. CONCLUSION

In this article an architectural model of a distributed information system based on Web services for automated generation of input data sets is proposed. The web services as a tool for developing distributed software systems are presented briefly. A three-layer architecture scheme of an information system, which consists of a client layer, service layer and data layer is presented. A web service and the realization of the offered web methods are described. For both Web methods pseudo code for their development is presented. Web methods are implemented in a real application and are tested.

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Sliding spectrum analysis

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Abstract*: The standard method for spectrum analysis in DSP is the Discrete Fourier transform (DFT), typically implemented using a Fast Fourier transform (FFT) algorithm. The reconstruction of the time-domain signal is then performed by the IFFT (Inverse Fast Fourier transform) algorithm. The FFT calculates the spectral components in a window, on a block-by-block basis. If that window is move by one sample, it is obvious that most of the information will remain the same. This work describes sliding spectrum analysis techniques whose spectral bin output rates are equal to the input data rate, on a sample-by-sample basis. Here we review the basic ideas and describe Sliding Discrete Fourier transform implementation. A MATLAB program was written using this technique and validated. Future work includes computational cost analysis, synthesis issues and a viability study regarding the use of the algorithms for computing SDFT with high performance on graphics processing units (GPUs).*

Keywords: *Sliding Discrete Fourier transform (SDFT), Fast Fourier transform (FFT).*

1. INTRODUCTION

The discrete Fourier transform (DFT), for transforming the time signal into its frequency domain counterpart, Is a popular signal analysis tool in science and engineering. Frequency and time are orthogonal. But some signals do have frequency components that change with time (for example speech having pitch that rises and falls over time). The solution to such problems is the sliding DFT algorithm [2]. With this method, the computational complexity for calculating DFT of each window is $O(N)$ as compared to $O(N^2)$ for standard DFT computation and $O(N \log_2 N)$ for FFT.

We are proposing an approach to the implementation of a discrete sliding DFT where the spectrum of the signal is estimated by realizing the DFT through a bank of IIR Filters. The technique has all the advantages inherent to the IIR filters, including the capacity of doing sample by sample

processing, and can estimate the spectrum at the exact frequencies of interest.

First we review the DFT approach followed by fast Fourier transform (FFT). The sliding DFT algorithm is then derived and proposed.

1.1. DFT and FFT

The discrete Fourier transform (DFT) plays an important role in the analysis and implementation of discrete-time signal-processing systems because its properties. The DFT is identical to samples of the Fourier transform. Computation of the *N*-point DFT corresponds to the computation of *N* samples of the Fourier transform at *N* equally spaced frequencies $\omega_k = 2\pi k / N$ (bins[1]), i.e. at *N* points on the unit circle in the z-plane. The DFT of finite – length sequence is [1]

$$S^k = \sum_{n=0}^{N-1} x[n] W_N^{kn}, \tag{1}$$

where S^k represent the k-th frequency point (bin), $x[n]$ is sampled input data windowed by rectangular window size *N* and $W_N = e^{-j2\pi/N}$.

Since in (1), both $x[n]$ and S^k may be complex, *N* complex multiplication and (*N*-1) complex addition are required. Computational complexity of each successive *N*-point output is approximate $O(N^2)$ where $O(\cdot)$ denotes order of. It is evident that the number of arithmetic operations required to compute DFT becomes very large for large values of *N*.

There are several properties of the DFT that play important role for improving the efficiency of computation of the DFT:

$$W_N^{(n+mN)(k+pN)} = W_N^{kn} \qquad \text{periodicity} \tag{2}$$

$$W_N^{k[N-n]} = W_N^{-kn} \qquad \text{symmetry} \tag{3}$$

The set of algorithms known as the fast Fourier transform (FFT) use (2, 3) for reducing the time required to compute DFT. Fast Fourier transform have a computational complexity that cannot be less then $O(N \log_2 N)$, but

[1] Frequency bins k corresponds to the band of frequencies centred at $\omega_k = 2\pi k / N$ with a bandwidth of approximately $2\pi / N$

in some practical cases can improve performance by a factor of 100 or more.

What is important to note is that the FFT is “fast” when all the *N* values of S^k are needed and the number of samples N is a power of two. But if we are only interested in the k-th value of the DFT, we have to compute the entire DFT - sequence and discard the unwanted values.

On the other hand, in the case of DFT, it has been noted that the algorithm can be implemented with $O(N)$ complexity, for any (non power of two) value of *N*. This can be achieved by using a set of parallel recursive digital filters [1] - this is called sliding DFT (SDFT). In the current literature, the term running DFT has also been used for this purpose.

2. SLIDING DISCRETE FOURIER TRANSFORM

The principle used for the SDFT is known as the circular shift property. It states that if the DFT of a sequence is S^k, then the DFT of that sequence, circularly shifted by one sample, is $S^k e^{j2\pi k/M}$. Thus the spectral components of a shifted time sequence are the un-shifted spectral components multiplied by $e^{j2\pi k/M}$, where *k* is the DFT bin of interest. We use this shift principle to express sliding DFT process as [2][3][4]

$$S_{[n]}^k = \left[S_{[n-1]}^k - x[n-M] + x[n] \right] W_M^k, \quad (4)$$

where $S_{[n]}^k$ is the new spectral component at the time index [n] and $S_{[n-1]}^k$ is the previous spectral component at the time index [n-1]. The superscript *k* is an integer in the range $0 \le k \le M$ associated with the *k*-th DFT bin. There is no requirement for the window size to be a power of two and we use *M* for sample data points, instead of the usual convention *N*. The difference between the current sample $x[n]$ and the last sample $x[n-M]$ can be computed once for each $S_{[n]}^k$.

The sliding algorithm (4) performs an M=16 point DFT on time samples is depicted in Fig. 1.

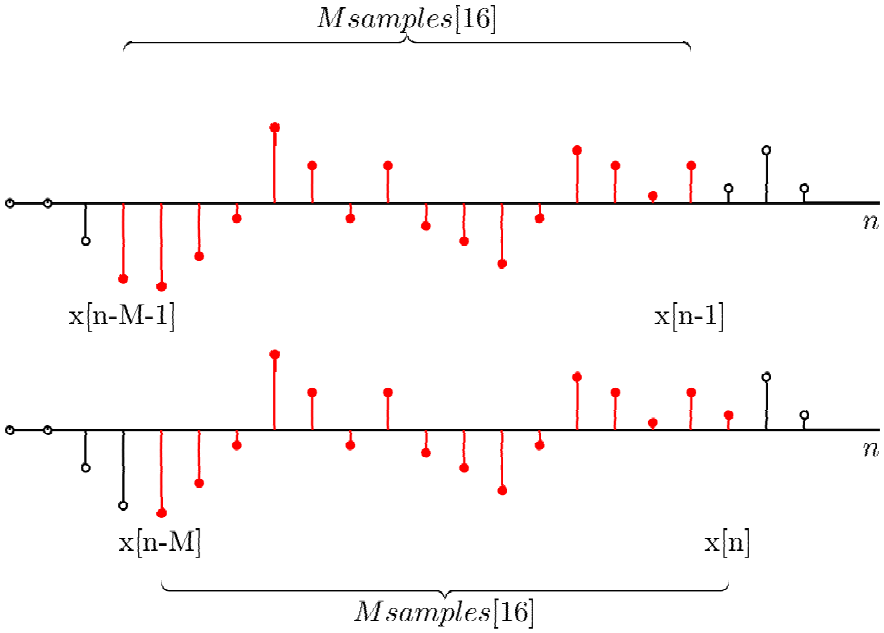

Fig. 1: Data samples at the time index [n] and [n-1].

First the SDFT computes the DFT at the time index [n-1], second at the time index [n]. For this we forget the oldest sample $x[n-M]$ and accept new sample $x[n]$.

The z transform which corresponds to a (4) is

$$S_{[n]}^{k} = \left[S_{[n]}^{k} z^{-1} - x[n] z^{-M} + x[n] \right] W_{M}^{k}. \tag{5}$$

And transfer function is

$$H(z) = \frac{\left(1 - z^{-M}\right) W_{M}^{k}}{1 - z^{-1} W_{M}^{k}}. \tag{6}$$

The transfer function (6) has *M* zeros located at the *M* root of 1. The single pole is located at $z_1 = e^{(j2\pi/M)k}$ .The *k* is an integer and we see that the single pole cancelled the k-th zero (i.e.) transfer function having (M-1) zeros and zero poles. However, since the poles of its corresponding recursive filters are on the unit circle (or close to the unit circle) it is very sensitive to roundoff error accumulation [5].

As example, Fig 2. shows the zero – pole plot for the *M*=16 and *k*=3.

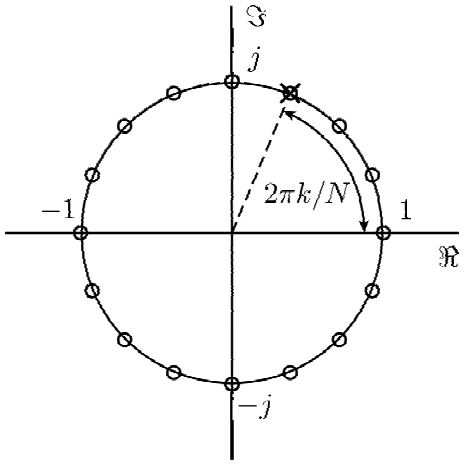

Fig. 2. Zero-pole plot for the M=16, k=3

The frequency response can be obtained by evaluating the magnitude of the it’s system function at

(7) $z = e^{j2\pi f / f_s}$

In the range $0 \le f / f_s \le 1$, were f_s is the sampling frequency. From (6) we have for the *k*-th bin

(8) $$H_k\left(z = e^{j2\pi f/f_s}\right) = \frac{\left(1 - e^{(j2\pi f/f_s) - M}\right) W_M^k}{1 - e^{(j2\pi f/f_s) - 1} W_M^k} = \frac{\sin \pi M \, f/f_s}{\sin\left[\pi\left(f/f_s - k/M\right)\right]}.$$

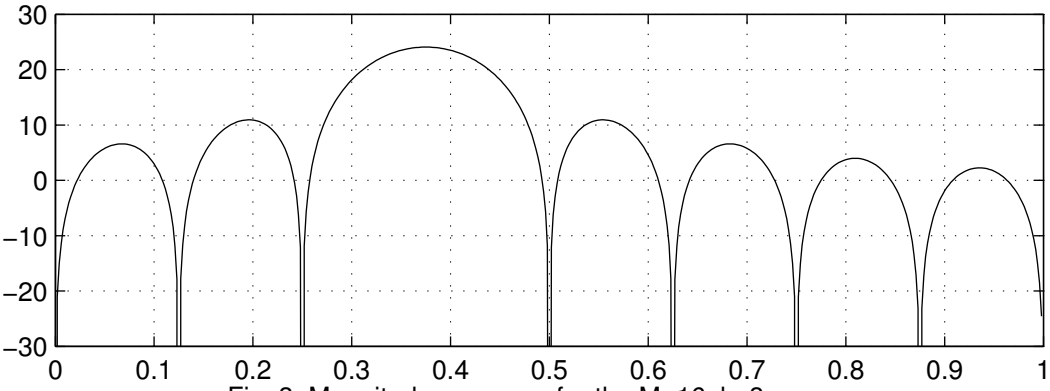

Fig. 3. Magnitude response for the M=16, k=3

Equation (6) leads to the single - bin SDFT filter structure shown in Fig. 4. The single - bin SDFT algorithm is implemented as an IIR filter with a comb filter followed by a complex resonator [2].

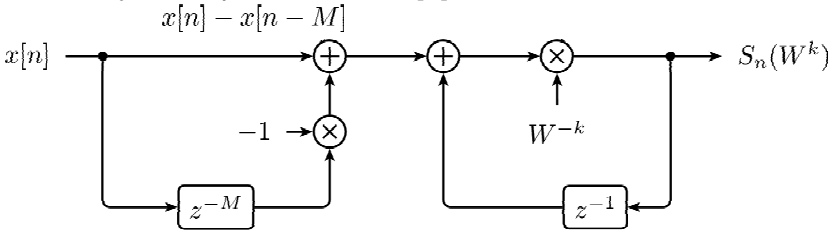

Fig. 4: The single - bin SDFT filter

If we want to compute all M DFT spectral components, M resonators with k=0 to M–1 will be needed, all driven by a single comb filter. The comb filter delay of M samples forces the filter's transient response to be M–1 samples in length, so the output will not reach steady state until the Sk(n) sample.

The SDFT structure for all spectral components is shown in Fig. 5 where we see that the DFT operates as a bank of narrow-band bandpass filters. The frequency responses for the filters associated with two adjacent bins are shown in Fig. 6, demonstrating that they have a large degree of spectral overlap.

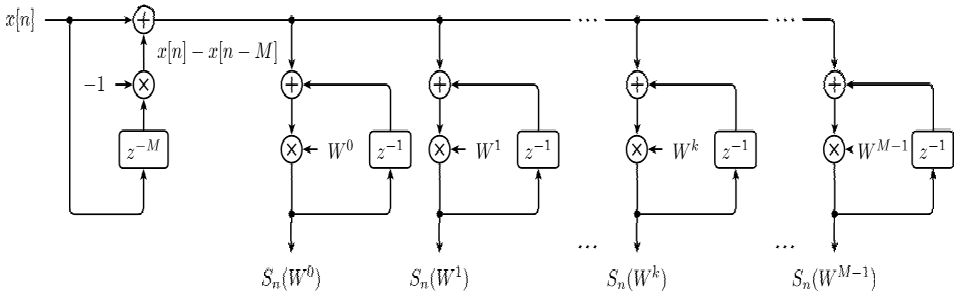

Fig. 5: Filter Bank structure for all spectral components.

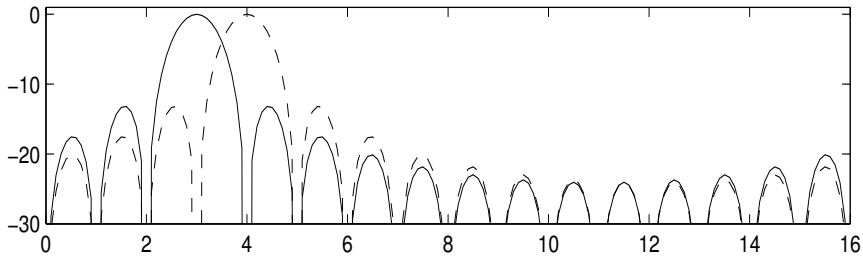

Fig. 6: Filter Bank Spectra. The frequency responses of two adjacent DFT bins for the case of N = 16.

This filter bank representation suggests that it may be possible to use other filter designs which have less spectral overlap, for example fast filter bank.

3. RESULTS, DISCUSSIONS, CONCLUSIONS

We are proposing an approach to the implementation of a discrete sliding DFT where the spectrum of the signal is estimated by realizing the DFT through a bank of IIR Filters. This filter bank representation suggests that it may be possible to use other filter designs which have less spectral overlap, for example fast filter bank.

A MATLAB program was written using this technique and validated. Future work includes computational cost analysis, synthesis issues and a viability study regarding the use of the algorithms for computing SDFT with high performance on graphics processing units (GPUs).

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Development of digital PMR dispatcher system based on DMR technology

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Abstract: *Two-slot 12.5 kHz TDMA-based systems, providing 6.25 kHz equivalency, is the right choice for most mobile professionals. Professional radio standards based on TDMA technology are already widely used around the world, and future requirements for even greater spectral efficiency are almost certain to be based on TDMA as well. Today and tomorrow, TDMA technology provides advantages of feature flexibility, lower equipment costs, longer battery life, futurereadiness and the proven ability to increase spectral efficiency without risking increased congestion or radio channel interference.*

Keywords: *TDMA, DMR, PMR, dispatcher systems*

Construction of PMR operational equipment system on the basis of DMR technology for a wide range of consumers of professional mobile radios can be established utilising a specific group of services, which activity requires maximum operational management.

Staff managing the said system need to be engaged within the implementation of the system's requirements, they need to be able to respond freely on the relatively large territories in both horizontal and/or vertical directions, they must be in a position of constant readiness, with a high level of awareness and to be able to respond to either individual or group requests in any or all live situations.

Opportunity for the individual or group response to a situation in the light of the above is composed of the following characteristics in any live current situation.

The most common cases in the composition of these services may come from:

1. Operational services - emergency aid, fire, and mountain rescue, etc;
2. Power structures;
3. Private security organizations;

4. Taxi services;
5. Collection and others.

Problems of operational management of assistants in each one of those listed services shall be decided with the help of an operational dispatching system built on the basis of a network of professional radios, which is a set of technical and daily software allowing users to work in real time. Since the subscribers of operational central dispatch system are people working under tension, in stressful situations, it is necessary for them to have besides the requirement for operability, a relaxed and comfortable environment allowing them to perform their duties efficiently effectively.

The main functional requirements of the system are:

1. High operability of access to the voice calls to all subscribers;
2. Opportunity for block and MSC call;
3. Automatic Identification of subscribers;
4. High Reliability and low noise and interference protection.

In order to increase the efficiency of the management and from the standpoint of maximum protection of the operators it is desirable that the operational central dispatch system maintain the following services:

1. Determining the location of subscribers and calculating the optimal routes for the movement to identifying purpose;
2. Transmission of information about the status of the subscriber or the result of the implementation of the task, through depiction of information to the specialized terminals or PC;
3. Coding (Encryption) of the transmitted information;
4. Access to databases.

In a case study on the condition of the market of similar systems recently , the authors established that:

1. Stock market shares occupy classical analogue systems for feedback, on the basis of approved be protocols. Their insufficient flexibility in ensuring the additional services or decision-making in specific situations is compensated for on the basis of a parallel system utilising existing cellular systems;
2. Potential clients monitor carefully the standards and the new trends and are ready to invest in the creation and development of corporate systems for professional radio;
3. Operators and users of the networks for radio seek not only to improve the quality of communications, but also to expand the set of services offered.

Analogue technology and systems for radio have proved to be a vital instrument, necessary for the work of many organizations, which is confirmed by the system being utilised effectively worldwide and with a high degree of daily commitment in resolving the problems in a variety of

different situations. In many respects however, they have reached high standards in fulfilling needs and opportunities. For most of their existence from as far back as half a century, they tried, tested and realized almost everything in the direction development and improvement.

Until recently TETRA the standard was seen as the only digital alternative to the analogue trunking systems, due to its unique location in the market and certain details, such as comprehensive pricing structure or clumsiness of the equipment were accidental or deliberate neglected by the producers of said systems, therefore not affording the consumers to make flexible decisions. For several years, however, ETSI - the European standardisation Institute for telecommunication approved two digital standard DMR and dPMR, which now allows the implementation and achievement of relatively inexpensive solutions in all configurations.

While ETSI dPMR systems are relatively new with route to market offers, DMR systems have spread widely in the last 2-3 years, and the reaction and response of consumers has been very positive.

dPMR with the option NXDN standard is offered at the moment, but based mainly with the needs and the characteristics of North American market.

Noting the importance of comparisons on number indicators most authors give their preference for the work of DMR standard in the establishment of medium-sized and large systems with a capacity exceeding 500 subscribers. The use of dPMR is justified in a working environment where direct feedback is required, without the use of connection or in relatively small systems i.e.100 - 200 subscribers.

The Standard DMR(digital mobile radio) has been developed by ETSI as a single open pan-European standard, enabling the user to use of fulfilling their requirements utilising equipment from different manufacturers, without concern about the compatibility of the various products. The seriousness of the manufacturers and their intentions is further illustrated by the fact that they signed the MoU , most of the main stream producers such as Tait, Fylde Micro, where, Motorola, Vertex Standard, Kenwood, etc. signed the said agreement to meet open standards.

Mainly mutation receives radio interface , which in the case reflects the physical and channel level of network model OSI. The network level is use the protocol IPv4. In this way Protocol for the transmission of data (PDP) of DMR allows to be seen radio network as IP subsystem, which provides manufacturers opportunity for the design of different applications in well standardized environment.

Characteristics of the standard DMR is triggering before everything from the technology for access to the channels principle (Time Division Multiple access), using working band 12.5 kHz.

Mainly mutation receives radio interface, which in the case reflects the physical and channel level of network model OSI. The network level is use the protocol IPv4. In this way Protocol for the transmission of data (PDP) of DMR allows to be seen the radio network as IP subsystem, which provides developers the opportunity for the design of different applications in well established and standardized environment.

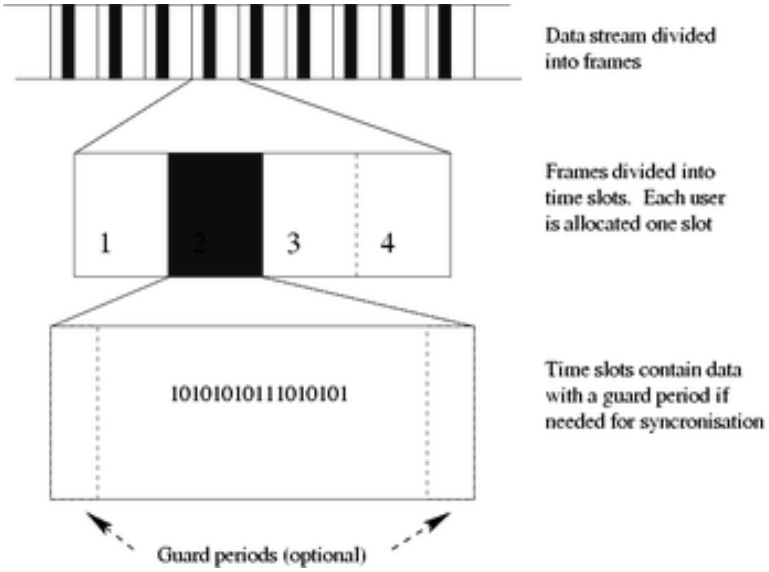

Fig.1

The required spectral efficiency is to be achieved by the provision of the total time of existence of a signal of a series of two independent time slots, each of which forms a single independent logical channel, so that within the framework of a working frequency may be carried out two conversation at the same time or to be organised transmission of data accompanied by call. In the most common type one single site radio network is presented to the fig.2.

From a physical point of view can be argued that the main parameters of broadcasting signal 12.5 kHz principle are analogous to the parameters of emitted an ordinary analogue signal with the same band. Despite some problems caused by the need for time sync, independent experts believe principle for the digital and therefore for the promising of the proposed other technologies of the market.

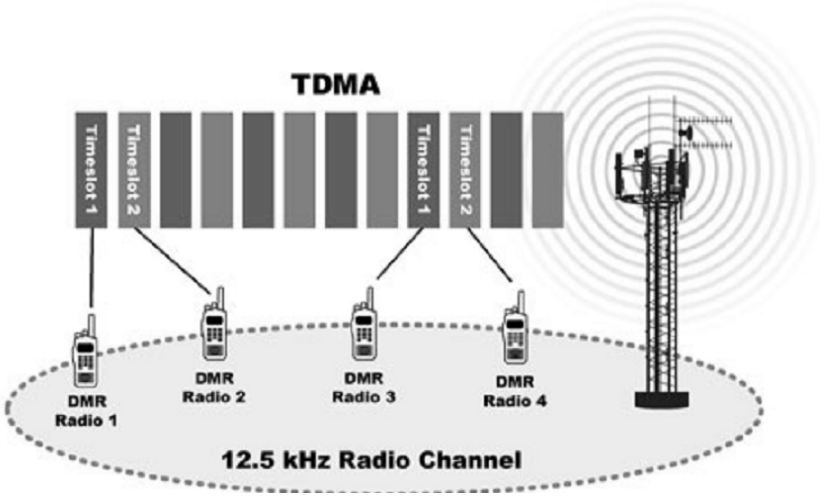

Fig.2

Taking into account the way the organization of radio interface, the main advantages of DMR to traditional analogue lines are as follows:

High spectral efficiency;

A large area of radio coverage - despite the fact that the spread of electromagnetic energy does not depend on the nature of broadcasts signal and its weight loss will be equally, in the case of a digital character of its contents contained adjustments for errors will allow adoption of the information with minimum losses. The same will happen and the impact of interference in channels - the receiver is trying to iron out any distortion of the signal. From here and the next advantage:

Better sound quality;

Greater duration of the work of battery. Since the DMR technology is used only one temporary slot, consumption of energy is active only for brief time employed by time slots. Respectively battery gives only half of its load for full cycle of transmission. Referring to the transmitter is a major consumer of energy is its economy reaches 40% in comparison with the work in analog mode;

Protection of the talks on the basis of the digital character of transmission;

Opportunity for integration in different networks.

The items listed above at first glance can be so insufficient to speak of a revolution in the field radio. Actually a network, located on the restricted area with a number of subscribers not more than 30-50 described advantages could appear to be an not particularly necessary, to some extent controversial and in all cases more expensive system.

Digital technology, however, provide such opportunities for communications to which line technique it is hardly touches. At- a simple, while for selective call by the analogue radio stations is necessary to have mounted circuit board SELECT 5, development of an addressing plan and drawing up of telegrams for each call, in digital entire exchange of identifiers and ex officio information runs automatically, as soon as free hires radio station.

Work on improving the DMR under the plan for development continues, as foreseen by the end of 2011 to be placed new relies - platform 2.0 , which will include:

Implementation of the Protocol XCMP (Extended command and management Protocol) . This Protocol will form yet another level, to work with peripheral devices XNL (network level XCMP), as the basis of IP, as well as without. In this way station capable of working with readers of stroke-code, with mobile printers, to be IP gate to telephone network;

New version of the operating circuit board GOB 2.0 on the basis of microprocessor Atme;

Support for Bluetooth devices, such as radio station only serves to channel of communication between the device and access point.

For professional users, digital two-way radio in licensed bands is the wave of the future. Whether they’re using analog radio today, or looking to implement their first two-way radio system, business organizations of all kinds will soon be choosing their first digital two-way radio solutions. DMR is the best established digital technology in the market today and is the clear choice for organisations looking to deploy new digital two-way radio systems, or to upgrade their existing analogue radio to digital.

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Using of programming system LabView in electrical engineering

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***Abstract**: This paper presents the utilization of LabVIEW (Laboratory Virtual Instrument Engineering Workbench) in the study of measuring methods for direct current. Graphical programming languages allow a natural, intuitive man-machine interaction. As a result, graphical programming has gained much popularity over the past several years, primarily because many scientists and engineers have experienced improvements in programming efficiency due to the natural understandability of graphical programming tools.*

***Keywords:** LabVIEW, virtual instruments, direct current, voltmeter, ammeter, DC circuits.*

1. INTRODUCTION

A virtual instrument (VI) is a program in the graphical programming language G. Virtual instrument front panels often have a user interface similar to physical instruments. G also has built-in functions that are similar to VIs, but do not have front panels or block diagrams as Vis do. Function icons always have a yellow background [1].

To be able to make meaningful statements about these quantities in circuits, we need to be able to describe their quantities in the same way that we might quantify mass, temperature, volume, length, or any other kind of physical quantity. For mass we might use the units of "kilogram" or "gram." For temperature we might use degrees Fahrenheit or degrees Celsius. Here are the standard units of measurement for electrical current, voltage, and resistance [2, 3]:

Table. 1. Measurement for electrical current, voltage, and resistance:

Quantity	Symbol	Unit of Measurement	Unit Abbreviation
Current	I	Ampere (Amp)	A
Voltage	E or V	Volt	V
Resistance	R	Ohm	Ω

Direct current is produced by such sources as batteries, thermocouples, solar cells, and commutator-type electric machines of the dynamo type. Direct current may flow in a conductor such as a wire.

The theoretical considerations regarding electrical current measurement in DC circuits and applications for their study and analysis using the LabVIEW graphical programming is analyzed in this paper [4-6].

2. COMPUTER SIMULATION OF ELECTRIC CIRCUITS

Computers can be powerful tools if used properly, especially in the realms of science and engineering. Software exists for the simulation of electric circuits by computer, and these programs can be very useful in helping circuit designers test ideas before actually building real circuits, saving much time and money [2, 5, 6].

These same programs can be aids to the beginning student of electronics, allowing the exploration of ideas quickly and easily with no assembly of real circuits required. Of course, there is no substitute for actually building and testing real circuits, but computer simulations certainly assist in the learning process by allowing the student to experiment with changes and see the effects they have on circuits [4, 6].

2.1. Calculating the currents in DC electric circuit

This example calculates the currents in the circuit shown. Supply the initial voltage V and the resistances R1, R2, R3, and R4 [2, 4, 7].

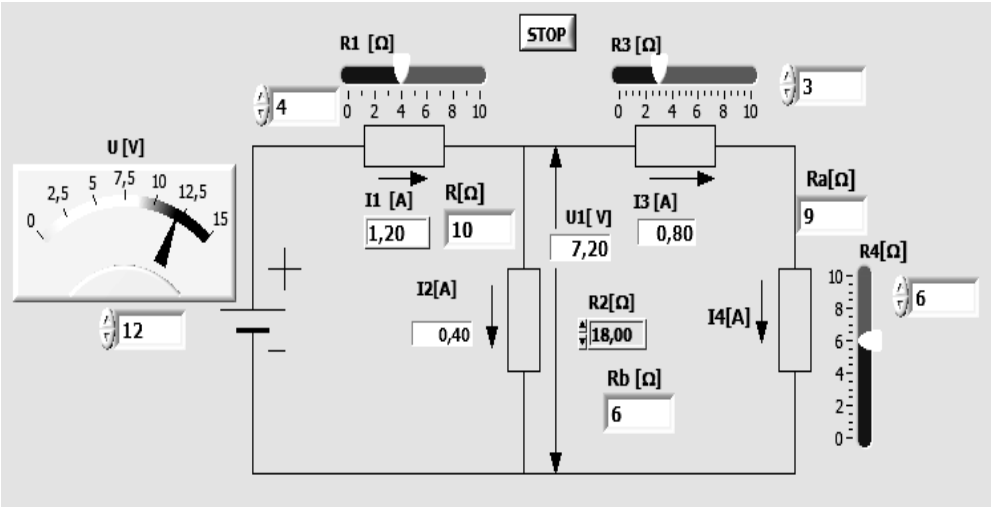

Fig.1 Calculating the DC currents in electric circuit-LabVIEW application, front panel.

The example will calculate the currents I1 through R1, I2 through R2, and I3 through R3, and R4. Find the current I in the circuit shown below and confirm the two Kirchhoff's Laws [2-5].

The method of calculation is as follows:

- Find resistances.

(1) $$R_a = R_3 + R_4, R_b = \frac{R_2 * R_a}{R_2 + R_a},\ R = R_b + R_1$$

- Find the current in the circuit.

(2) $$I_1 = \frac{U}{R}\ , I_2 = \frac{U_1}{R_2},\ I_3 = I_4 = \frac{U_1}{R_3 + R_4}$$

- Find the voltage to the parallel circuits and the currents through each of them.

(3) $$U_1 = U - R_1 * I_1$$

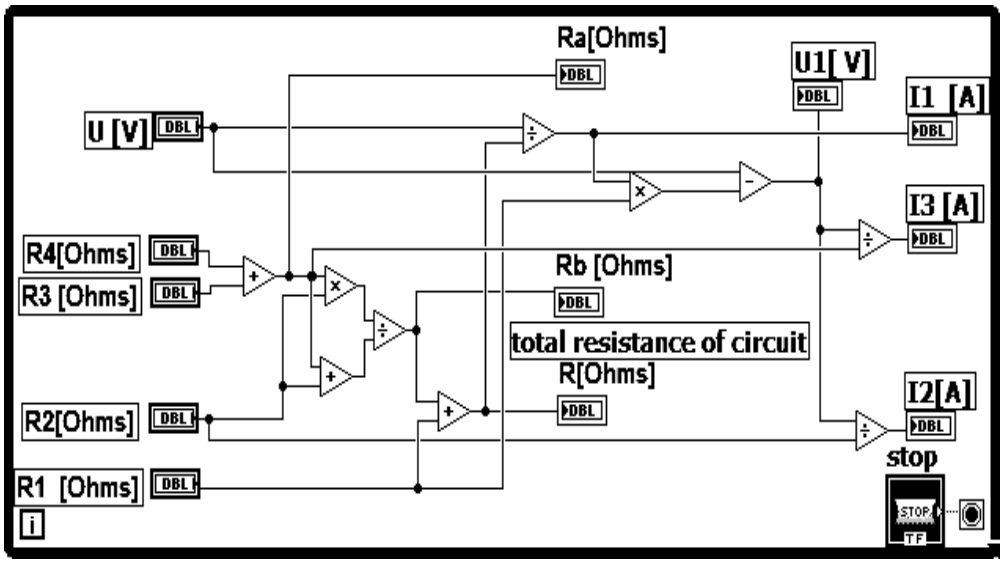

Fig. 2 Calculating the DC currents LabVIEW application, block diagram.

3. MEASURING RESISTANCE WITH A VOLTMETER AND AMMETER

3.1. Indirect method of voltmeter and ammeter

The determination of resistance through this method is based by Ohm law [2,6]:

(4) $$R = \frac{U_V}{I_A}, R_X = \frac{U_X}{I_X}$$

3.2. Scheme VA

It is necessary to be measured the voltage at the resistor terminals and inside current, then the resistance is calculated.

(5) $$R_X = \frac{U_V - U_A}{I_X} = \frac{U_V - R_A \times I_A}{I_A}$$

where R_A is the internal resistance of the ammeter.

The absolutely error is:

(6) $$\Delta R_X = R - R_X = R_A$$

The relative error is:

(7) $$\delta\% = \frac{R_A}{R_X} \times 100$$

This application gives the possibility for method analysis, having the following facilities: measurement range selecting at ammeter and voltmeter, tension and current change for measurement of different values resistance, as well as the error calculation [3-6]. The error decreasing imposes condition such as $R_X >> R_A$.

Determining resistance from measurements of potential difference (p.d.) and current.

Apparatus and materials.

- Power supply, low voltage 0 to 30 V, DC
- Voltmeter, 0 to 30 V, DC
- Ammeter, 0 to 5 A, DC
- Resistor 10 ohms (10 watt) to 1200 ohms (2 watt)
- Various other components

LabView application for VA scheme is presented in figure 3 [1, 5-8].

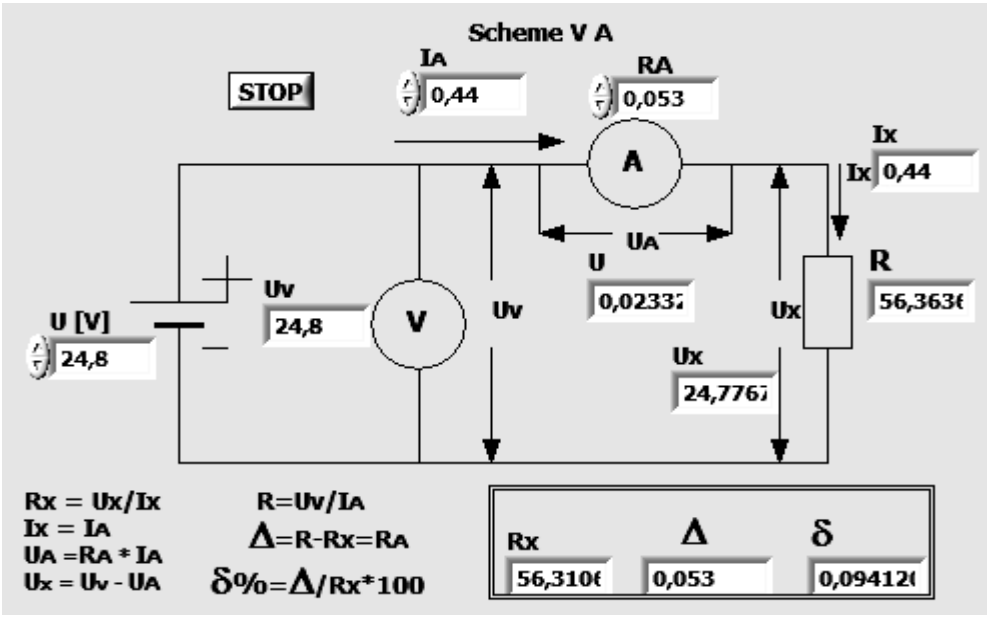

Fig. 3 Electric resistance measurement with voltmeter and ammeter VA scheme LabVIEW application, front panel.

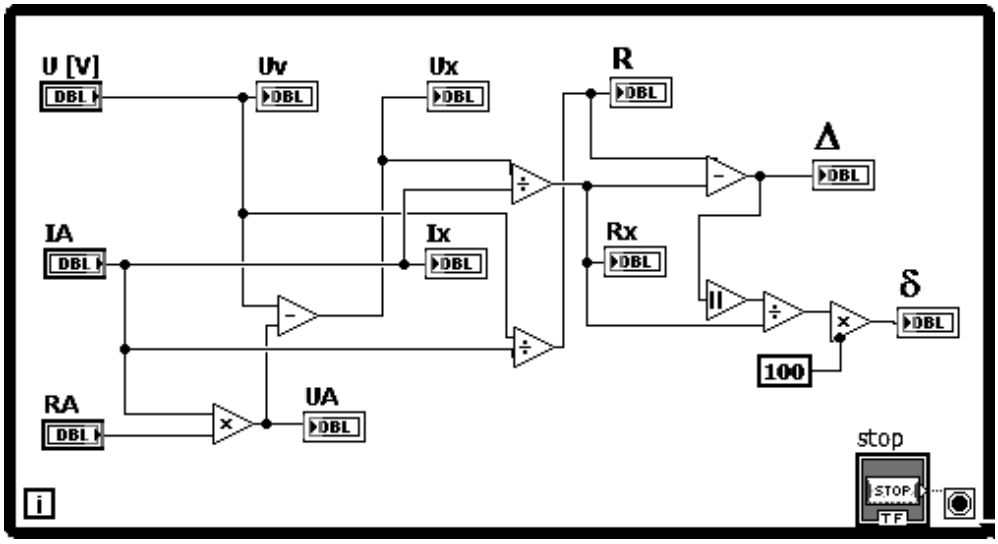

Fig. 4 Electric resistance measurement with voltmeter and ammeter VA scheme LabVIEW application, block diagram

3.3. Scheme AV

(8) $$R_X = \frac{U_X}{I_X} = \frac{U_V}{I_A - I_V} = \frac{U_V}{I_A - \frac{U_V}{R_V}} = \frac{R}{1 - \frac{R}{R_V}}$$

where R_V is the internal resistance of voltmeter.

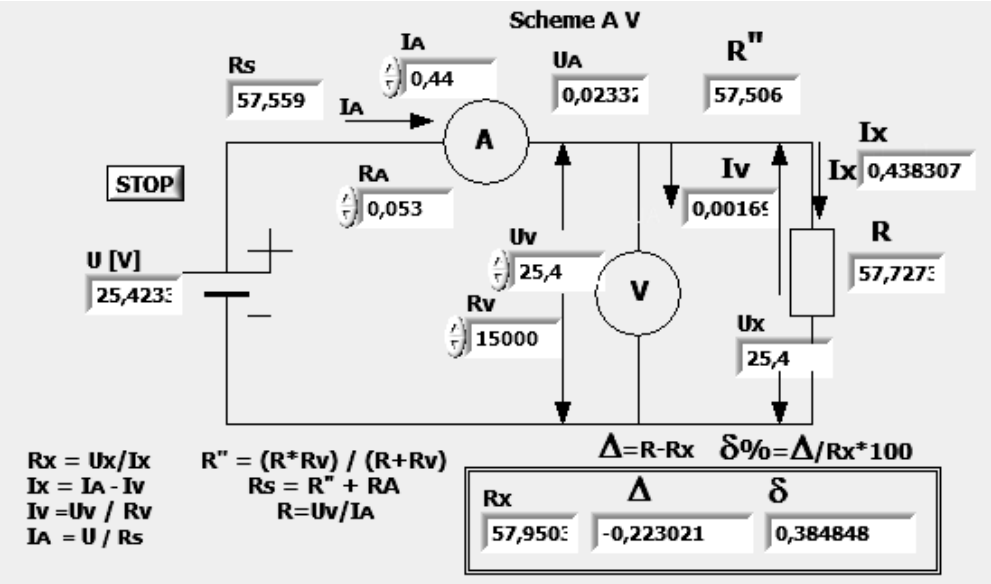

Fig. 5 Electric resistance measurement with voltmeter and ammeter AV scheme LabVIEW application, front panel.

The absolutely error is:

(9) $$\Delta R_X = R - R_X = \frac{U_V}{I_A} - \frac{U_V}{I_A - \frac{U_V}{R_V}}$$

The relative error is:

(10) $$\delta\% = \frac{\Delta R_X}{R_X} \times 100 = \frac{1}{1 + \frac{R_V}{R_X}} \times 100$$

The error decreasing imposes condition such as $R_X << R_V$.

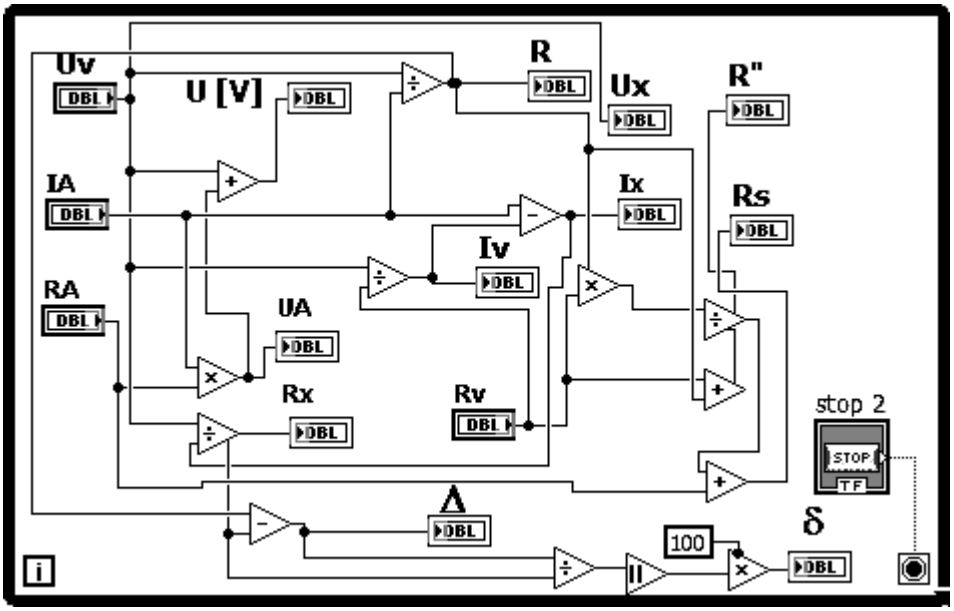

Fig. 6 Electric resistance measurement with voltmeter and ammeter
AV scheme LabVIEW application, block diagram

4. CONCLUSIONS

- The LabView software is applied in this work to calculation the DC current in linear electric circuits. The complete block diagram is shown in details in this paper.
- Using of LabVIEW, the analysis and the study of the electric resistance measurement methods in DC is assured. This analysis is useful in lab application.
- A grafical user interface (front panel) is desined in the developed LabView voltneter-ammeter scheme testing program. The made applications allow the input parameters change by means of the specific control elements.

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MEANS TO FORM KEY COMPETENCES BY TEACHING „CHEMISTRY AND ENVIRONMENTAL PROTECTION” IN GRADE 8

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Abstract: *A comparison was made of expected results set in grade 8 „Chemistry and environment preservation” curriculum and requirements to form one of eight key competences „Mathematical literacy and basic knowledge in science and technologies”. The results obtained allow to make some recomendations towards improvement of teaching through a more effective use of science content to form key competencies.*

Keywords: *teaching, science, chemistry, key competences, curriculum.*

Bulgarian education was set the important task to provide means for key competences acquirement and in this way to prepare young people for a wholesome life in present-day conditions. It is time to acquire not simply knowledge, skills and attitudes corresponding to different science areas but to put an emphasis on formation of key competences [1,2]. In the field of science some activity related to this objective has been conducted and a national contest in key competences has been held for three consecutive years [3,4,5].

When the secondary school curriculum now existing was prepared the ideas about key competences were not yet elaborated in our country [7]. That is the reason why there is no data about to what extent requirements to form key competences are introduced in different subject curriculum.

The objective of this paper is to asses grade 8 „Chemistry and environmental protection” curriculum related to the capacity to provide means to form and develop key competences in the field of science and technologies. The results could be of help to the elaboration of proposals for curriculum change because of its forthcoming actualization, as well as to outline some recomendations to teachers for its more effective and purposeful implementation.

„Basic competences in science and technologies” is a part of one of eight key competences recommended in the European referent frame „Mathematical literacy and basic knowledge in science and technologies” [1]. The outlined requirements for key competences in that part are used

and are compared to related expected results (standards) at curriculum level [8]. The results are shown in Table 1.

Table 1.

KNOWLEDGE
Knowledge of basic principles of nature and of basic concepts, principles and methods of science, and also comprehension of environmental consequences The student describes: - layer structure of electronic atom shell - physical and chemical properties (physical condition, rigidness, electrical and heat conductivity, relating to hydrogen, oxygen, and metals) characteristic for nonmetals from group VI A of the Periodic table - hydrocarbons (methane, ethane, propane, butane), alcohols (methyl and ethyl), organic acids (acetic), carbohydrates (glucose, sugar, starch, cellulose), fats, and proteins by composition - substances with important biological functions (proteins, fats, carbohydrates – sucrose, glucose, starch, cellulose, and amino acids) - harmful effect of some substances on man and environment (pollution with plastics, tires, car gases and fuels, acid rains) - oxidation-reduction processes as processes related to electron exchange
SKILLS
Capability to use scientific data for reaching a given objective as well as for making a decision or for communicating a conclusion based on facts - The student draws a general conclusion about the relation between the position of elements in the Periodic table and the properties of their simple substances and compound substances. - The student classifies already studied substances in basic classes of inorganic substances (simple substances, oxides, hydrogenous compounds, bases, acids, salts) by their composition and properties. - The student draws a general conclusion about the physical and chemical properties characteristic for metals from IIA and aluminum (IIIA group of the Periodic table). - The student shows relation of properties of already studied inorganic substances (caustic and hydrated lime, carbonates, sulfur acid, aluminum and its alloys) to their use. - The student uses the series of relative activity of metals.

- The student shows by chemical equations characteristic properties of already studied substances (Ca, CaO, $Ca(OH)_2$, Mg, S, SO_2, SO_3, H_2SO_4, sulfates, Al).
- The student shows by chemical equations the genetic relations: element – oxide – base (acid) – salt.
- The student determines metal activity.
- The student works out mole ratios.

Capability to identify basic characteristics of research as well as to communicate the reasoning and conclusions that had lead to them.

- The student identifies organic and inorganic substances by composition.
- The student distinguishes compounds of elements from IIA and VIA group of the Periodic table and aluminum by their behavior relative to water, bases, and acids.
- The student identifies acids and bases by their properties (characteristic ions in solutions, change of color of litmus, phenolphthalein, and a universal indicator, behavior relative to metals, oxides, acids, and base).
- The student traces the areas of application of some plastics (PVC, polyethylene, polystyrene), liquid and gaseous fuels (oil, natural gas, propane-butane mixture), fibers, and rubber.
- The student plans elementary chemical experiments and uses the obtained data to draw conclusions.
- The student uses pH to determine solution acidity.
- The student calculates mole masses, mole volume, mass part and yield.
- The student uses qualitative reactions to identify sulfates by $BaCl_2$, acids and bases by indicators, $Ca(OH)_2$ by CO_2, calcium and its salts by flame coloring.

ATTITUDES

Readiness to evaluate critically and curiosity towards research advancement

- The students study properties of Ca, Mg, $Ca(OH)_2$, $CaCO_3$, S, diluted and concentrated H_2SO_4.
- The students study interaction of aluminum with acids and bases.
- The students range metals by activity based on experimental data.
- The students foresee interaction of salt and metal using the series of relative activity.

Comprehension of advancement but also of limitations and risks of scientific theories

- The student estimates the necessity of secondary processing of metals, glass, plastics, rubber, paper, fibers.
- The students asses organic substances as: materials, substances that build up living nature and sources of environment pollution.

Interest towards ethical problems and expression of respect to security and sustainability of scientific advancement and comprehension of its relations to any man and any community.

- The student applies rules of work with already studied substances and ways to make them harmless (work with acids and bases).
- The student describes possible ways to solve ecological problems (recycling, decomposition to harmless substances, wasteless technologies.

The comparison of requirements for basic competences and curriculum, made in Table 1, shows that a significant part of grade 8 "Chemistry and environment preservation" curriculum is related to acquiring of knowledge. For example, a rather great part of the curriculum is directed to expressing interactions among different substances by chemical equations. At the same time there are requirements to distinguish different classes of substances, to relate their properties to areas of use, and also to investigate autonomously some of them.

It is necessary to find appropriate forms and approaches to develop key competences but that to a great extent depends on teachers. It is evident that conventional forms of teaching are ill suited for that purpose. One possible way is to use active and interactive methods more intensively and purposefully. Independent or team work of students to solve appropriate problems related to transfer of knowledge from other sciences could result in comprehension of possible use of substances and processes in practice, and also safe work, as well as in cultivating interest and critical assessment of scientific advancement and also all other characteristics of key competences. That is why we assume that the most effective way to form and develop key competences could be realized using appropriate problems containing generalization, revision, control and assessment [6, 7]. In that way the subject material could be related to key competences clearly and directly.

It creates the impression that different elements of discussed key competences are represented to a different extent. For example, cultivating "Interest to ethical problems and display of respect to safety and to sustainability of scientific advancement and comprehension of its relation to any man and any community" occupies an insignificant space in grade 8 "Chemistry and environment preservation" curriculum. However, these

competences are formed through the teaching of other subjects from the cultural and educational area “Science and ecology” and are developed in following grades too. It is necessary to make analyses of the whole science content and to decide whether it is necessary to make corrections and additions to the curriculum aiming a holistic development of key competences in that area.

As a result of the completed research the following conclusions could be made:

1. In State educational requirements to subject content and in grade 8 “Chemistry and environment preservation” curriculum is set the bases for acquiring elements of the key competence “Mathematical competence and basic competences in science and technologies”.
2. Effective use of curriculum to form key competences could be realized using interactive methods and appropriate problems.
3. It is necessary to reformulate some of the curriculum elements in order to support key competences formation.

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Non-standard mathematical problems in classes

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"I lost that day and time, which I have not learned anything new ."
.. Jan Amos Komenskiy, XVI century

Abstract*: The article examines the role of non-standard tasks to motivate students to learn activity, to analyze the effectiveness of training in solving unusual problems, to stimulate students' motivation and activity.*

Keywords: *non-standard tasks, students' motivation and activity.*

1. INTRODUCTION

An important goal of modern education is to educate people who think in a non-standard way when resolving important issues. When doing non-standard problems, students receive non-standard knowledge. Non-standard knowledge includes signs that allow distinguishing knowledge of this type. The distinctive features of non-standard knowledge are: its relationship to activity that psychologists call "productive", "creative", an independent search of ways and options for solving the given problems, unusual working conditions; reproducing actively earlier knowledge obtained in unknown conditions [3]. If the student participates actively in the learning process, they are able to penetrate deeply in the material studied and to absorb it to the level of regularization and leading ideas. Therefore the correct selection of material is very important for the motivation.

2. ROLE AND PLACE OF NON-STANDARD PROBLEMS

According to Friedman and Turetskiy [4] the types of mathematical problems solved in the school course can be classified: **in accordance with the nature of the objects** in them, into *practical (real) and mathematical*, **in terms of theory**, which is used to solve them - into *standard and non-standard*, according to **the type of requirements in them** – into *calculation problems*; *conception* or *transformation problems* as well as *proof* and *explanation* problems.

Non-standard problems are those for which the school course in mathematics doesn't have common rules and principles for determining the precise algorithm for their solution [4, p.45]. They can be posed as problematic situations, role-plays, active-plays and problems with elements

of entertainment - life and fantastic situations, puzzles and more. They can be used in mathematical lessons not only as a motive for the introduction of new material, but also to show the application of new knowledge and to solve specific practical problems as well as to beak the monotony of the learning process. Such tasks encourage students to be active and creative. They are important means of education through which pupils can form a sustainable interest in the learning process, take down the tension, help to develop habits for school activity and have an emotional impact so that students can form deeper and profound knowledge.

The process of resolving non-standard problems is composed of the consistent application of two activities: 1) minimize non-standard problems to another, equivalent to it, but now standard problem (using transformations or reformulation of the problem), 2) breaking the non-standard problem into several standard subproblems. Depending on the nature of non-standard problems we apply one of them or both, and in more complex problems - repeated implementation of them both.

As we already noted there are no common rules to solve non-standard problems, as well as some more specific rules to reduce the non-standard problems to standard except for general guidelines or recommendations. These guidelines typically called heuristic rules do not have a binding nature, but only contain advice which may lead to solving (or not) the problem. The solutions of some mathematical problems might be reduced to a few basic recommendations:

1. Read the problem and determine which type it belongs to - standard or non-standard;
2. If you have already recognized a familiar standard problem, use for its solution a well-known standard algorithm.
3. If the task is non-standard then:
   a) Try to break the problem into subproblems of a standard form;
   b) initiate in the condition subsidiary elements such as parameters, additional conceptions etc.
   c) reformulate the problem or replace it with another equivalent to it.
4. To materialize the steps listed above, try to make a visual subsidiary model of the problem - write it schematically.

Solving non-standard problems is an art that can be managed with the help of profound and continuous analysis of the performed actions for

finding a solution of such problems and constant practice by solving various problems.

Non-standard problems can be used in different types of lessons – revision lesson, lesson for new knowledge, to acquire the knowledge, with different training methods - narrative, discussion, individual work and others. Systematic use of non-standard problems in mathematical classes contribute to the activation of the cognitive activity of students and developing different thinking qualities and memory (flexibility, etc.).

3. EXAMPLES OF NON-STANDARD TASKS

We will suggest some ideas for using the non-standard problems in studying certain subjects.

Pythagorean triads. It is known that if the numbers *a, b* and *c* form a Pythagorean triad then ka, kb and kc are also Pythagorean triad. Moreover, the numbers $a, (a^2-1)/2, (a^2+1)/2$ also form a Pythagorean triad and change values to get different Pythagorean triads - 5, 12 and 13, 7, 24 and 25. A random number of fractional Pythagorean triads can be worked out, where the numerator of the fraction is equal to the whole part of the number and the denominator is an arbitrary positive number, identical to all numbers of the triad. Since 8, 15 and 17 form a Pythagorean triad then $8\frac{8}{9}$; $15\frac{15}{9}$ and $17\frac{17}{9}$ are also Pythagorean triad. Knowledge of the Pythagorean triads allows an oral problem solving such as:

Problem 1. If $\operatorname{tg}\alpha = -\frac{24}{7}$ и $\frac{\pi}{2} < \alpha < \pi$, find $\sin\alpha$ and $\cos\alpha$.

Answer: $\sin\alpha = 24/25$ and $\cos\alpha = -7/25$.

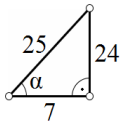

Fig.1

Students do not need formulas, but the definitions of sinus, cosine, tangent and cotangent of an acute angle in a orthogonal triangle and the signs of these functions in the interval $[0°, 2\pi]$.Using of Pythagorean triads provides the opportunity for oral solutions of most mathematical problems of this type and test the knowledge of more students.

Some types of square equations. Sometimes students have to solve square equations with relatively large coefficients and get discriminant of which is difficult to extract square roots. This is the equation: $2011\cos^2 x - 2008\cos x - 3 = 0$, which can be solved verbally,

$(x_1 = 1,\ x_2 = -3/2011)$. That is why it’s better for students to learn some little "tricks" for verbal solution of certain square equations. If $ax^2 + bx + c = 0,\ a \neq 0$ is a quadratic equation then: a) with $a + b + c = 0$, b) with $a - b + c = 0,\ x_1 = -1$ and $x_2 = -c/a$; c) if $a \pm b + c \neq 0$ the equation $y^2 + by + ac = 0$ is solved verbally, then $x_1 = y_1 : a$ and $x_2 = y_2 : a$. For example, the equation $5x^2 - 11x + 2 = 0$ is fulfilled $5 \pm 11 + 2 \neq 0$ and the roots of $x^2 - 11x + 10 = 0$ are 1 and 10. Then the given equation has roots 1/5 and 2.

Bisectrix's problems. In some cases it is appropriate to give additional problems to the subject taught to enable students to look at the studied material from another angle and thus to deepen and expand their knowledge. Math problems similar to the following three ones may be proposed for self-study, after examining the theme "Bisectrix of an angle", and their solutions have to be reported by the students in the coming hours or extracurricular work.

Problem 2. To construct the bisectrix of acute angle between the straight lines *a* and *b* if their intersection point is not available (Fig. 2)

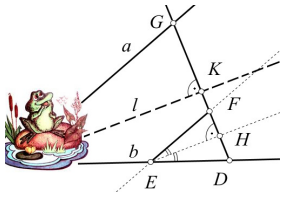

Fig.2

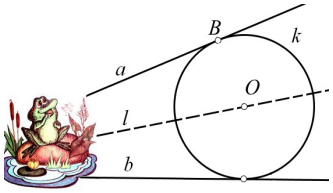

Fig.3

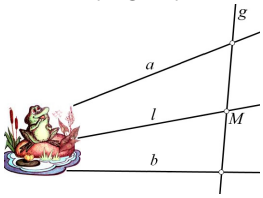

Fig.4

One possible way to solve the problem is: To construct a) a straight line through an arbitrary *E* from b – parallel to *a* and point F from which that $EF = ED$, where $D \in b$; b) the bisectrix *EH* of $\sphericalangle DEF$; c) the intersection *G* of the half-line *DF* and the straight line *AB*; d) midperpendicular *l* to *DG* is the bisectrix to find (Why?).

Problem 3. We have the straight lines *a* and *b* as their point of intersection is not available. To construct a circle (Fig. 3) which is tangential to the line *a* in point *B* and to line *b*.

Problem 4. We have the lines *g*, *a* and *b* and, as the intersection of a and b is not available. (Fig. 4). Find a point M from line g, which is at regular intervals from lines *a* and *b*.

The tasks above can be formulated as **practical** ones: In a meadow close to a swamp, students must find points of the bisectrix of two lines that intersect at an inaccessible point and students only have stakes and rope.

In other cases it is useful for students to be shown how by means of elementary mathematics we can prove certain allegations, which they use without knowing their proof. For example:

Problem 5. Prove that the medians have a point of intersection.

Solution: If AA1, BB1 and CC1 are the medians of triangle ABC and O is the point of intersection . Let S_1, S_2, S_3, S_4, S_5, S_6 be the surfaces respectively of $\triangle AOC_1$, $\triangle BOC_1$, $\triangle BOA_1$, $\triangle COA_1$, $\triangle COB_1$ and $\triangle AOB_1$. We will use the fact that every median divides the triangle by two triangles with the same surface (they have same base and common altitude), then we have $S_1 = S_2, S_3 = S_4$ and $S_5 = S_6$ (fig.5). If $S_{\triangle ACC_1} = S_{\triangle CAA_1} = 0{,}5S_{\triangle ABC}$ and $S_1 = S_{\triangle OAC_1} = S_{\triangle ACC_1} - S_{\triangle AOC} = S_{\triangle CAA_1} - S_{\triangle AOC} = S_{\triangle OCA_1} = S_4$, so $S_6 + 2S_1 = S_5 + 2S_4$ and $S_{ABOB_1} = S_{CBOB_1}$. Besides the median BB_1 separates triangle ABC into two triangles with the same surface and the point O must be on the segment BB1.

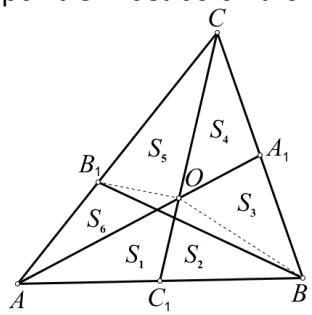

Fig.5

Students should be advised to answer the following questions after the solution:

- What kinds of ideas have lead to the solution and how is this mathematical problem similar or not to another one already solved one?
- What conditions are used and will the statement be true if some of the conditions are missing or their importance is decreased?
- Is it possible for conditions and solutions to change places?
- Can we generalize this mathematical problem or could it be reached to interesting results?

It is better for students to do a sum for a day in order to analyze it than to do many sums but in a perfunctory manner. Lifted spirit of finding the solution of a non-standard problem is a sign for useful and successful work. The knowledge they get that way is thorough and lasting.

In some cases it is good to formulate the conditions again in more understanding way as: “we define that…..”We can reckon that”…etc.

Problem 6. From a sheet of paper in a shape of a triangle we cut a parallelogram and we must prove that the half of the surface of the triangle is equal to the surface of the parallelogram.

Solution: The difficulty is to find the position of the parallelogram in the specified triangle ABC. We will reform the parallelogram in a way to decrease its surface.

a) We “prolong” $MNPQ$ of MN_1P_1Q, so that some of its apex to lie on the AB side of $\triangle ABC$ (Fig.6a) and obviously $S_{MN_1EF} < S_{HTRK}$

b) We reform the parallelogram MN_1P_1Q in the parallelogram MN_1EF (Fig.6b), so that one of its sides to lie on one of the apexes of given triangle and $S_{MN_1P_1Q} = S_{MN_1EF}$, so that all his apexes to lie on triangle ABC and $S_{MN_1EF} < S_{HTRK}$

c)We prolong the parallelogram MN_1P_1Q so that all of the apexes to lie on the sides of $\triangle ABC$ (Fig. 6c) и $S_{MN_1EF} < S_{HTRK}$.

d) We reform the parallelogram $HTRK$ to the parallelogram $HALK$ without changing its surface in a way one of its apexes to coincide with an apex of $\triangle ABC$ (Fig. 6d).

e) We coincide the parallelogram $HALK$ with $\triangle HKC$ and $\triangle LBK$ (Fig.6 e), supplemented to the triangle ABC. We get that $S_{ALKH} = S_{\triangle HKC} + S_{\triangle BLK} - S_{\triangle TLX} < S_{\triangle HKC} + S_{\triangle BLK}$ and $S_{ALKH} \le S_{\triangle ABC} / 2$

We get the equation when KH is the middle segment of the triangle ABC

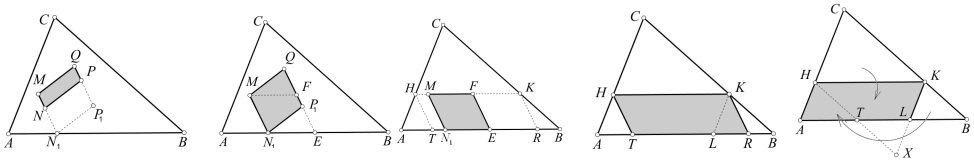

Fig. 6 a) *Fig. 6 b)* *Fig. 6 c)* *Fig. 6 d)* *Fig. 6 e)*

One of the most important qualities of thinking in man is their logic, the ability to draw true conclusions of known facts and statements. Mathematical study develops not only the logical thinking of a person but other valuable qualities such as quickness of mind, punctuality, critical attitude, patience to achieve their aims, ability to find the right way in complicated situations, etc.

Different ways of finding the solution of one and the same mathematical problem helps the students to understand advantages and disadvantages of one or another method depending on the content of the sum. It is not rare for a solution found to be used later in another sum. Finding different ways of solving a sum is interesting thing to do, requirng knowledge of different math courses, for example sum number 7:

Problem. 7. There is a rectangular triangle ABC. Through the apex C CD is drawn. If M and N are the medians of segments CD and DB, prove that $AM \perp CN$.[*1, 65 page*].

Solution: Method 1: (appropriate for lessons about “The Middle Segment in a Triangle”). In triangle BDC, MN is the middle segment (Fig.7).

Then $MN \| CB$ and respectively $MN \perp AC$, i.e. M is the orthocenter of triangle ACN and $AM \perp CN$.

Method 2: (appropriate for lessons about "Scalar Creation of Vectors") As N is the median of BD, there fore $\overrightarrow{CN} = 1/2\left(\overrightarrow{CD} + \overrightarrow{CB}\right)$. Besides $\overrightarrow{AM} = (1/2)\overrightarrow{CD} - \overrightarrow{CA}$, then $\overrightarrow{CN}.\overrightarrow{AM} = 1/2\left(\overrightarrow{CD} + \overrightarrow{CB}\right) \cdot \left((1/2)\overrightarrow{CD} - \overrightarrow{CA}\right) =$ $(1/4)\overrightarrow{CD}\left(\overrightarrow{CD} - \overrightarrow{CA} + \overrightarrow{CB} - \overrightarrow{CA}\right) = (1/4)\overrightarrow{CD}.\left(\overrightarrow{AD} + \overrightarrow{AB}\right) = 0$ and $\overrightarrow{AM} \perp \overrightarrow{CN}$.

Method 3 (appropriate when doing sums about transforming in tangenital plane) Let $h = h\left(D, k = CD : AD\right)$ and $\varphi = h \circ \rho$ be respectively homothety and rotation. It can be proved that applying $\varphi = h \circ \rho$ represents points D, A and C as, accordingly, the points D, C and B. Then $\varphi\left(DC\right) = DB$ and the median M of DC will apply in the median N of DB. Therefore $\varphi\left(AM\right) = CN$ and $AM \perp CN$.

The first and second methods are standard ones.

Problem 8. An ant is on the apex M of a transparent cube (Fig.8). Find the shortest way of the ant to the grains of wheat in the apex P.

The studenst are involved in real situation from life by this sum, to find the shortest way from one point to another. The student's knowledge improves about the shortest distance in the plane – the segment that combines them and it is underlined that this is a more difficult task in space. If we manage to bring the mathematical problem to a plane one, it becomes then a standard one. A colective analysis of the solution can be done in the following way: to cut the cube in our thoughts and to place the upper base and surounding side (Fig.8), where apex P in one plane is, then the sum becomes known to us. It is obviuous that $ME + EP = ME + EP' < MT + TP' = MT + TP$ for an arbitrary point $T \neq E$.

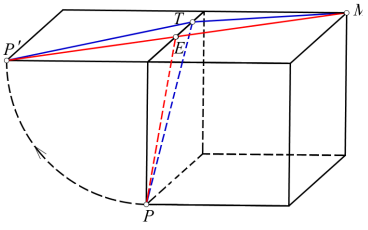

Fig. 8.

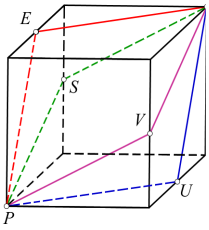

Fig. 9.

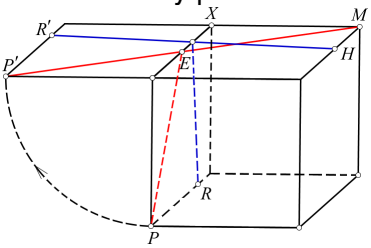

Fig. 10.

Suitable questions after examining the mathematical problem solution are: how many solutions one can find (fig.9); is it ossible to use this way of solving the sum if the position of points M and P is changes, for example M=N and P=R (Fig. 10), etcr.

4. CONCLUSION

There are not enough non-standard sums in the mathematical classes and it is usually explained with the time limit for developing the creativity of people taught, the lack of material in textbooks and methodological literature and lack of training for accomplishing tasks of explorative nature and so on. The motivation of solving non-standard sums is based on conceptions of a complex and synergetic approach. Students find solutions not only by using standard algorithm but also by new, untraditional methods of solving the problem found on their own. The non-standard sums are an obstacle regarding harmful mechanical transfer of algorithms for solving problems, they destroy wrong associations, contribute to find new ways in what already is acquired as knowledge, help to transfer knowledge in new conditions and to use new methods of mental activity. The non-standards sums should not be chosen by chance – they must be connected with the school material and their difficulties to be comfortable to talents of the students. They are more beneficial when their solutions are found without preliminary preparation and when they vary in content and ways of solving them. Students should be given non-standard sums according to their abilities, which improves the knowledge acquired in the mathematical classes.

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KEY COMPETENCES IN STATE MATRICULATION EXAMS IN CHEMISTRY

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Abstract*: To report the key competencies in natural science and technologies the results from the matriculation exam 2010 of chemistry and environmental protection are used. In the article are shown some opportunities for optimization of tasks for external and internal assessment of students' achievements and forming of key competences.*

Keywords: *chemistry education, matriculatoin tests, key competences.*

In according with the approach assumed by the European Commission working group, competencies are defined as combination of knowledge, skills and way of thinking that fit the given circumstances. Key competencies are the competencies needed by each person for their personal knowledge and development, active civil behavior, social integration and employment [1].

The integration of the European and worldwide requirements in the Bulgarian education system during the last years bring out the question about development of key competencies in the future generation. If built skills in people should support them in achieving their individual life goals that depend on their personal interests, dreams and will for lifelong learning, then it is necessary to evaluate the role of the undergraduate education for development of key competencies.

In the last years matriculation was established as basic method for evaluation the achievements of the students at the end of their undergraduate education. The results from the last couple of years have been edited, published and analyzed by specialists of different areas [2, 3]. This information is important not only for following the achievements of a particular student, class or school. This feedback is necessary for the success of the implemented educational programs and the effectiveness of the standards in the area of the natural sciences determined in the educational programs and state educational requirements. The analysis of

the results can provide the teachers with an exact outlook on what should be taken into consideration during the preparation of the future undergraduates. On the other side this is also a reminder for the responsible authorities that should answer the question if it is necessary to restate some elements of the educational programs in order to support the development of key competencies [4].

The aim of the present article is to point out to what extent the key competencies can be detected through tasks by means of open-end questions in the public matriculation examination in Chemistry and Environmental protection. The analysis that has been done is consistent having set requirements for one of the eight key competencies "Mathematical literacy and basic knowledge in science and technologies" in its part "Basic competencies in the natural sciences and technologies":

- skill to use scientific data in order to achieve given aim, as well as to make decisions or to come to conclusions based on facts;
- adjustment for critical evaluation and curiosity for the scientific progress;
- awareness of the progress, as well as of the limits and risks of scientific theories;
- interest in ethic issues and respect to safety as well as to scientific progress stability and understanding of its links with every person and every community, etc. [1].

The public matriculation examination in Chemistry and Environmental protection consists of solving 50 text tasks, divided in 2 groups. The first group contains 35 tasks each of which with 4 possible answers. The second group includes 15 tasks with open answers. Each of them is valued with different points depending on the number of components included in it and their relative difficulty level. The highest point number for the tasks in the second group is 65. The evaluation is based on 434 assessed examination works of students who held the public matriculation exam on May 17th, 2010.

The analysis of the second part of public matriculation examination in Chemistry and Environmental protection shows that it includes tasks from all categories in Bloom's Taxonomy. The biggest percentage is for the tasks from the domains of knowledge, comprehension and application the lowest percentage is in the domains of analysis and synthesis. As it could be expected, the undergraduates coped well with tasks from the first 2 domains (knowledge and comprehension) while they had much more difficulty in the domains of application, analysis and synthesis.

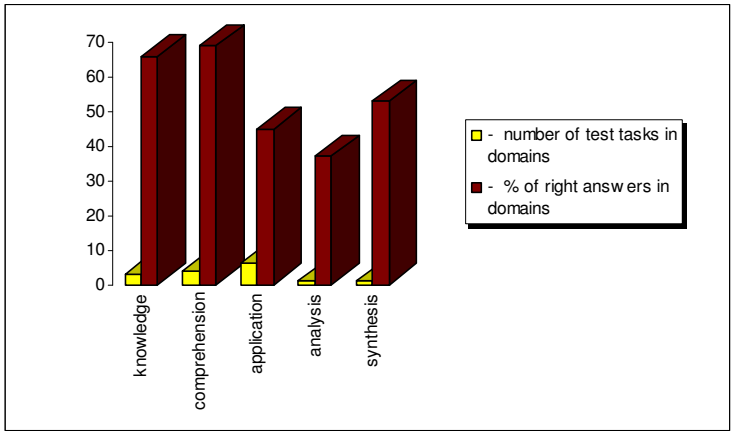

Fig. 1. Distribution of tasks and % of correct answers in different domains

Task 46 from domain analysis is linked with one of the important for natural sciences key competencies (namely the ability to use scientific data in order to achieve a set goal as well as to make decision or draw conclusions based on facts). It is:

In three test-tubes there are colorless solutions of:

a) sodium chloride

b) barium dinitrate

c) phenol

Suggest reagents you can recognize these substances with.

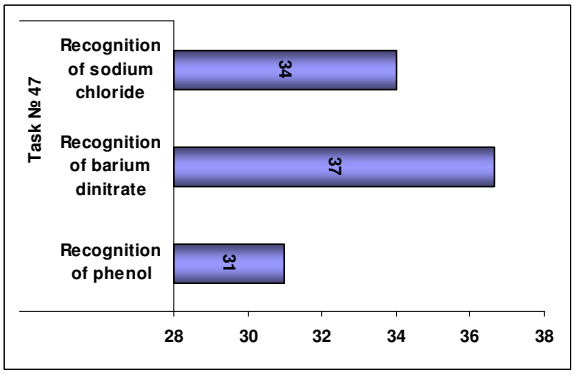

Fig. 2. Distribution of correct answers for the given examples

The results are low in all three cases – from 31 to 37 % correct answers. The question that appeared is why the students didn't manage to recognize even the sodium chloride having in mind that the silver nitrate is explored as reagent already in grade 7. The students remember mostly what they see in class but unfortunately chemical experiments are rarely used in class nowadays. Very often there is a lack of reagents, the teacher doesn't feel prepared or just there is not enough time in class.

The lowest results shown by the students are for question 38 where the percentage of the correct answers is only 19. The task requires to write down a known equation and to consider the conditions for the process to take place.

38. Express with chemical equation the reaction for incision of calcareous rocks to form caves.

It must be pointed out that the task is from the open type and the graduates have to write down the equations required. Probably they would have done better if they had been given possible answers. Another reason for these results is the insufficient linking between the studied facts and regularities with real processes in nature and in practice during the education.

The results for task 50 confirm this conclusion:

50. Methane is one of the basic fuels in industry.

a) How many m^3 oxygen are needed for the complete burning of 1 m^3 methane?

b) How is the mixture of methane and air in coal mines called?

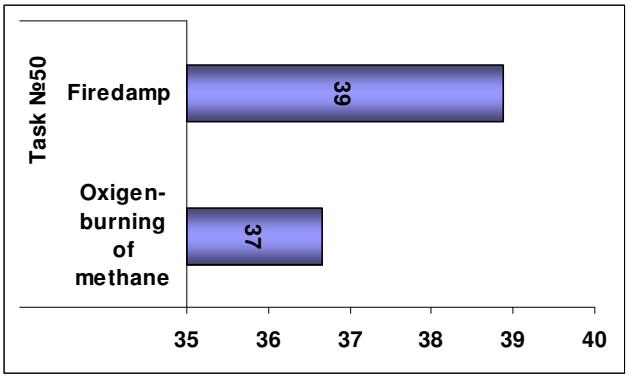

Fig. 3. Distribution of correct answers for a) and b)

Only 39% of the examined students identified the methane and air mixture in coal mine as firedamp-something that they should know as general knowledge. A little bit better is the data for task 49 that is related with classification of some substances often used in practice.

49. Which of the substances cellulose, saccharose, polyester, nylon are:

a) natural products?

b) polymers?

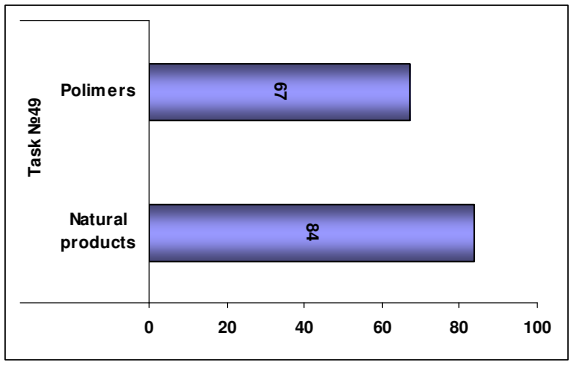

Fig. 4. Distribution of correct answers for a) and b)

The failures here are due to insufficient clarification of the link between obtaining and characteristics of substances and possibilities for their use.

Based on the conducted analysis for the possibilities to define key competencies assessment through tasks from the public matriculation examination in Chemistry and environmental protection, it can be concluded that many of the skills underlying the key competencies "Mathematical literacy and basic knowledge in science and technologies" are not learned at a sufficient level. The undergraduates manage with easier tasks which require choice between given possible answers or comparison. They have difficulties when they have to consider and write down the correct answers by themselves, to find out regularities, and finally to formulate conclusions.

The fact that the students are not able to express themselves correctly in their mother language causes special concerns as this is the first key competency according to the European referent framework. In the exam papers there are words like «атмосвера» instead of атмосфера; «замръсява» instead of замърсява; «катализатъра» instead of катализатора, etc.

The question that rises is if the education at school gives possibility for development of one the following competencies: skills for independent learning and gathering of information. It is alarming that the student nowadays is used to getting all the needed information without any efforts. In this way, they present their own papers obtained through “copy” and “paste” techniques and do not find it necessary to check any information.

The present results show that in preparation of the future undergraduates attention should be paid to the following:

- Work out of different test tasks — with different cognition levels, as well as from different types. This will allow the development of key competencies for using scientific facts, independent solution finding, valuation based on analysis of the link between the reason and

consequence, and for realizing role of every individual in the nature and society.

- Aiming at maximum linkage between the theoretical knowledge with the praxis: by doing as many chemical demonstrations as possible, to link the areas of application of the studied substances with their characteristics and their influence of the environment and the human health.

Teachers as well as students and parents should realize the fact that it becomes more and more important to prepare not only in accordance to "I know" but to "I can". The time spent at school should give the new generations the possibilities to develop competencies which should help them to manage with real situations in real life.

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Симетрията като съизмерност и закономерност на хармоничния Космос.

д-р Янко Бицин

Математическата схема на питагорейците принципиално не би могла да включи в сферата на своите натурфилософски определения множествеността от реалните качества на нещата и явленията. Този факт обуславя настъпилото значително увеличение на познавателния интерес към изясняването на първоосновите, първопричините на многообразието в последващото развитие на философската мисъл. От друга страна, абстрактното определение на всичко съществуващо в действителността като генетическо порождение на числото и хармонията не може да има своето конкретно продължение в питагорейския контекст на това определение, тъй като в техните интерпретации на числото не се проявява и не се указва конкретния механизъм на органгзирането и осъществяването на космическия ред и на съизмеримостта на нещата, процесите и явленията. Поради това, питагорейското определение на "космоса" се оказва само едно застинало понятие, а техния модел на реалния космос – само една лишена от каквато и да била активност инвариантна завършеност.

И на края, функциите на числата, които се опредметяват в рамките на питагорейската натурфилософия и като материална, и като разумна, и като фантастическо-мистическа основа на нещата, са напълно лишени от своето съдържателно основание – реалната непосредственост на мярата. За това в питагорейското учение числото, макар и да се оказва формална мяра на вичко съществуващо, осъществява мярата единствено в нейното абстрактно представяне, защото то, концентрирайки в своята гносеологическа специфика всички методологически несъвършенства и философски затруднения и спекулации, все още не може да изрази мярата чрез конкретни измерения.

Конкретните числа в питагорейското учение представляват сбор, съчетание, синтез от единици, т.е цели положителни числа (άρίθμζ). "Начало /архе/ на всички неща, коментира Диоген Лаерций, е единицата /монада/, от единицата се хипостезира неопределената двойка /диада/... От единицата и неопределената двойка /се хипостезират/ числата..."*1 Единиците, изграждащи числото, се смятали от питагорейците и се изобразявали от тях като точки, които те разполагали във формата на правилни геометрически тела и така

те получавали “... от числото – линии, от линиите – плоски фигури, от плоските – телесни фигури, а от тях – чувствените тела...”*2 От получените по този начин “триъгълни”, “четириъгълни”, “петоъгълни” и други “фигурни” тела възниквал качествено-геометрическия образ на числата. “Значителна част от тяхната математика, отбелязва Р. Брамбо, не е била чиста математика, а изцяло е зависела от рисунки и от въображението.”*3 Още по-точен е У.А. Гатри: “Да представят числото във вид на геометрически образи, пише той, било обичайната практика на питагорейците; вероятно това е било най-ранната практика и у гърците и у другите народи.”*4 Такова представяне на числата прави още по очевидна противоречивата природа на трактовката им в натурфилософското учение на Питагор, трактовка, в която вече методологически явно се конкретизира имананнтно присъщото за това учение противоречие между интуитивизма и натурализма в разбирането на числата.

В интуитивиското разбиране на числото нагледното му представяне под формата на геометрическа фигура се приема спекулативно като чиста фигурност, като откъсната от конкретните предмети идеална форма. За питагорейците, при такъв подход, числата съществено се различават от геометризираното си предметно, сетивно представяне, защото за тях числото е действително геометризирано, но единствено мислимо геометризирано вън от конкретната пространствено-времева определеност на сетивно съществуващите предмети. Числата при такава трактовка на питагорейците са единствено мислими, рационални реконструкции, фигурации и формализации вън от конкретните неща.

При натуралистическото осмисляне на числото неговото представяне чрез определена геометрическа конфигурация вече не е само илюстрация, защото числото не съществува вън от предметното си пространствено-времево въплъщение в реално съществуващата геометрична форма. Числото отново не е тъждествено на геометрическото си предметно представяне, но в този случай, защото по своята онтологическа природа е нещо много повече от геометрическа фигура – то е първооснова, първопричина, първообразец на всичко съществуващо. Именно в това “се проявява, пише А.Ф. Лосев, натурализмът, творческата стихийност: няма число като такова, то не съществува без нещата, то е геометрическата структура на самите неща, то е техен ритъм и симетрия, то е, от гледна точка на досократовото разбиране на света, – тяхна душа.”*5

Противоречието между интуитивизките и натуралистически представи за числото, което е вътрешно присъщо на питагорейското натурфилософско учение, очертава не само два варианта в

трактовката на числата, но и на две отчетливо открояващи се в развитието на философията тенденции във философското осмисляне на света, тенденции водещи своето начало от Питагор и ясно разграничаващи се в традициите на Платон и Аристотетел. “Това става, пише Б.Г. Кузнецов, когато отразяващите света числа станат форма на материята, а управляващите света числа станат самостоятелни идеи.”*6 Приемайки същността на оценката на цитирания автор, оценка, която в своя вулгаризиран вариант отдавна е придобила христоматийна категоричност в историята на крайно идеологизираната през периода на тоталитаризма материалистическа традиция, все пак е необходимо да констатираме, че в нея има логическо противоречие: числата, като математически понятия, ако се превърнат във форми на материята – това си е отново идеалистическа концепция за света – рационалните форми на мисленето се оказват форми на битието. Явно, че в случая имаме несъзнателно подчиняване на необходимостта от точни и детайлни формулировки на желанието на автора да постигне ефекта на афористично обобщение. Необходимо е, следователно, уточнението, че става въпрос за числата, не като рационални, идеални отражения на количествените отношения, а за самите количествени отношения – именно те като формалната структура на битието са негови форми.

Представянето на числата чрез пространствени геометрически фигури поражда още една гносеологическа специфика на питагорейското натурфилософско учение – аритметиката и геометрията в него са тясно свързани. В тази взаимовръзка приматът все пак принадлежи на аритметическото начало. Приятелят на Платон, питагореецът Архит пише: “Аритметиката, според /моето/ мнение, се отделя сред другите науки със съвършенството на своите знания, включително и от геометрията /тя е по-съвършенна, тъй като/ тя е по-ясна от геометрията, и разглежда всеки /предмет/”*7.

Числовите отношения се разглеждат от питагорейците в изключително тесните рамки на “крайната аритметика”, която напълно изключва конструктивните особености и евристическия потенциал на прилагането, на използването на “безкрайността” и преди всичко на “нулата”. “Нулата за питагорейците в античната математика, отбелязват Дж. Реалье и Д. Антисери, е напълно неизвестна.”*8 Функциите на нулата притежават значителна евристическа значимост, защото “нулата, както отбелязва Фр. Енгелс, по своята природа е по-важна от всички останали ограничени числа. Действително, нулата е по-богата със съдържание, отколкото всяко друго число”*9. Но за да се осмисли нулата, образно казано “да се направи нещо от нищото, да се даде на това нещо име и да се изобрети за него символ”*10, е необходимо да се разкрие

многообразието и определеността на “нищото”, които се разкриват единствено в процеса на съотнасянето на мисълта с действителността. Това е невъзможно в рамките на питагорейското учение за числото, защото нулата като число, лишено от величинна, метрична определеност на съдържанието /и в този смисъл като чиста абстрактна понятийна форма/, може да бъде разбрана единствено чрез разкриването на богатството на реалното “безкрайно”, т.е чрез разкриването на съдържанието на качественото многообразие в действителността. Именно поради това “нулата за питагорейците в рамките на собствения им дедуктивен математически метод си остава неизвестна, а следователно, и неизползваема”*11, а нейната смисловата функция в практиката на естествознанието е била открита не в сферата на тяхното учение за числото, а от древногръцките астрономи. В древногръцката астрономия за пръв със знака „0” започват да обозначават “пустото място” чрез съкращението на думата “οὔδέν“. “Ако в реда от цифри се стрещало пусто място, нашата (άρίθμζ) – 0, описва формата на употреба на “нулата” Ш. Рюел, то гърците го заменяли понякога с вертикална черта, например, 10 098 – ΜΙΙΩή; или пишели думата “οὔδέν“ – нищо, както прави Теон, коментаторът на Птоломей, или пък поставяли просто точка, както правел самият Птоломей.”*12

Геометрически зрителното представяне на числата, следователно, лишава “нулата” от изображение, затова Питагор и неговите последователи превръщат в изходна основа на своите числови конфигурации точката, изобразяваща единицата, двойката, отъждествявана с правата /две точки/, тройката – с плоскостта /три точки/, четворката – с елементарния обем /четири точки, единици/. Най-простото, т.е. най-елементарно тяло се оказва пирамидата. Нулата, както е очевидно, не е стуктурен елемент на даденото геометрично образование, затова и природата на “неопределеността”, чиито съществени моменти са отразени в “нулата”, не се съотнася с понятието “число”.

Този момент е особено важен за правилното разбиране на питагорейската философиа на числата и на нейното място в развитието на античната философия. Тъй като “нулата”, изразяваща “пустотата”, “нищото”, “отсъствието” и съдържателно противостояща на “безкрайността”, която обобщаваща “запълнеността”, “всичкото”, “безусловното наличие”, отсъствуват от тяхните числови конфигурации, а тяхното наличие и последователен синтез под формата на взаимовръзката между “определеното” и “неопределеното” определя най-непосредствено бъдещата тендеция на формирането на философските принципи на конструктивното и рационалното обяснение на света, – тенденция вербално

представена като линията на Демокрит и линията на Платон в развитието на философската мисъл – то, тяхната математическа философия на крайните числа остава в страни от нея.

Питагорейският модел на космоса и нещата в него се основава не просто върху първоосновата на крайните числа въобще, а само върху положителните крайни числа (άρίθμοζ). Питагорейското разбиране за света – е изцяло цялочислено разбиране. Всичко в света е хармонично и симетрично устроено, именно защото първопричината за този ред са целите положителни числа. Всичко в космоса е съизмеримо с помоща на тези числа. Самото човешко познание е възможно именно благодарение на целочислените конструкции на нещата, а истинното обяснение на света се постига единствено с тяхна помощ. Резултатите от изследването на света чрез аритметическите операции с целите положителни числа се превръща във философско основание на питагорейския светоглед и на цялата им научно-изследователска методология и гносеология. “Това довежда питагорейците до мисълта, отбелязва И.Г. Башмаков, че всички закономерности на света могат да бъдат изразени с помоща на числата, ”че елементите на числата се явяват елементи на всички неща и че светът като цяло се явява като хармония и число” /Аристотель. Метафизика. М. Л., 1934, с 27- 28./”*13.

Абсолютизацията и мистификацията на целите положителни числа в натурфилософското учение на питагорейците ги довежда до единствено възможното логическо заключение в техните гносеологически ограничения, а именно, че построеният целочислен, съизмерим и симетричен модел на света – е единственият истинен свят, а самото му рационално обяснение задължително трябва да изхожда от принципите на целочислената математическа методология и гносеология.

Абсолютната увереност на питагорейците в истинността и логическата бедупречност на техния целочислен, съизмерим, хармоничен модел на света е унищожена в един миг от откриването и научното доказване на факта, че отношенията между диагонала на квадрата и неговите страни са несъимерими, че “тяхното отношение не може да бъде изразено с “число”, т.е. с това, което ние сега наричаме рационално число /цяло число или дроб/, а само такива числа са допустими от питагорейската аритметика”*14.

Анализът на Питагоровата теорема в рамките на парадигмалната и гносеологическа специфика на питагорейското натурфилософско учение, закономерно води до следните методологически изводи: Ако 1 е дължината на квадрата, а X е дължината на диагонала, то величината на диагонала X би трябвало да бъде : $X^2=1+1=2$, защото в случая диагонала на квадрата е

хипотенуза на равностранен триъгълник с дължина 1. Но числото 2 няма точен квадратен корен. “Може да се докаже, отбелязва Роже Каратини, че ако съществува число Х, което да е равно на корен квадратен от 2, то това число би трябвало да бъде едновременно четно и нечетно, което е абсурдно; това, възможно, е било разбираемо доказателство за питагорейците от първото поколение…”*15.

Това научно откритие разрушава най-фундаменталната основа на светогледа на Питагор и неговите последователи – идеята, че първоизточник на организираността, хармонията и разумността на света са целите, съизмерими, рационални числи. А. Н. Чанишев така описва краха на питагорейския космологически модел: “Числата, мислели питагорейците, се състоят от еднакви /съизмерими – Я.Б./ единици. Така че в основата на света лежи единицата. И ето, изведнъж се оказва, че в основата на света лежат като минимум най-малко две единици, несводими една към друга. Така че неразумното, несъизмеримото и ирационалното се оказва в самото ядро на света.”*16 Роже Каратини е още по-точен и категоричен в оценката на кризата на питагорейското учение:“Разбираемо е, пише той, че проблемът за неизчислимостта на диагонала провокира логически скандал в питагорейския свят: да признаеш, че всички неща са числа, едновременно с това да признаеш, че нещо, което ти се струва, че е лесно измеримо като отрязък от права линия, а в същото време не може да бъде обозначено с никакво число – това е в състояние да предизвика шок.”17

Най-парадоксалното в случая е, че откриването на “несъизмеримостта между страната и диагонала на квадрата, две отсечки, чиито относителни величини са ни толкова привични, на отсъствието на обща мяра, даже и възможно най-миналната, между тях”*18, откритие, “предизвикало най-дълбокия кризис на основите на гръцката математика”*19, е направено от самите питагорейци в рамките на собствената им школа. Най-непосредственото последсвие от откриването на несъизмеримостта – “ математическа идея, значението на която майче може да бъде сравнена единствено с откриването на неевклидована геометрия в XIX век, или на теорията на относителността в началото на XX век”*20 – е, че питагорейското учение за целочислените числа и геометрическите конструкции и величини, чрез които те се изразяват, повече не може да бъде признавано за самоочевидно истинно, защото основният принцип на това учение, че “целите числа се явяват мяра на всички неща се натъква на непреодолимо логическо противоречие благодарение на откриването на ирационалността”*21.

Откриването на ирационалните числа не само "поставя проблем, станал централен за цялата древногръцка математика"*22, но и формулира задачата за търсенето на ново обоснование на питагорейските идеите за първоначалото и първоосновата на всички съществуващите неща. Първата евристическа реакция е мистификацията на квадрата. "Оказали се пред факта на съществуванетето в света на несъизмерими /неизразими чрез цели положителничисла/ величини, отбелязва Ф.Х. Кессиди, питагорейците били толкова обезкуражени от това, че виждали в свойствата на квадрата нещо "непостижимо от ума", нещо /alogus/ или дори "ръката на зъл демон."*23 Втората реакция е свързана с новата фаза на мистификацията и социоморфната трактовка на самите числа. "Съществени /и неразрешими за тях – Я.Б/ трудности за питагорейците, пише В.В. Илин, представлявало обяснението на отношението на несъсъизмеримост. Един от изходите от създалата се ситуация става приписването на числата на духовни и нравствени характеристики."*24

Новият характер на парадигмалната ситуация детерминира съществено изменение в структурата на математическото знание. Този етап е непосредствено свързан с творческата дейност на Питагор. Прокъл описва новия етап в развитието на математиката по следния начин: "Питагор преобразува тази наука във формата на свободно образование. Той изучава тази наука, изхождайки от нейните първи основания, и се стараел да получи теореми при помощта на чисто логическото мислене, вън от конкретните представи. Той открива теорията на ирационалните /или пропорции/ и построяването на петте космически тела."*25

В гръцкия език език ирационалността се изразява чрез три термина: "асимметрон", означаващ отсъствието на обща мяра, "арретон" – неизразимо с цели числа; и "алогон" – като неопределяемо от "логоса". За самите питагорейци най-важен в математическите им анализи се оказва първият термин – "асимметрон". Използувайки го за обозначение на ирационалните величини, в своите математически интерпретации самата ирационалност те разбирали преди всичко като праволинейни отрязъци, нямащи обща мяра и поради тази причина неизразими чрез отношението на цели числа, т.е. като противоположна на рационалността, която самите питагорейци изразяват чрез съизмеримите, имащи обща мяра цели числа, а рационалните числа те представят като двойка цели числа. Следователно, самите използувани за обозначаването на ирационалността термини от питагорейците, показват, че те правилно са разбирали нейната противоречива природа – да отразява не отделните величини, а

асиметричното отношение на една величина относно друга. “Ако един катет е равен на 1 см и другият – също, то по теоремата на Питагор, хипотенузата трябва да бъде равна на корен квадратен от 2. Макар това число да е ирационално, то при това е хипотенуза – нещо съвсем реално, най-обикновена линия, която може да се измери, колкото си искаме точно, и само цялата нейна особеност се заключава в това, че нейната дължина е несъизмерима с дължината на катета.”*26 Това разбиране за ирационалността се превръща в изходен пункт при преодоляването на кризата на питагорейската математическа конструкция на света.

Математическата мисъл на Питагор и на другите древногръцки учени се обръща към идеята за построяването на математиката не върху аритметиката на рационалните числа, защото на този етап тя не може да разреши породеното от откриването на ирационалността свое вътрешно противоречие, а върху основата на геометрията на отсечките и фигурите. Новият характер на математиката обуславя превръщането на всички алгебрически операции в определени конкретни геометрически величини и фигури. “На пръв поглед, отбелязва Г.Г. Цейтен, преимуществата на геометрическото представяне на величините въобще могат да се покажат нищожни, тъй като който и да е отрязък притежава такава определена величина, както и взетото произволно число, но, в действителност, нарисуваната фигура служи само за материален знак при изразяването на понятието за фигурата, а тук величините могат да приемат всички значения, съвместими с изискванията на такова понятие.”*27 Геометрическото изразяване на общите отношения между величините обективно довежда до създаването на “геометрична аритметика”: традиционното за питагорейците изобразяване на числата с точки, разположени във вид на правилни фигури, било отхвърлено, и числата сега се представят чрез отсечки и построения, осъществявани с тях. От тук възниква обичайната за древните гърци употреба на понятията “плоски” – и “пространствени” числа. Плоски те наричат числата, являващи се произведение от два множителя, и ги разглеждали като изобразяващи конкретна правоъгълна площ, а пространствени – са числата изобразявани с помощта на паралелепипед, т.е. представляват произведение от три множителя, при това, когато множителите са равни по между си – такива числа били определяни в първия случай като квадратни, а във втория – като кубически. Всяка обобщена величина при геометрическото представяне на числата – рационална или ирационална – би могла вече да бъде представяна като дължина на праволинейна отсечка. Алгебричните операции за изваждане и събиране на изобразените по този начин величини били

разглеждани като наслагване на една отсечка върху друга, а произведение между съответните отсечки се наричал построения чрез тях правоъгълник.

Геометрично-аритметическия подход в своята крайност довежда до геометрическата алгебра, в която геометрическото представяне на величините се асоциира в двумерния случай с площта на фигурата, а в тримерния – с обема на паралелепипеда, а аритметическите операции, свързани с изчисляването и сравнението на математическите величини, неминуемо придобиват опростен и нагледен характер.

Сетивно-нагледното представяне на математическата наука поражда и съответната форма на обяснения на нейните теореми и закони с помоща на рисунки и чертежи, която, апелирайки към наслагането и съотнасянето на конкретни отсечки, линии и фигури, неминуемо ориентира познанието към непосредственото зрително съзерцание. Следователно, геометризацията на аритметиката като специфичен опит за представяне на ирационалните числа създава гносеологическата нагласа за отсъствие на необходимостта от рационални доказателства и на самите рационални доказателства, защото тя се основава на самоочевидната истинност на изходните теоретически предположения – аксиомите. “Влиянието на геометрията върху философията и научния метод, отбелязва Б. Ръсел, било дълбоко. Геометрията в такъв вид, в който тя се установява при гърците, се отправя от аксиомите, които се явяват като самоочевидни или се приемат за такива, и чрез дедуктивните разсъждения отива до теоремите, които са далече от самоочевидността.”*28 Почти аналогична е позицията на А.Ф. Лосев:”Теоретико-числовите операции, пише той, се разценят от питагорейците като най-необходимия априоризъм, който се трактува като най-самоочевиден и като не изискващ доказателства.”*29 Такова разбиране на гносеологическия процес на достигането до истината последователите на Питагор наричат “интуиция” и го превръщат в една от най-съществените специфики на цялото антично мислене. “...За нас сега, отбелязва А.Ф. Лосев, е съвършенно очевидна връзката на античния геометризъм с исконната интуиция, върху която израства цялата антична култура, а именно – с интуицията на ярко оформеното и очертано, напълно веществено и напълно материално тяло.”*30 Тази “исконна интуиция” е етимологически свързана с латинската дума “intuitus”, която буквално означа “съзерцание”, “възприемане”, “виждане”. В еквивалента на гръцки език интуицията е представена в платоновската “теория” – “teorius”, която, в оценките на същия автор “се явява от само себе си все пак самото реално “съзерцание”, определящо своите особености в съответствие с

термина “ейдос” и “ейдолон”, израстнали от едно и също “виждане”, различаващо се само в тези аспекти, че в единия случай става дума за пасивното запечатване на външните възприятия, а в другия – за чистото съзерцание, възприемане на обективния свят, равносилно на активното създаване на този образ в съзнанието.”*31

Следователно, най-непосредственото гносеологическо последствие от геометризацията на математиката е приемането “на интуитивния характер на познанието, в описанието и обяснението на което голяма роля играе аналогията му със зрителното възприятие”*32.

Абсолютизацията на значимостта на зрителните възприятия е харектерна специфика и на гносеологията на Платон, който е най-бележитият последовател на питагорейската традиция в представянето на числата и алгебрическите операции и теореми чрез геометрически отсечки и фигури. “Очите, пише той, ни откриха числото, дадоха ни понятие за времето и ни подбудиха да изследваме природата на Вселената, а от това възникна нещо, което ние днес наричаме философия.”*33 Без зрителните усещания, още по-категоричен е той в редица разсъждения от по-общ познавателен характер, “ние не бихме могли да кажем нито една дума за природата на Вселената, за звездите, за Слънцето и небето.”*34

Обобщавайки трактовката на симетрията в натурфилософскитото учение на питагорейците, на нейната взаимовръзка с техните представи за хармонията, реда, мярата, числото и съизмеримостта на нещата, от една страна, и неспособността на питагорейците да обяснят природата на несъизмеримостта и на породените от нея ирационални числа – от друга, бихме могли да формулираме следните теоритически изводи:

Първо: Симетричната картина на света, която питагорейците изграждат върху натурфилософските си разсъждения за съизмеримите, цели, положителни числа като първооснова на космоса и на всички съществуващи неща, е напълно разрушена след откриването на несъизмеримостта, на ирационалността;

Второ: Асиметричният модел на космоса, който е единствено възможният модел, основаващ се върху несъизмеримостта на нещата и на ирационалността на техните отношенията, не може да бъде логически непротиворечиво обяснен и разбран в рамките на питагорейските натурфилософски принципи за числата, защото самото научно осмисляне на асиметричния модел обективно е възможно само в гносеологическата специфика на една закономерно недостъпна за тогавъшното ниво на античната мисъл нова диалектическа концепция, концепция, обединяваща в противоречиво

единство единство симетричността и асиметричността, измеримостта и несъизмеримостта, рационалните и ирационалните числа.

Трето: Питагорейците не насочват своите натурфилософски изследвания на числата към разширяването и задълбочаванията на собствените си прозрения за противоречивата природа на рационалните числа, а се ориентират към обосноваването на алгебрическите закони и теореми чрез геометрически сетивно възприемани построения. Геометризацията на математиката, като опит за решаване на проблема за ирационалността и на несъизмеримостта ориентира познанието към сенсуалистичното пренебрежение на необходимостта от логически доказателства на математическите формула, към интуитивната самоочевидност на истинното знанието.

Разрушаването на питагорейския симетричен модел на света, последвало тяхното колосално научното откритие на несъизмеримостта на нещата, разбира се, не е отхвърляне на обективното съществуване на симетрията въобще. Нещо повече, последователното преодоляване на теоретическите затруднения на питагорейците при обяснението и рационалното осмисляне на ирационалните числа, осъществено от учените на Новото време в сферата на математическите анализи на действителните числа и на тяхната интерпретация като диалектическо единство на рационалните и ирационалните числа, не само възстановява симетричната картина на света, но и непосредствено формира по-задълбоченото научно разбиране на симетрията – като обобщен израз на инвариантноста на диалектическото единство на ирационалните и на рационалните числа.

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Sulfur and Its compounds: experiments, models and tasks

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***Abstract**: An overview of the visual means on the topic "Sulfur and its compounds" in the textbooks for "Chemistry and Environmental protection" for 8th grade and in the Internet is made. Suitable virtual experiments are selected and corresponding tasks that can be worked out at school as well as autonomously by the students are formulated. Their combination with appropriate models and diagrams allows both a visualization of the processes on a micro-level and enrichment of the students concepts on the properties of substances, as well as on their application in practice and finally their impact on the environment and human health.*

***Keywords:** education in chemistry, visualization, sulfur, sulfur compounds, environment protection.*

INTRODUCTION

The cultural and educational area *Natural Sciences and Ecology* allows the students to form a system of contemporary scientific knowledge about nature and to acquire competencies for their application [1, 2]. Chemistry as a subject of this cultural and educational area provides respectable selection of knowledge and competencies. For their proper formation a maximum visualization and revealing of possible connections and dependencies is required [4].

Chemical experiments are an important part of the visual means in the educational and cognitive process. The necessary equipment which is in the school chemical laboratories does not often allow the implementation of lab chemical experiments – reagents, glasses, apparatuses are not available. Another reason which makes difficult the implementation of experiments in the chemistry education is the duration: some of them which are not compatible with the duration of the usual school class [6]. One possible solution of these problems could be found in using multimedia technology for a presentation of some chemical experiments, as well as for a presentation of various samples, models and schemes, some of which could be found in Internet. The selection of such suitable visual means is a very slow and labour-consuming process for the teacher.

The aim of the present paper is to create an optimal selection of visual means for the section *Sulfur and its compounds* which is included in the curriculum of Chemistry and Environmental protection for 8th grade. This section allows the use of visual means with different types and purposes: models, ouflines, apparatures, virtual experiments, etc., which helps students to be aware of some basic physical and chemical properties of the sulfur and its compounds (sulfur dioxide, sulfur trioxide, acid sulfur) which are harmful and dangerous when working directly with them. This selection is meant to support teachers by the selection of proper visual means for this section, as well as to provide students with formulated tasks linked to them for autonomous work.

RESULTS AND DISCUSSION

The comparative analysis of the visual means used in different textbooks for 8th grade is made. It shows that they are in conformity with the content defined in the syllabus, including pictures of sulfur samples, models of a sulfur molecule with 8 atoms, its compounds, as well as outlines of experimental implementation and description of real chemical experiments [1, 3, 5, 7, 8]. The review of the available materials in Internet on this topic shows a considerable number of virtual experiments linked with sulfur and its compounds [9, 10]. Some of them provide additional information which remains hidden by observation without a certain purpose. This fact directed our attention to selection of materials which allows formulation of different tasks and could be used at school, as well as for autonomous students' work.

One suitable example of this selection is the combination of video about the changes of sulfur by heating it, pictures of the basic stages of these changes and the outline which shows the transformations on atomic-molecular level. The respective task is as follows:

Compare the changes of sulfur caused by heating shown in the video with their model in the diagram. Explain the different agility of the melting and getting of plastic sulfur using the changes in the sulfur structure. Conduct the experiment in a school laboratory by observing the rules for safe working.

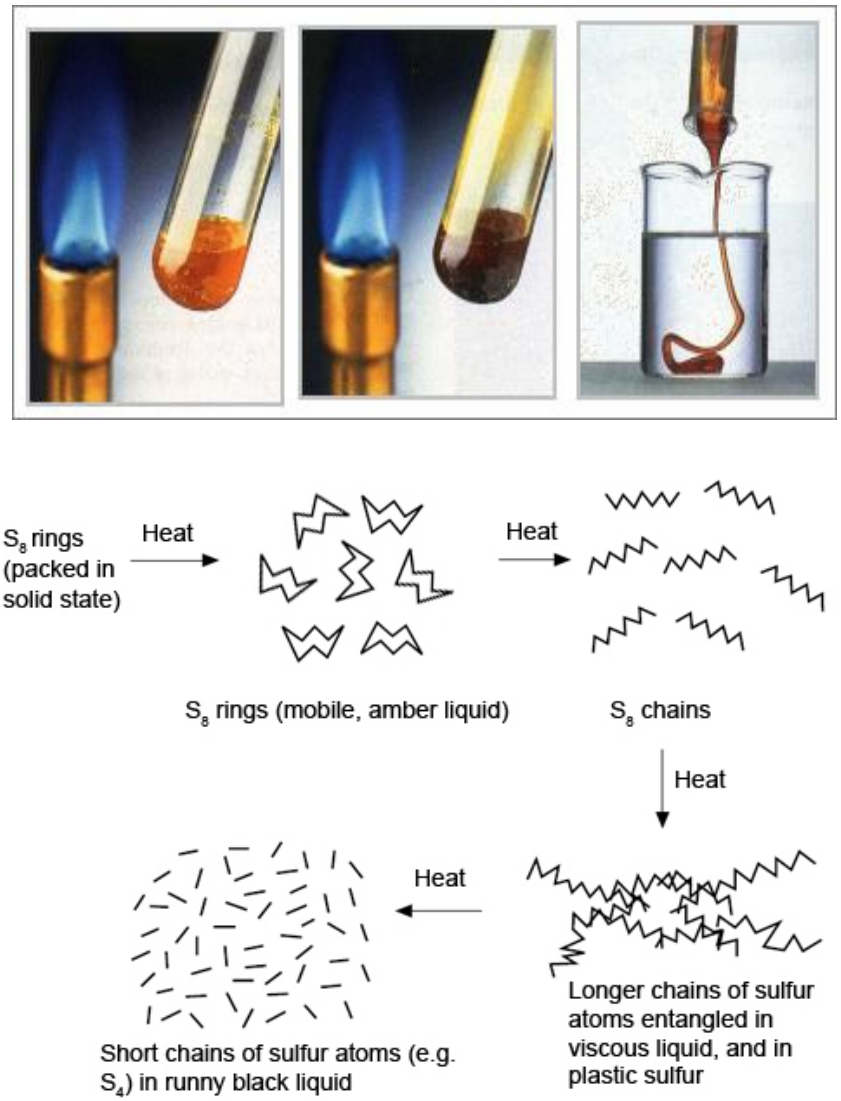
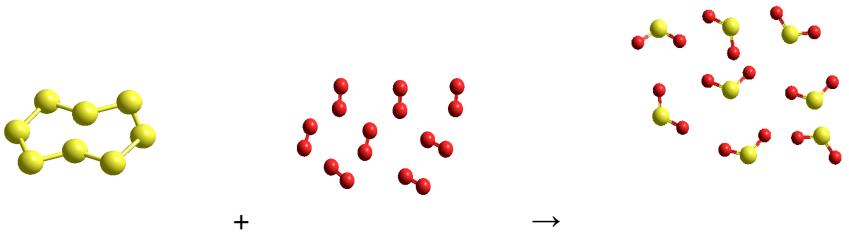


Fig. 1. Temperature changes in structure of sulfur

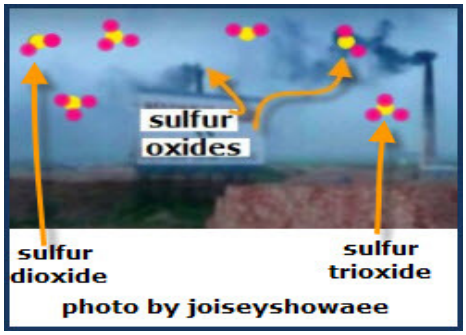
Another suitable example for selection of materials refers to the structure and properties of sulfur oxides. It includes a video about obtaining sulfur dioxide, demonstration of its acid characteristics and its bleaching effect, a diagram of the properties of sulfur dioxide and sulfur trioxide as well as their respective models and a scheme about the formation of acid rain. The respective task is as follows:

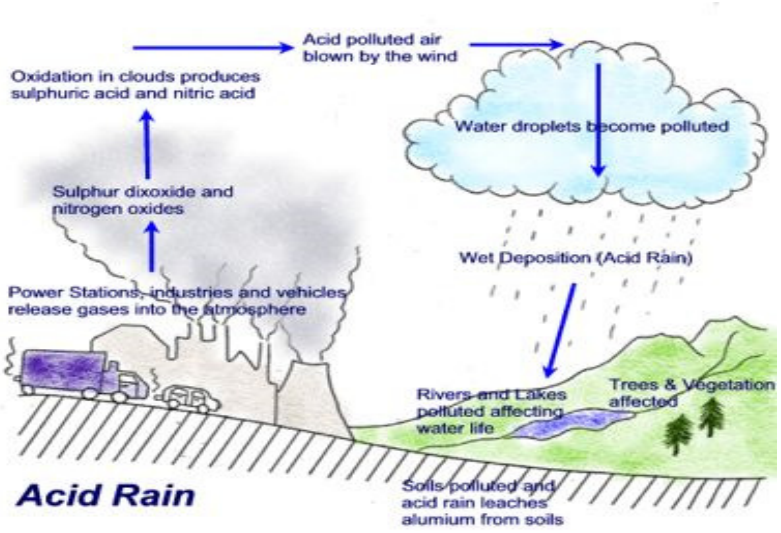
Explain the formation of acid rain. How human activities influence on the purity of rain? What are the consequences for the environment and human

health? Suggest a selection of measures for decreasing the sulfur oxides contamination.



S	+	O_2	→	SO_2





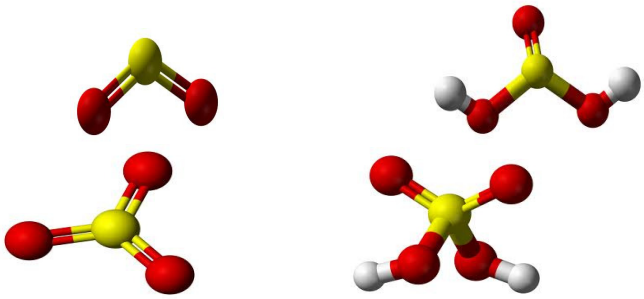


Fig. 2. Sulfur oxides and acid rain

CONCLUSIONS

A number of visual means for the section “Sulfur and its compounds” studied in 8th grade has been created. It contains:

- 16 videos of chemical experiments
- 25 figures (pictures, models, schemes)
- 20 tasks for independent work.

Visualization of the sulfur properties and its compounds has been carried out and on the other hand would require following certain rules for safety work which can not be provided easily at school.

Part of the selected virtual experiments shows some subjects which are not included in the educational program. By the teacher decision they could be used for an autonomous work of the students. In this way a certain differentiation and an individual approach can be achieved toward students with special interests in chemistry.

The bilingual labeling in some of the used schemes allows learning of respective terminology in English, too.

The selection proposed can be used as a model for creating a combination of visual means for different topics of the syllabus in Chemistry and Environmental protection. It can be used by teachers and students, as well as by students who are trained to be teachers in Chemistry in the future.

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ESTERS OF ACYCLOVIR WITH PEPTIDOMIMETICS - SYNTHESIS AND ANTIVIRAL ACTIVITY

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***Abstract**:A series of esters of the antiherpetic drug acyclovir with peptidomimetics was designed and examined for in vitro antiviral activity against herpes simplex virus type 1 and type 2 (HSV-1, HSV-2). The esters were synthesized from the amino acids valine, glycine, alanine, and leucine containing a thiazole ring and acyclovir. N-ethyl-N’-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) served as the coupling reagent for their synthesis. Boc-alanine-thiazol-4-yl-acyclovir showed moderate activity against HSV-2. The remaining compounds were considerably less effective.*

1. INTRODUCTION

Acyclovir, 9-[(2-hydroxyethoxy)methyl] guanine (ACV), is an acyclic guanine nucleoside analogue that is widely used clinically as an antiherpetic agent [1]. However, ACV and similar acyclic nucleosides suffer from low solubility in water and low bioavailability following oral administration antiviral, antioxidant [2-3]. Several amino acid esters of acyclovir were developed to overcome this problem, valacyclovir, the valine ester of ACV, being among the first of this series of compounds that were readily metabolized upon oral administration to produce the antiviral nucleoside *in vivo*, thus increasing several times the bioavailility [4]. Thus, valacyclovir, L-valyl-ACV, is a prodrug derived from ACV by

esterification of ACV with L-valine. Upon administration, valacyclovir is rapidly and completely converted to acyclovir, the active parent drug, by enzymatic hydrolysis. The prodrug increases the oral bioavailability of acyclovir three to five fold in humans. Enhanced oral absorption of acyclovir has been attributed to the human peptide mediated transport of valacyclovir. The compound is recognized as a peptidyl derivative and absorbed by peptide transporters, even though there is no peptide bond in its structure. Prodrug strategies have been employed to improve the properties of potential small-molecule chemotherapeutic agents, including their solubility, stability, organ selectivity, and duration of action [5-14]. Recently, we reported on the use of the peptidomimetics as the basis for a new series of esters of acyclovir. Modification of anti-herpes agents (such as acyclovir) by peptidomimetics, with chemical structures different from the natural peptides but maintaining the same ability to interact with specific receptors, is of great interest. Based on the known structure-activity relationship we designed a new series of analogues of acyclovir in which the natural amino acid was replaced by amino acids containing a thiazole ring.

2. RESULTS AND DISCUSSION

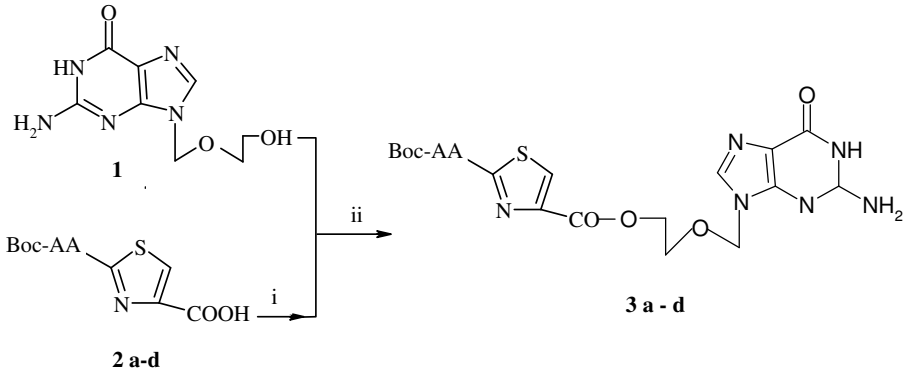
In the last two decades, unprecedented biologically active natural products containing directly linked azoles, have been isolated from natural sources [16-18]. Many of these compounds are candidates for drug development. In particular thiazole, oxazole and imidazole amino acids that may play a key role in biological activities of unusual peptides are also important intermediates for natural product synthesis and peptidomimetics [15-20]. Acyclovir derivatives modified with amino acids and peptides have been reported [5-14]. but acyclovir containing peptidomimetics are not known at all. In order to obtain analogues with more desirable characteristics, we synthesized new esters of acyclovir containing Boc-2-aminomethyl-thiazole-4-carboxylic acid, Boc-2-Val-thiazole-4-carboxylic acid, Boc-2-Leu-thiazole-4-carboxylic acid, and Boc-2-Ala-thiazole-4-carboxylic acid.

Synthesis of thiazole containing amino acids

Boc-2-aminomethyl-thiazole-4-carboxylic acid, Boc-2-Val-thiazole-4-carboxylic acid, Boc-2-Leu-thiazole-4-carboxylic acid, and Boc-2-Ala-thiazole-4-carboxylic acid were prepared according to the literature [21-22]

Synthesis of esters of acyclovir

A mixture of thiazole containing amino acid 2 a-d and 1-[3-(dimethylamino)-propyl]-3-ethyl carbodiimide hydrochloride (EDC) in dimethylformamide (DMF) was stirred for 1 h at 0°C under nitrogen atmosphere. A solution of acyclovir (1) (Fig. 1) and 4-*N*, *N*-(dimethylamino)-pyridine (DMAP) was added to the reaction mixture and stirring continued for 24 h. Then DMF was evaporated *in vacuo* and the residue was chromatographed on silica gel, using 1:4 MeOH:CH_2CH_2. The ^1H and ^{13}C-NMR, mass-spectra were consistent with the expected structures.



(i)EDC, DMF, 0 ^{0}C, 1 h; (ii) DMAP, rt, 24 h.

Protected AA: **2 a)** Boc-2-aminomethyl-thiazole-4-carboxylic acids; **2 b)** Boc-Val-thiazole-4-caboxylic acid; **2 c)** Boc-Ala-thiazole-4-carboxylic acid; **2 d)** Boc-Leu-4-carboxylic acid.

Fig. 1.

I. Antiviral activity

*Effect of the compounds (**3 a-b**) on the replication of HSV-1(Fig.1.) and HSV-2 (Fig. 2.).*

The guanosine analogues did not affect the cell morphology at the investigated concentrations. Acyclovir was not cytotoxic according to data in the literature [23]. Results from the application on their two derivatives were not unexpected – concentrations as high as 20 µg/ml did not affect the cells. The esters of acyclovir were tested against HSV-1, strain Da, and HSV-2, strain Ba. Compounds **3 a-b** were tested in concentrations of 10, 5, 1 and 0.5µg/ml. Unfortunately, the inhibitory effect on the replication of HSV-1 was weak in comparison with the antiviral effect of acyclovir. Acyclovir, applied in a concentration of 10µg/ml, inhibited the replication strongly – over 99%. Compound **3a**, applied in the same

concentration, slightly suppressed viral replication (by 20 %), whereas the antiviral effect of valine and alanine thiazole esters of acyclovir was unessential, with inhibition of only 11% and 8%, respectively (Fig. 2). Boc-Leu-ACV did not affect the replication. Using the same doses, acyclovir completely inhibited the replication of HSV-1.

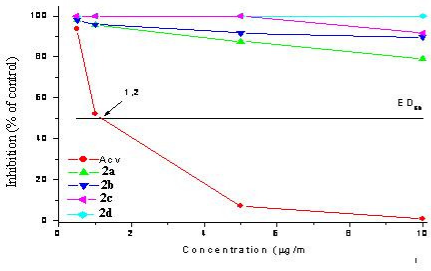


Fig. 2.

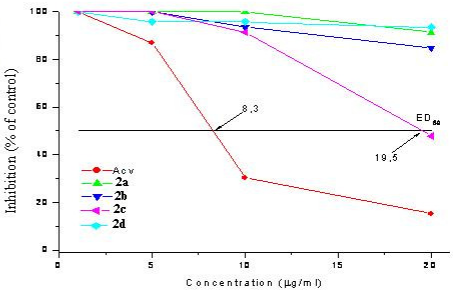


Fig. 3.

The results of the inhibition studies on the replication of HSV-2 were similar for compounds **3 a**, **3 b**, and **3 d** (Fig. 3.). In contrast, the inhibitory effect of the alanyl ester of acyclovir was remarkable. The value of its ED_{50} (19.5µg/ml) is comparable to the ED_{50} of acyclovir, 8.3µg/ml. Differences between the values of the inhibitory effect of Boc-Ala-thiazolyl-ACV against HSV-2 and HSV-1 could be attributed to different activities of the viral thymidine kinase and immediately early regulator proteins (IE gene products)of the two types.

Table 1.

Virus / Compound*	HSV-1, strain Vic	HSV-2, strain Ba
2a	20.8	8.7
2b	10.4	15.1
2c	8.3	52.1
2d	0	6.4
Acv	99.2	84.7

- in maximal applied concentrations: toward HSV-1 was
- 10µg/ml and toward HSV-2 was 20µg/ml.

** Inhibition (% of viral control)

In conclusion In this study we extended the scope of modification of acyclovir with various peptidomimetics.

Firstly, four novel esters of acyclovir with peptidomimetics were synthesized. Thiazole containing dipeptide mimetics from glycine, valine, alanine and leucine were used. The ESI-MS and NMR analysis proved the structures of the final products **3 a-d.**

Secondly, the results of antiviral activity testing of compounds **3 a, 3 b,** and **3d** showed that the replication of HSV-1 and HSV-2 was slightly affected. In contrast, the inhibitory effect of the alanyl ester of acyclovir was unessential (Tabl.1.).

Thirdly, our investigations showed that modification of acyclovir with amino acids (Gly, Val, Leu) through a thiazole linker reduced the antiviral effect in comparison with modification with natural amino acids.

The measured inhibitory effect of Boc-2-alanine-thiazol-4-yl-acyclovir against HSV-2 suggests that this compound could be attractive for antiviral chemotherapy. Further research *in vivo* is required for complete antiviral characterization of the effectiveness of this compound against acyclovir resistant strain of the herpes simplex viruses.

3. MATERIALS AND METHODS

Chemicals

The amino acids were purchased from Sigma, and DMAP and 1-[3-(dimethylamino) propyl]-3-ethyl carbodiimide hydrochloride (EDC) from Merck.

TLC analysis was performed on aluminum silica gel sheets 60 F_{254} plates (Merck) and spots were detected using an UV lamp at 254 nm.

NMR Spectroscopy: Bruker Avance DRX-600 spectrometer; chemical shifts referenced to the solvent peaks [δ (^{1}H, ([D_6]-DMSO) = 2.49 and δ (^{13}C, ([D_6]-DMSO) = 39.5

Mass Spectrometry: API III triple quadrupole mass spectrometer equipped with an electrospray ion source at atmospheric pressure (Sciex, Thornhill, Canada); electrospray ionization mass spectra (ESI-MS) were recorded in the positive mode.

Synthetic procedures

*N-α-tert-Butoxycarbonyl-Gly(Thz)-acyclovir **(3 a)***

A mixture of *N*-α-tert-butoxycarbonyl-2-aminomethyl-thiazole-4-carboxylic acid (**2 a**) (0.8 mmol, 0.210 g) and 1-[3-(dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (EDC) (0.4 mmol, 0.740 g) in dimethylformamide (DMF) was stirred for 1 h at 0 ℃ under a nitrogen atmosphere (Boger at al. 1999). A solution of acyclovir (**1**) (0.4 mmol, 0.1 g) (**Figure 1**) and 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) was added to the reaction mixture and stirring continued for 24 h. Then DMF was evaporated *in vacuo* and the residue was chromatographed on silica gel,

using 1:4 MeOH:CH_2Cl_2. Yield: 0.140 g, (68 %). ^{1}H-NMR ([D_6]-DMSO): δ = 1.36 (s, 9H, 3xCH_3), 3.69 (m, 2H, CH_2O, ACV), 3.76 (m, 1H, α CH), 4.23 (m, 2H, $CH_2OC(O)$, ACV), 5.36 (s, 2H, N-CH_2-O, ACV), 6.64 (s, 2H, 2-NH_2, ACV), 7.82 (s, 1H, H-8, ACV), 8.15 (s, 1H**,** CH_{Thz}), 10.77 (s, 1H, ACV-NH); ^{13}C-NMR ([D_6]-DMSO) δ = 28.3 (Boc–CH_3), 42.0 (CH_2), 64.13 (CH_2OCO, ACV), 66.28 (CH_2O, ACV), 71.68 (NCH_2O), 78.7 (Boc-Cq), 116.84 (C-5, ACV), 128.9 (C^5_{Thz}), 137. 55 (C-8, ACV), 148.2 (C^4_{Thz}), 151.08 (C-4), 155.8 (Boc-CO), 156.63 (C-6, ACV), 162.2 (C^2_{Thz}), 168.71 (C=O, ACV); ESI-MS: *m/z*: 468 $[M+H]^+$.

*N-α-tert-Butoxycarbonyl-Val(Thz)-acyclovir **(3 b)***

N-α-tert-Butoxycarbonyl-Val(Thz)-acyclovir (**3 b**) was prepared as described for compound **3 a**. Yield: 0.148 g, (60 %). NMR ([D_6]-DMSO) δ = 0.89 (d, 6H, $(CH_3)_2$), 1.36 (s, 9H, 3xCH_3), 2.11 (m, 6H, $CH(CH_3)_2$), 3.71 (m, 2H, CH_2O, ACV), 3.82 (m, 1H, α CH), 4.33 (m, 2H, $CH_2OC(O)$, ACV), 5.33 (s, 2H, N-CH_2-O, ACV), 6.76 (s, 2H, 2-NH_2, ACV), 7.83 (s, 1H, H-8, ACV), 8.15 (s, 1H**,** CH_{Thz}), 10.90 (s, 1H, ACV-NH); ^{13}C-NMR ([D_6]-DMSO) δ = 18.3, 17.24 ($(CH_3)_2$), 28.3 (Boc–CH_3), 29.23 (CH), 57.09 (α CH), 64.13 (CH_2OCO, ACV), 66.28 (CH_2O, ACV), 71.68 (NCH_2O), 78.7 (Boc-Cq), 116.84 (C-5, ACV), 129.0 (C^5_{Thz}), 137. 55 (C-8, ACV), 148.2 (C^4_{Thz}), 151.08 (C-4), 155.8 (Boc-CO), 156.63 (C-6, ACV), 162.9 (C^2_{Thz}), 169.91 (C=O, ACV); ESI-MS: *m/z*: 508 $[M+H]^+$.

*N-α-tert-Butoxycarbonyl-Ala(Thz)-acyclovir **(3 c)***

N-α-tert-Butoxycarbonyl-Ala(Thz)-acyclovir (**3 c**) was prepared as described for compound **3 a**. Yield: 0.31 g, (71 %). ^{1}H-NMR ([D_6]-DMSO): δ = 1.36 (s, 9H, 3xCH_3), 1.32 (d, 3H, CH_3), 3.70 (m, 2H, CH_2O, ACV), 4.03 (q, α CH), 4.32 (m, 2H, $CH_2OC(O)$, ACV), 5.54 (s, 2H, N-CH_2-O, ACV), 6.65 (s, 2H, 2-NH_2, ACV), 7.81 (s, 1H, H-8, ACV), 8.15 (s, 1H**,** CH_{Thz}), 10.79 (s, 1H, ACV-NH); ^{13}C-NMR ([D_6]-DMSO) δ = 15.51 (CH_3), 28.3 (Boc–CH_3), 29.23 (CH), 47.66 (α CH), 64.29 (CH_2OCO, ACV), 66.11 (CH_2O, ACV), 71.74 (NCH_2O), 78.7 (Boc-Cq), 116.33 (C-5, ACV), 129.0 (C^5_{Thz}), 137. 55 (C-8, ACV), 148.2 (C^4_{Thz}), 151.30 (C-4), 154.06 (C-2), 155.8 (Boc-CO), 156.62 (C-6, ACV), 162.9 (C^2_{Thz}), 169.91 (C=O, ACV); ESI-MS: m/z: 481 $[M+H]^+$.

*N-α-tert-Butoxycarbonyl-Leu(Thz)-acyclovir **(3 d)***

N-α-tert-Butoxycarbonyl-Leu(Thz)-acyclovir *(***3 d***)* was prepared as described for compound **3 a**. Yield: 0.303 g, (58 %). ^{1}H-NMR ([D_6]-DMSO): δ = 0.99 (d, 6H, $(CH_3)_2$), 1.32 (d, 3H, CH_3), 1.36 (s, 9H, 3xCH_3), 2.11 (m, 6H, $CH(CH_3)_2$), 3.72 (t, 2H, CH_2O, ACV), 3.87 (m, α CH), 4.28 (m, 2H, $CH_2OC(O)$, ACV), 5.36 (s, 2H, N-CH_2-O, ACV), 6.70 (s, 2H, 2-

NH_2, ACV), 7.97 (s, 1H, H-8, ACV), 8.35 (s, 1H**,** CH_{Thz}), 10.87 (s, 1H, ACV-NH); ^{13}C- NMR ([D_6]-DMSO): δ = 17.3, 18.24 (($CH_3)_2$), 28.3 (Boc–CH_3), 42.0 (CH_2), 58.31 (α CH), 64.49 (CH_2OCO, ACV), 66.21 (CH_2O, ACV), 72.08 (NCH_2O), 78.7 (Boc-Cq), 128.9 (C^5_{Thz}), 137. 56 (C-8, ACV), 147.3, 148.2 (C^4_{Thz}), 151.00 (C-4), 154.20 (C-2), 155.8 (Boc-CO), 156.0 (C-6, ACV),162.2 (C^2_{Thz}), 168.73 (C=O, ACV); ESI-MS: m/z: 522 $[M+H]^+$.

Biological activity

Assay of antiviral activity of the synthesized esters of acyclovir against HSV-1 and HSV-2

Viruses: Herpes simplex virus type 1, strain DA, (HSV-1) and Herpes simplex virus type 2, strain BA, (HSV-2) were kindly provided by Prof. S. Dundarov, NCPID.

Cell culture: Cell line MDBK (Madin-Darby Bovine Kidney), grown in growth medium RPMI-1640 (Flow Laboratories) with 10% newborn calf serum. Serum concentration was reduced to 5% for growth of viruses and for testing the prodrugs.

Cytotoxicity assay – determination of the maximum tolerable concentration (MTC). To compare the MTC values of substances to that of ACV confluent monolayers were covered with media containing different concentrations of prodrugs or reference substance (ACV) and cultured at 37°C for 96h. Samples of cells grown in test prodrug-free medium served as a control. The maximum concentration, which altered neither the morphology nor viability of the cells, was recognized as MTC.

Antiviral assay. Experiments were done in multicycle growth experimental setup. Confluent cell monolayers were washed and infected with 320 cell culture infectious doses ($CCID_{50}$) per 0.1 ml of the respective virus strain. After 1 hour of adsorption, the maintenance solution containing compound tested in appropriate concentrations was added. One set of infected cells served as untreated control. The effect on viral replication was determined 48h after cultivation at 37°C as the reduction of infectious virus titres as compared to that in untreated virus control. The 50% inhibitory concentration (IC_{50}) for virus-induced cytopathic effect (CPE) was evaluated.

ACKNOWLEDGEMENTS

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QSAR STUDY AND CYTOTOXIC ACTION OF ISATIN DERIVATIVES

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Abstract

The antiproliferative action of seven isatin derivatives: 5-fluoroisatin, 5-chloroisatin, 5-bromoisatin, 5-iodoisatin, 5-methylisatin, *N*-methylisatin and *N*-ethylisatin was investigated *in vitro* on two neoplastic cell lines, HeLa (human cervix carcinoma) and Fem-x (human malignant melanoma). Target cells were seeded (2000 cells per well) in the nutrient medium. Twenty hours later, five different concentrations of examined agents were added to cells. 48 hours after isatin derivative action, the cell survival was determined by the MTT test, and by the neutral red uptake test.

All the analyzed compounds affected target cells proliferation. Morphological examination of treated cells shows that halogen derivatives of isatin induced the fragmentation of HeLa cells. *N*-methyl and *N*-ethyl derivatives induced Fem-x cell vacuolization and cell necrosis. The neutral red uptake test was more reliable than the MTT test in IC50 determination. All the compounds showed marked Hansch-type relationship between IC50 values and molecular parameters of lipophylicity and substituent steric effect.

Introduction

Cancer is the leading disease-related cause of death of the human population in some areas of the world, and it is predicted to continue this trend within the coming years [1]. Chemotherapy, or the use of chemical agents to destroy cancer cells, is a mainstay in the treatment of malignancies. A major advantage of chemotherapy is its ability to treat widespread or metastatic cancers, whereas surgery and radiation therapies are limited. The chemotherapy has aroused many researchers' interests and a great deal of current efforts has been focusing on the design and development of varied anticancer drugs. The search for new

compounds that could be potential anticancer drugs is the ultimate goal in modern medicine.

The isatin molecule (1H-indole-2,3-dione) is a versatile moiety that displays diverse biological activities [2], including anticancer activity [3, 4]. *N*-alkylated indoles have also been reported to exhibit anticancer activity. For example, the indolyl amide D-24851 has been found to be block cell cycle progression in a variety of malignant cell line including those derived from the prostate, brain, breast, pancreas and colon [5].

The quantitative structure-activity relationship (QSAR) is a powerful tool for rationalization and understanding of the biological activity of chemical compounds. It enables to pick up the most interesting new compounds among innumerable organic substances. The type of QSAR depends on the class of the compound and on the target system. Therefore, there is a need for an extensive study of various classes of compounds and their effects on living tissues.

In this sense the aim of this work was to test the action of seven synthetic isatin derivatives: 5-fluoroisatin, 5-chloroisatin, 5-bromoisatin, 5-iodoisatin, 5-methylisatin, *N*-methylisatin and *N*-ethylisatin (Fig.1) towards survival of two human neoplastic cell lines *in vitro*.

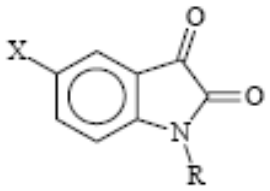


Fig. 1 Structure of isatin derivatives, X=F, Cl, Br, I, CH_3; R=H, CH_3, C_2H_5

Experimental

Synthesis of isatin derivatives was reported earlier [6].

Stock solutions of investigated compounds were made in DMSO, in concentration range 5.8-9.9 mM. Afterwards were diluted by nutrient medium (RPMI 1640 medium supplemented with L-glutamine (3 mmol/L), streptomycin 100 μg/mL and penicillin 100 IU/mL, 10% heat inactivated fetal bovine serum, FBS and 25 mM Hepes, adjusted to pH 7.2 by bicarbonate solution.) to various final concentrations. The 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazoliumbromide

(MTT) and neutral red (NR) were purchased from Sigma Chemicals (St. Luis, MO, USA) MTT was dissolved, 5 mg/mL in phosphate buffer saline pH 7.2 and filtrated through milipore filter, 0.22 μm, before use. RPMI

1640 cell culture medium and fetal bovine serum (FBS) were products of Gibco (Paisley, Scotland, UK)

Cell culture. Human malignant melanoma Fem-x cells and human cervix carcinoma HeLa cells were maintained as a monolayer culture in the same nutrient medium. The cells were grown at 37℃ in 5% CO_2 and humidified air atmosphere by twice weekly subculture.

Treatment of Fem-x and HeLa cells. Target cells were seeded in triplicate (2000 cells per well), into 96-well microtiter flat-bottomed plates. Twenty hours later, five different concentrations of investigated compound were added to the wells to various final concentrations, except to the control wells where a nutrient medium only was added to the cell. All samples were set up in triplicate. Nutrient medium with corresponding concentrations of compounds, but void of cells was used as blank, in triplicate too.

Determination of HeLa and FEM-x cell survival. Cell survival was determined as reported earlier [7-9] by MTT test, 48 h after the addition of drug. Briefly, 50 μL of MTT solution (5 mg/mL PBS) was added to each well. Samples were incubated for further four hours at 37℃ in 5% CO_2 and humidified air atmosphere. Then, 100 μL of 10% SDS in 0.01M HCl were added to the wells. Optical density (OD) at 570 nm was red the next day. To get cell survival (%), optical density at 570 nm of a sample with cells grown in the presence of various concentration of investigated agent (OD), was divided with control optical density ODc, (The OD of cell grown only in nutrient medium)×100. (It was implied that OD of blank was always subtracted from OD of corresponding sample with target cells.) Concentration IC50 was defined as the concentration of a drug needed to inhibit cell survival by 50%, compared with vehicle-treated control.

Neutral Red uptake test [10] was also used for determination of cell survival. Forty-eight hours after the agents' action nutrient medium was discarded and fresh medium with 40 μg/mL of neutral red was added to the cells. After three hours of the cell incubation with dye the medium was removed and the cells were washed with 1% $CaCl_2$ – 0.5% formaldehyde solution, which both removes the unincorporated dye and fixes the cells to the substratum. The dye was extracted into the supernatant by addition of 0.2 mL of 1% glacial acetic acid – ethanol solution. After 1 h at room temperature OD570 was red. Cell survival was calculated in the same way as in MTT test.

Methods of calculation. The quantitative correlation of the obtained IC50 values was done with lipophilicity, log (P), the substituent steric constants, Es, and with dipole moments. Estimation of logarithm of partition coefficient [n-Octanol/Water] log (P) =log (KOW) was done by Crippen's fragmentation method [11]. Substituent steric constants were taken from published compilations [12]. The geometries and dipole

moments of the molecules were determined by the AM1 method (using a MOPAC package, version 7.01 [13]), employing full geometry optimization and imposing no *a priory* symmetry constraints. The MNDO-AM1 method was proven to be accurate for the calculation of various molecular species [14-17].

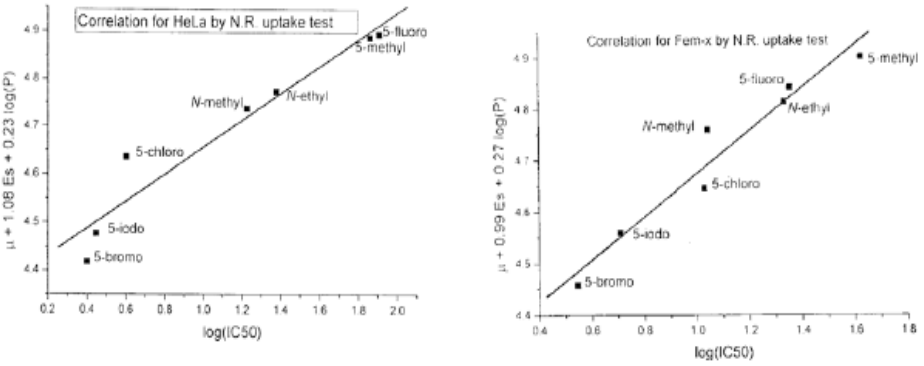
Results and discussion

The effect of the investigated compounds on Fem-x and HeLa cell survival, 48h after the continuous action of agents, was shown on Fig.2, on graphs A-C. Investigated drugs expressed the dose dependent antiproliferative action toward investigated cell lines. In order to compare the extent of the antiproliferative action between members of this group of compounds, IC50 were determined under exactly the same conditions. HeLa cells were more sensitive to the cytotoxic action of investigated isatine derivatives. The sequence of cytotoxic potency determined by MTT test was 5-iodo- > 5-chloro- > 5-bromo- > 5-fluoroisatin > alkylisatin. The same sequence was obtained by MTT test from Fem-x cells. *N*-alkyl and 5-methyl isatins appeared to be without cytotoxic effect, having extremely high IC50 values.

Morphological examination of treated cells on inverted microscope showed that cytotoxic action of 5-halogeno- and 5-methyl-derivatives of isatin induced the fragmentation of HeLa cells. This fragmentation was accompanied by abortive mitosis in approx. 5% of cells in the presence of 5-iodo- and *N*-methylisatins. The main effect of the investigated isatin derivatives on Fem-x cells was necrosis. *N*-methyl, *N*-ethyl- and 5-iodo-derivatives were particularly efficient in cell vacuolization, cell enlargement and cell membranelysis. A morphological examination of Fem-x cells treated with alkylisatins showed the presence of many dead (necrotic) cells, while MTT test showed no cytotoxic effect. Therefore we used alternative test for evaluation of cytotoxic potency of chemicals, *i. e*. neutral red uptake test.

A neutral red uptake test was more consistent with morphological evidence than MTT test in IC50 determination.

The sequence of cytotoxic potency determined by NR uptake test was 5-bromo- > 5-iodo-> 5-chloro- > *N*-methyl >*N*-ethyl > 5-fluoro-isatine for HeLa and Fem-x cells.



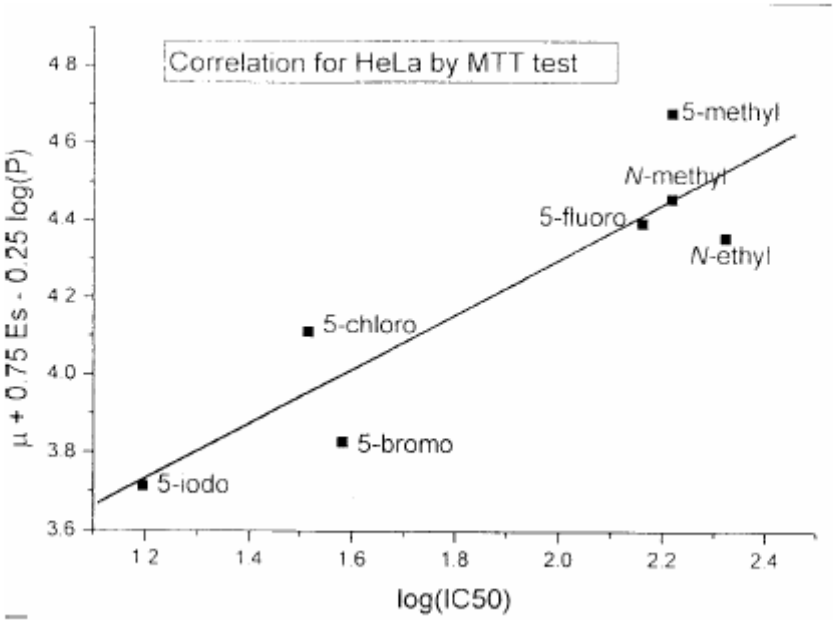


Fig.2 a) Correlation for HeLa by NR uptake test, b) Correlation for Fem-x by NR uptake test, c) Correlation for HeLa by MTT test

Structurally analogous derivatives have excellent correlations with single molecular parameter, such as the regression coefficients for various linear regressions of log (IC50) with calculated molecular properties for the investigated molecules. It could be seen that different behavior of halogen- and alkyl-substituted isatins, inferred from

morphological evidences, is mirrored in their different regression patterns. Generally, halogen derivatives correlate with Es and log (P) values, while alkyl-derivatives have best correlation with dipole moments.

However, using quadriparametric Hanch-type equation:

$$\log (IC50) = A \cdot (\mu + B \cdot Es + C \cdot \log (P)) + D \quad (1)$$

a very good correlation for all sets of experiments could be obtained.

An explanation for the observed discordance between data obtained by MTT test, NR uptake test and morphological evidence could be the production of some substances, during the cell necrosis, capable to reduce the MTT to formazan. Due that effect, the erroneously high cell survival values were obtained by MTT test.

Conclusions

Isatin is reported to be an endogenous natural inhibitor of monoamine oxidase B [18].

This study shows that IC50 values obtained by different methods produce different QSAR equation. This must be taken in account when results from various sources are compared.

Acknowledgement

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Determination of sugars in some ripe and dehydrated tomato varieties

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Abstract. *Five different tomato varieties: Pik Ripe 748 Imp LSL F1, Alexandar F1, Arizona, Rio Grande and Florida 47 F1, picked up in full technological maturity from Ovče Pole, Republic of Macedonia, in period of 2009 and 2010 have been analyzed for sugars in both forms, fresh and dehydrated. The dehydration by Armenian solar drier and preparation of samples prior to analysis is described. The method using Carrez reagents was found to be efficient preparation tool. Laborious volumetric Loof-Schoorl method was adapted to detect and quantify microgram amounts of sugars in tomatoes. The reducing sugar content is ranged from 1.51 % (w/w) of fresh mass in cultivar Arizona for 2009 and 1.78 % (w/w) in 2010 to 3.02 % (w/w) of fresh mass in cultivar Rio Grande for 2009 and 3.21 % (w/w) in 2010. The absence of sucrose amount was explained by similar values obtained for reducing sugars before and after inversion. According to results, processing tomatoes into dehydrated products improved their nutritional quality and sugar content mainly by concentration effect.*

1. INTRODUCTION

Tomato (Lycopersicon esculentum) is the most cultivated herbaceous plant in the Republic of Macedonia with 66% of vegetables production according to the literature data [1]. Tomato is a valuable source of carotenoids in particular lycopene, flavonoids, ascorbic acid, vitamin E, proteins, dietary fibers and potassium, so is widely consumed product in both fresh and processed form. Tomatoes are processed into sauce, paste, puree, ketchup, but also can be conserved by solar drying which applies cheap, safety and clean energy. All scientific researches show that the Republic of Macedonia is country with high insolation, average 2200 sun

hours per year [2], and this possibility for exploitation of solar energy was used for processing dehydrated tomatoes by Armenian solar dryer.

The efficiency of tomato processing operations depends on the type and concentration of carbohydrates that are present in analyzed samples. Carbohydrates are one of the most important components in many foods. As well as being an important source of energy and dietary fiber, carbohydrates also contribute to physicochemical properties of foods such as the sweetness, appearence, stability and textural characteristics. Furthermore, favorable ratio between sugars and titrable acids is one of the most important parameters for assessment the quality of tomatoes as potential vegetables for conservation.

In vegetables such as tomatoes, carbohydrates are present in low levels making their isolation and quantification very difficult. Traditionally, the carbohydrate content of foods can be determined by calculating the percent remaining after all the other components have been measured:

% carbohydrates = 100 % – (% moisture + % protein + % fat + % ash)

The carbohydrate estimated in this fashion includes fibre, as well as some components such as organic acids [3]. Also, this method can lead to erroneous results due to experimental errors in any of the other methods, and so it is usually better to directly measure the carbohydrate content for accurate measurements.

During the last years, a large number of analytical techniques have been developed to measure the total concentration and type of carbohydrates present in foods. Mixture of carbohydrates can be resolved into individual components by differential or isopycnic centrifugation, ion-exchange chromatography and gel filtration. Monosaccharides obtained by hydrolysis with strong acids are separated and quantified mostly by chromatographic methods [4]. HPLC and ion chromatography [5], are currently the most important methods for analyzing carbohydrates because of their capability for rapid, specific, sensitive and precise measurements, whereas samples can often be analyzed directly. In addition, GC requires conversion to suitable volatile derivatives [5]. HPLC and GC are commonly used in conjunction with NMR or mass spectrometry, so the chemical structure of the molecules can be identified. Electrophoretic separations of carbohydrates [5] after their derivatization to charged molecules are also followed by spectroscopic measurements. Enzymatic methods and specific colorimetric assays [6] enable analyses to be performed quantitatively as well as adding certainty to the identification. Qualitative analysis of monosaccharides, frequently obtained by hydrolysis of higher saccharides and isolated by chromatographic methods, planar chromatography and colour tests, are inexpensive and easy to carry out, requiring standard reference compounds, but it is not possible to distinguish between

enantiomers by such means. Monosaccharides and oligosaccharides in foods are determined using a number of chemical methods based on the fact that many of these substances are reducing agents that can react with other components to yield precipitates or colored complexes which can be quantified gravimetrically, spectrophotometrically or by titration [7].

The objectives of this work was to develop a sample preparation procedure for determination of carbohydrate content in ripe and dehydrated tomatoes, using a method which is easy to carry out and not required expensive equipment. In this study reducing sugars content was determined by Luff-Schoorl method, which is widely used to detect and quantify microgram amounts of reducing sugars. Furthermore, the aim was to observe the processing effect of solar drying on the nutritional composition of tomato varieties.

2. MATERIALS AND METHODS

Pik Ripe 748 Imp LSL F1 is a high quality hybrid variety for fresh consummation with spherical appearance and average weight 200-250 g.

Alexandar F1 is industrial variety of tomato with spherical crop and weight 160-180 g.

Arizona is well known industrial variety with high content of dry matters and permanent color, using for process into sauce and puree. The average weight is 160 g.

Rio Grande is industrial tomato variety with oval shape, 100g weight and high content of dry matters.

Florida 47 F1 is Nederland tomato hybrid for fresh consummation and average weight 230 g.

Reagents

Carrez solution I: 15 % (w/v) water solution of potassium hexacyanoferrate (II) trihydrate $K_4[Fe(CN)_6]\cdot 3H_2O$.

Carrez solution II: 30 % (w/v) water solution of zinc sulfate heptahydrate $ZnSO_4\cdot 7H_2O$.

Luff-Schoorl reagent: The citric acid solution (50 g citric acid octahydrate $C_6H_8O_7\cdot 8H_2O$ dissolved in 50 mL of water) was added to the sodium carbonate solution (388 g sodium carbonate decahydrate $Na_2CO_3\cdot 10H_2O$ dissolved in about 300 mL of warm water) in a one litre volumetric flask with gentle swirling. Then the copper (II) sulphate solution (25 g copper (II) sulphate pentahydrate $CuSO_4\cdot 5H_2O$ dissolved in 100 mL water) was added and filled up to 1 L with water. The prepared Luff-Schoorl solution was allowed to stand overnight and filtered if it was necessary. The molarity and pH of the reagent were checked before analyses. The

procedures for standardization of the Luff-Schoorl reagent were included: titration with sodium thiosulphate of acidic solution when potassium iodide was added; and titration of heated mixture of 0.75 mol/L hydrochloric acid and diluted reagent with sodium hydroxide. The pH of the Luff-Schoorl reagent was between 9. 73 and 9. 74 at 20 ºC.

Potassium iodide solution, 1 mol/L
Sulphuric acid, 25 % (w/v)
Sodium thiosulphate solution, 0,1 mol/L
Starch solution, 2 % (w/v)
Hydrochloric acid, concentrated.
Sodium hydroxide, 20 % (w/v)
Methyl rod solution, 0.1 % (w/v)

Experimental Procedure

Preparation of dehydrated tomato samples

The ripe fruits of different tomato varieties were selected, calibrated and washed up with microbiological and chemical accuracy drinking water. Then tomatoes were strained, cut to small peaces and placed on wooden hurdle gate with metal sieving grids (10 kg fruits/ 1 m^2 surface hurdle-gate) of Armenian solar dryer with 100 kg capacity. Tomato fruits were dried for approximately 2 days (48 hours) in the end of the August 2009 and 2010, respectively.

Procedure 1: Preparation of tomato solution for determination of sugars

Carbohydrates were extracted from aliquots of 10 g of both forms of tomato with 30 mL hot water, at least for five minutes on water bath with stirring. Then the homogenized mixture was quantitatively transferred to a 100 mL volumetric flask, and filled with water. After vacuum filtration, 50 mL of obtained extract for fresh fruit and 25 mL for dried form was transferred in 250 mL volumetric flask, clarified with adding an equal volumes of Carrez solutions, mixed well and filled up with water. Reducing sugars were determined in acquired solution after filtration.

Procedure 2: Determination of reducing sugars before inversion by the Luff-Schoorl method

25 mL of the prepared tomato solution in Procedure 1 and 25 mL of Luff-Schoorl reagent were pipetted into a 300 mL conical flask fitt with a reflux condenser. The liquid was heat to boiling point over a period of about two minutes on direct Bunsen flame, which was followed by gently simmer on asbestos wire gauze for exactly 10 minutes. After cooling the sample solution for two minutes, 9 mL of potassium iodide solution was added and immediately with caution (because of effervescence) 25 mL of 25 % sulphuric acid. The excess of copper II was determined iodometrically. Control test was carried out using 25 mL of water in place of the 25 mL tomato solution.

Procedure 3: Determination of total sugars after inversion by the Luff-Schoorl method

5 mL concentrated hydrochloric acid was added to 50 mL of tomato solution prepared in Procedure 1 into a 100 mL volumetric flask. Inversion of non-reducing sugars was achieved by heating of acidic solution in thermostat bath on temperature 67-70 °C, for exactly 5 minutes. The mixture was neutralized to pH 6 with sodium hydroxide solution and the flask was making up with water. The obtained solution was further used for determination of reducing sugars following the Procedure 2.

3. RESULTS AND DISCUSSION

Cultivar quality is defined by different parameters that give an integral picture of selected fruit. The relationship between total soluble solids and total acidity is very important in determining fruit quality. In numerous researches of different tomato varieties, the total soluble TSS/TA ratio was found to be very important, because it provides information about the balance of sugars and acids in the fruit. Recently, this ratio was considered as main parameter for determining fruit quality [8], along with the fruit color. In this investigation reducing sugars were determined in five different tomato varieties: Pik Ripe 748 Imp LSL F1, Alexandar F1, Arizona, Rio Grande and Florida 47 F1. Samples of fresh tomato fruit were picked up in full technological maturity from Ovče Pole, Republic of Macedonia, in period of 2009 and 2010. Tomato fruits were dried in Armenian solar drier.

In order to extinguish the high level of variation caused by low level of sugar content in tomato, the procedure of sampling for ripe and dried tomatoes was developed. According to literature data [9], 25 mL of analyzed solution must contain not less than 15 mg and not more than 60 mg reducing sugars expressed as glucose. The obtained results from Luff-Schoorl analysis were reproducible when the sample weight was 500 mg of ripe tomato and 250 mg of dry form.

Low molecular weight carbohydrates that are physically associated or chemically bound to other components were isolated from homogenized tomato matrix by extraction from water solution with refluxing. The soluble monosaccharides and oligosaccharides were separated from the insoluble proteins, polysaccharides and dietary fiber by filtering the boiled solution. The small molecules of amino acids, organic acids, vitamins, minerals and pigments contained in colored water extract were interfered with endpoint determination, so the solutions were clarified prior to analysis. In this work, Carrez reagent (zinc sulphate + potassium ferrocyanide) was used as clarifying agent to precipitate the amino acids and some proteins, forming insoluble complexes that were removed by filtration and centrifugation. The

best results were obtained when equal volumes of Carez I and Carez II reagent, 5 mL of each were added.

Total sugar content in clarified samples of tomato varieties were determined by Luff-Schoorl method as reducing sugars (% w/w) before and after inversion. The base medium of Luff-Shoorl reagent was necessity to achieve equilibrium between hemiacetal ring form of D-glucopyranose and open chain form of D-glucose (Fig. 1). Also, under these conditions hydrolysis of D-fructofuranose was followed by spontaneous tautomerization to corresponding aldohexose D-glucose (Fig. 2).

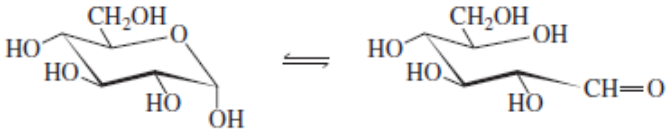

Fig. 1 Open chain form of D-glucose is dominant in alkaline medium

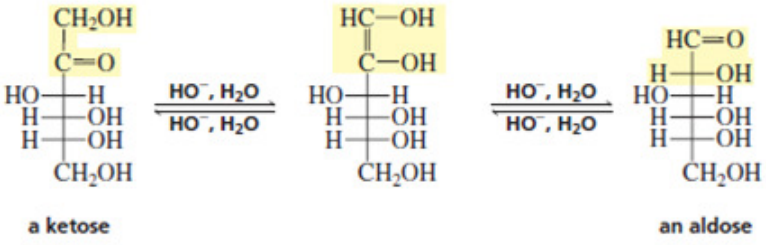

Fig. 2 Tautomerization of D-fructose to D-glucose

In presence of heat and excess of copper sulfate under carefully controlled conditions oxidation reaction was completed and copper oxide precipitate was formed:

reducing sugar + Cu^{2+} + base → oxidized sugar + CuO_2

In addition, the excess of copper II was determined iodometrically. The volume of sodium thiosulphate solution was directly related to the concentration of reducing sugars in the initial sample.

The reducing sugars content before and after inversion for analyzed tomato fruits in period of 2009 and 2010 are shown in Tab. 1. The similar values for reducing and total sugar content can be attributed to nonappearance of unreducing sugars, or sucrose occurred under the limit of detection.

Tab. 1 Sugar content in ripe tomato fruits from different variety

tomato variety	reducing sugars percentage (w/w) of the dry matter	total sugar content percentage (w/w) of the dry matter	sucrose percentage (w/w) of the dry matter
Florida 2009	2.523	2.528	0.0047
Florida 2010	2.72	2.72	0.00
Alexandar 2009	2.82	2. 80	0
Alexandar 2010	3.15	3.13	0
Pik Ripe 2009	1.81	1.80	0
Pik Ripe 2010	1.96	1.94	0
Arizona 2009	1.51	1.51	0.00
Arizona 2010	1.72	1.78	0.057
Rio Grande 2009	3.01	3.01	0.00
Rio Grande 2010	3.20	3.21	0.0095

Data are expressed as average value ± 0.01 standard deviation of three replicates.

The reducing sugar content is ranged from 1.51 % (w/w) of fresh mass in cultivar Arizona for 2009 and 1.78 % (w/w) in 2010 to 3.02 % (w/w) of fresh mass in cultivar Rio Grande for 2009 and 3.21 % (w/w) in 2010. Because of that, the variety of Rio Grande is recommended for industrial production of tomato puree and ketchup. The obtained results are in accordance with the investigations of other authors. According to Martinovski [10], the quantity of total sugars in the investigated cultivars ranged from 1.99 % to 2.25 %, while Vračar [11] reported values for total sugars from 3.5 % to 4.7 % depending on the tomato cultivar. In the research of Hossain [12], the range of reducing sugar content varied from 2.36 % for TM-152 to 2.74 % for TM-133. The differences exist due to different varieties, cultivation system, climatic conditions, etc. As can be seen from Tab. 1, a general trend of the highest sugar content was found with increasing insolation in the region of Ovče Pole in 2010 [2] for all tomato varieties.

The obtained results for reduced sugar content in tomatoes dehydrated by Armenian solar drier are shown in Fig. 3, expressed in terms of invert sugar or D-glucose as percentage (w/w) of the dry matter.

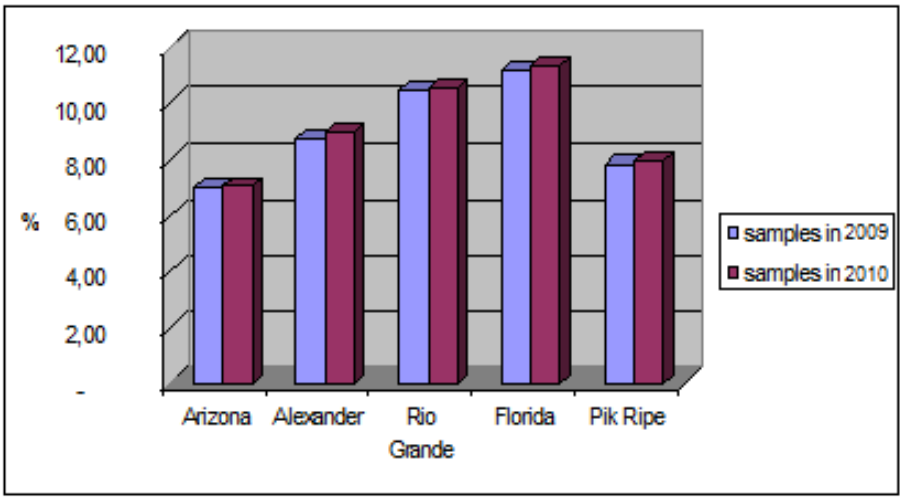

Fig. 3 Sugar content in different tomato varieties dehydrated by Armenian solar drier

According to the obtained results, processing tomatoes into dehydrated products improves their nutritional quality and sugar content mainly by concentration effect. Results acquired by Luff-Schoorl procedure were shown that there is no detectible amount of sucrose in these varieties of dried tomato fruit.

4. CONCLUSION

From the present study it could be concluded that Luff-Schoorl method shows very high accuracy of the determination of small amounts of reducing sugars and the results can be comparable with other automated methods, but suffers from the same disadvantages as the Lane-Eynon volumetric method. The disadvantages of this method are (i) the results depend on the precise reaction times, temperatures and reagent concentrations used and so these parameters must be carefully controlled; (ii) it cannot distinguish between different types of reducing sugar, and (iii) it cannot directly determine the concentration of non-reducing sugars.

The advantage over other volumetric procedures is non-interference with other types of molecules that act as reducing agents. Namely, under slightly alkaline conditions (pH 9.3) oxidation occurred only with aldoses and ketoses, not with aldehydes present in the matrix.

The tomato varieties Rio Grande and Alexander can be recommended for further solar drying because of the highest sugar content. Armenian solar dryer is convenient because it contributes to fruits and vegetables

conservation nearest to the place of production without other sources of energy.

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Antioxidant and anti-inflammatory effects of phenolic compounds

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Abstract*: Phenolic antioxidants in extra virgin olive oil, suppresses production of proinflammatory mediators. It is not clear however which of their structural features are responsible for this. Here we attempt to explain the reasons for this activity. We found that only phenolic compounds, which have two hydroxyl groups on a suitable position to form a stable quinones after oxidation inhibit production of the inflammatory cytokine interleukin -1 β and prostaglandin E2.*

Keywords: *phenolic antioxidants, extra virgine olive oil, quinines*

1. Introduction

There is a view in the nutrition science that the presence of Extra virgin olive oil (EVOO) decreases coronary heart disease death rates [1]. EVOO is an obligatory ingredient of the Mediterranean diet. In comparison to other vegetable oils, EVOO must be considered as a unique dietary food due to the prevalent presence of the monounsaturated oleic acid and hydrophilic compound such as phenolic alcohols and acids, flavonoids, lignans, and secoiridoids. [2]. The fatty acid fraction accounts for not less than 98% of the oil components and is characterized by a relative low level of polyunsatured fatty acids and a high level of monounsatured fatty acids [3].

Consumption of a dietary antioxidants may be beneficial in protecting low density lipoprotein against oxidative modification and coronary disease [4]. On the other hand, there are proves that, the development of cardiovascular disease includes a strong inflammatory component [5]. Some EVOO phenolics have been shown to inhibit eicosanoid production, suggesting that they might exert anti-inflammatory effects [6,7]. This is supported by experiments with phenolic compounds significantly decreased the production of the inflammatory cytokine interleukin (IL)–1β [8]. Others have demonstrated that different EVOO phenolics can increase or decrease the production of another inflammatory mediators [9,10].

In the citation [11] authors have investigated the effects of eight EVOO-derived phenolic compounds on the production of a range of proinflammatory mediators - IL-1β and IL-6, tumor necrosis factor-α, and

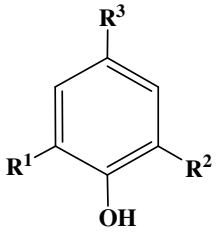
prostaglandin E2 [PGE2] by human whole blood cell cultures stimulated with bacterial lipopolysaccharide. The phenolics tested are vanillic acid, *para*-coumaric acid, syringic acid, homovanillic acid, caffeic acid, oleuropein glycoside, and tyrosol, kaempferol, which are commonly identified in EVOO (Fig. 1).

The results confirm the hypothesis - the tested compounds with antioxidant activity suppress production of IL-1β and PGE2, therefore have anti-inflamatory action.

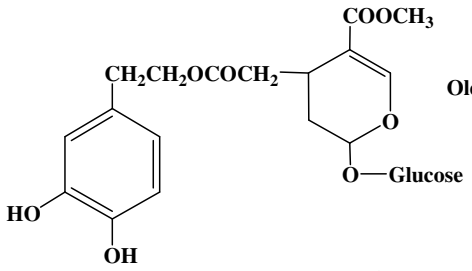
Antioxidant activity is modeled very well with structural descriptors generated by their ability to interact with active radicals. Such descriptors are spin density of the newly formed radicals in the reaction with active radicals and the bond length is the dissociable hydroxyl group.

The purpose of this work is to check which of the structural properties of the studied compounds could explain their activity against inflammatory mediators.

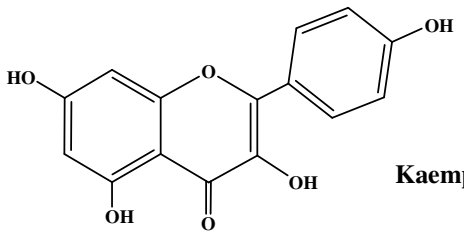
2. METHODS



	R^1	R^2	R^3
Vanilic acid	H	OCH_3	COOH
Homovanillic acid	H	OCH_3	CH_2CH_2OH
p-Coumaric acid	H	H	CH=CHCOOH
Syringic acid	CH_3O	OCH_3	COOH
Caffeic acid	H	OH	CH=CHCOOH
Tyrosol	H	H	CH_2CH_2OH



Oleuropein glycoside



Kaempferol

Fig. 1: Structures of the considered compounds.

Antioxidant descriptors of the considered compounds were calculated after quantum chemistry calculations. In the recent years, the hybrid DFT potentials have become the most widely used quantum-chemical methods for calculating descriptors of antioxidant activity [12]. The values were computed after geometry optimization of all investigated structures at the unrestricted DFT level of theory with the B3LYP functional [13] using the GAUSSIAN'09 program package [14]. It has been shown that the B3LYP functional gives more reliable results with respect to bond dissociation energies than the post Hartree-Fock methods [13]. Moreover, the utilization of post Hartree-Fock methods is usually more costly. The orbital basis set was chosen to be 6-31G(d,p) [14]. Further extension of the basis set usually does not increase the quality of the data [15]. The effect of the environment was neglected.

3. RESULTS AND DISCUTIONS

Tab. 1: Spin density (SD) and O-H bond distance in the compounds investigated in [Elizabeth A. Miles, Pinelope Zoubouli, Philip C. Calder, D.Phil Nutrition 21 (2005) 389-394].

Compounds	BA1 IL-1β	BA1 PGE_2	SD	R_{OH}
Caffeic acid	60%	59%	0.302	0.97
Kaempferol	15%	100%	0.341	0.966
Oleuropein	80%	60%	0.356	0.9691
p-Coumaric acid	20%	10%	0.356	0.967
Syringic acid	0%	38%	0.336	0.971
Vanillic acid	0%	0%	0.36	0.971
Tyrosol	8%	50%	0.431	0.966
Homovanilic acid	0%	47%	0.386	0.96534

Vanillic acid, Syringic acid and Homovanilic acid do not diminish the IL-1β concentration. *Para*-coumaric acid cause 20% lessening of the IL-1β concentration, kaemferole – 15%, tyrosole – 8 %, oleuropein – 80%, and caffeic acid – 60%.

Vanillic acid do not disturb the concentration of (PGE2). *Para*-coumaric acid diminish its concentration – 10 %, syringic acid – 38 %, homovanillic acid – 47 %, kaemferol – 100 %, tyrosol – 50 %, oleuropein – 60 %, and caffeic acid – 59 %.

On the other hand the most active antioxidant according to calculated descriptors in the group of phenolic compounds is caffeic acid, folowed by syringic asid, kaemferol, oleuropein and so on.

It turns out that according to the descriptors no link between the antioxidant activity of compounds and their ability to decrease production of IL-1β and PGE2.

However, these descriptors are relevant only to the dissociation of the first or single hydroxyl group in the molecule of antioxidant. If the molecule has a second hydroxyl group in a suitable position to form a stable diamagnitic quinone, the second hydroxyl group dissociates as easy as the first or easier and can therefore participate in the capture of free radicals.

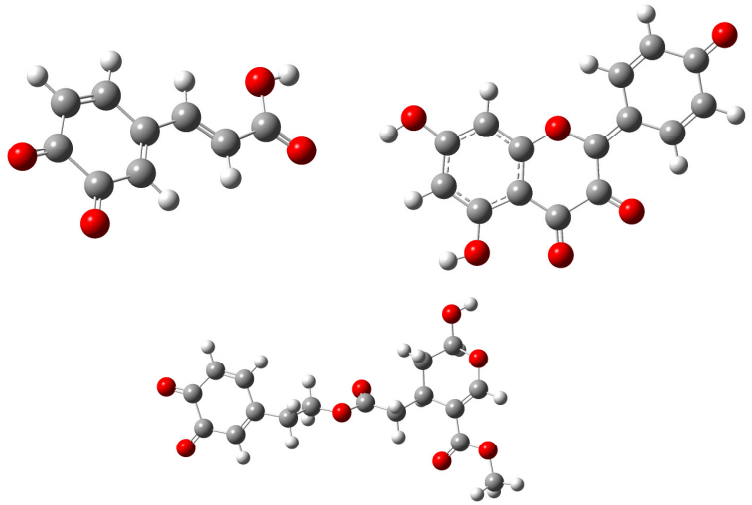


Fig. 2. Optimised geometry of the corresponding quinones.

Obviously, this is the case with the tested compounds. The most active among them are those which can form stable quinones - cafeic acid, kaemefrol and olevropein.

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On one possibility for application of new thermoelectric materials based on Ag_2Te

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***Abstract**: The thermoelectric characteristics of Ag_2Te and $Ag_{1,84}Cd_{0,08}Te$ (solid solution based on Ag_2Te) are investigated and analyzed. The main thermoelectric characteristics of the solid solution: α=118 μV/K; σ = 2230 S/cm and λ = 2,45.10^{-2} W/(cm.K) ensure coefficient of thermoelectric efficiency z = 1,27.10^{-3} K^{-1} (at 300 K), which increases this of the Ag_2Te. A composition for commutation material is developed, which connects the N- and the P-branches of a single thermo element (52 wt. % In + 48 wt. % Sn) with melting temperature of 390 K. The possibility for application of the $Ag_{1,84}Cd_{0,08}Te$ solid solution as N-branch of a thermo element in combination with the solid solution $Bi_{0,5}Sb_{1,5}Te_3$ (P-branch) is investigated. The thermo element guarantees values of z from 0,71.10^{-3} to 1,27.10^{-3} K^{-1} in the temperature interval 250 - 350 K. The maximum z value is registered at 300 K (z = 1,27.10^{-3} K^{-1}).*

***Keywords:** Silver telluride, Solid solutions, Thermoelectric properties, Thermoelement.*

1.INTRODUCTION

The fast development of the contemporary technologies during the last 10-15 years continuously requires more effective and reliable materials with better characteristics. Due to this reason the new materials have become a key section, from which to a great degree depends the success of the engineering solutions in different areas of the human activities. This leads to more effective assimilation of the already known classical materials and to widening of their spectra of properties, on the one hand, and to a purposeful research of new materials with new preliminary given properties, on the other. This is valid mostly for the energetic technologies: elaboration and increase of the efficiency of the already used materials, as well as searching of innovative solutions in this area. The thermoelectric phenomena, which form the basis of the thermoelectric energy transformation, mark a significant progress during the last years due to the

possibilities, which they offer for direct transformation of the heat energy into electricity, and also due to their wide application range in different thermoelectric devices: thermocouples, thermoelectric cooling devices and transformers for measurement of electrical constants, thermoelectric calorimeters, emission receivers, thermoelectric transformers, pumps and many others.

The main requirement towards the thermoelectric materials is that they have to possess high values of the thermoelectric efficiency coefficient (z), which have to be kept in a wide temperature interval ($z = \alpha^2\sigma/\lambda$; α – thermo-electromotive tension coefficient; σ – specific electroconductivity; λ – heat conductivity coefficient). The materials are qualified as thermoelectric, i.e. appropriate for a practical application, if their $z \geq 0{,}3.10^{-3}$ K^{-1} [1]). The most appropriate for thermoelectric application are the semiconductor materials, which to a great degree allow the managing of α, σ and λ with the aim the highest z values to be reached.

The increase of the z coefficient of the thermoelectric materials is a complicated task and a complex method is needed for its solution, since the change of certain thermoelectric parameters towards positive direction leads others to get worse. For example, the decrease of the charge carriers' concentration leads to increase of α, but in parallel with this σ decreases. Furthermore, if σ increases the λ significantly decreases, etc.

One of the most widely used methods for increase of the thermoelectric efficiency coefficient is this, by which isovalent substitution atoms are introduced in the one or in both sub-lattices of the semiconductor compound. By this way isomorphous solid solutions (partially or fully substituted) are formed, as depending on the substitution character and the valence of the participation atoms, a limiting influence on λ or on σ is reached [2].

The interest towards the Ag_2Te is not new and is owed to several reasons: it belongs to the self-compensating compounds [3], on the one hand. On the other it is part of the group of the narrow-gap semiconductors ($\Delta E \leq 0{,}3$ eV), on which basis a row of devices are constructed: thermoelectric transformers [4], optical quantum generators [5], photoelectric receivers, working in the near and far IR-region [6], heat switchers [7], etc.

It is known that the appearance of self-conductivity in Ag_2Te is masked by the conductivity of the "defect" zone and by its junction with the conductivity band, due to which the experimentally determined value of the thermal band gap (ΔE_o) varies in wide range: from 0,025 to 0,5 eV. The value of 0,18 eV is accepted as the most trustworthy [3,8].

The electrical conductivity (σ) of $Ag_{2-x}Te$ at room temperature varies in the range 250-1100 S/cm [9-11]. According to A.S.Okhotin et al. [12], the heat conductivity coefficient (λ) decreases from 2.10^{-2} at 300 K to $1{,}75.10^{-2}$

at 475 K, after which is increases again to $7,8.10^{-2}$ W/(cm.K) at 673 K. The thermo-electromotive tension coefficient (α) of $Ag_{2-x}Te$ changes its sign both with the temperature increase and the deviation from the stoichiometry [13]. α also decreases when the sample is not with stoichiometric composition [14]. The over-stoichiometric Ag-atoms cause negative values of α, while their insufficiency – to positive.

The stoichiometry deviation, the doping with appropriate admixtures and the development of solid solutions based on $Ag_{2-x}B^{VI}$ open possibilities for increase of z [15]. Data is reported in the literature about z of a doped Ag_2Te of about $(0,3\text{-}1,0).10^{-3}$ K^{-1} [1]. The silver telluride $Ag_{2-x}Te$ is characterized by structural disorder and strong intrinsic defectness, by complicated energetic structure and high concentration of the charge carriers, i.e. it covers the requirements of the highly effective thermoelectric materials [2,15].

The phase diagram of the Ag_2Te-CdTe system is investigated [16]. Existence of boundary solid solutions in the concentration interval $0 \le x \le 8$ mol % CdTe is observed. There is very small quantity of data in the literature about the properties and the application possibilities of solid solutions based on Ag_2Te. In our previous work, the main characteristics of the solid solutions $Ag_{2-2x}Cd_xTe$ ($0 \le x \le 8$ mol %) are investigated and it is established that the solid solution with composition $Ag_{1,84}Cd_{0,08}Te$ has the maximum thermoelectric efficiency coefficient [17].

The aim of the present report is to examine the possibility for application of the solid solution $Ag_{2-2x}Cd_{0,08}Te$, as an N-branch of a semiconductor thermo element, working in the interval 250-350 K.

2.RESULTS AND DISCUSSIONS

The initial components Ag_2Te and CdTe, as well as the $Ag_{1,84}Cd_{0,08}Te$ solid solution are obtained by direct monotemperature synthesis [18] from the elements with purity: Ag – 3N; Cd – 2N3 and Te – 3N.

For the α, σ and λ measurements of the polycrystalline samples Ag_2Te and $Ag_{1,84}Cd_{0,08}Te$, equipment for complex materials investigations in the temperature interval of 100÷500 K is used (developed and constructed in the Department of Non-Ferrous Metals Metallurgy and Semiconductor Technologies), which is protected by author certificate [19]. The construction of the equipment allows simultaneous measurement of all three temperature-dependent characteristics of the materials: $\alpha(T)$, $\sigma(T)$ and $\lambda(T)$ in the mentioned temperature interval.

The measurements were led at temperatures of 250, 300 and 350 K at residual pressure in the cryostat of $1,33.10^2$ Pa. Liquid nitrogen is used for reaching of the working temperature of 250 K. The methods used for the

measurements were: direct method for the α measurements, two-point probe for σ and absolute stationary method for λ. These characteristics of the thermoelectric materials were measured with accuracy of: ± 1 % for α, ± 3 % for σ and ± 5 % for λ.

The samples were welded to the forehead planes of a special holder with In-Sn solder (52 % In + 48 % Sn; T_m = 390 K).

The thermoelectric characteristics of Ag_2Te and the $Ag_{1,84}Cd_{0,08}Te$ solid solution are summarized in Table 1. The obtained values are in good conformity with the reported in the literature [17,20].

Tab. 1: Main characteristics of Ag_2Te and the $Ag_{1,84}Cd_{0,08}Te$ solid solution.

T	Ag_2Te				$Ag_{1,84}Cd_{0,08}Te$			
	α, 10^{-6}	σ	λ, 10^{-2}	z, 10^{-3}	α, 10^{-6}	σ	λ, 10^{-2}	z, 10^{-3}
K	V/K	S/cm	W/(cm.K)	K^{-1}	V/K	S/cm	W/(cm.K)	K^{-1}
250	103	850	2,30	0,392	80	2600	2,35	0,708
300	114	815	2,42	0,438	118	2230	2,45	1,267
350	95	780	2,57	0,274	102	2115	2,62	0,840
Characteristics of P-$Bi_{0,5}Sb_{1,5}Te_3$ at 300 K					160	850	1,60	1,360

The analysis of the results from Tab. 1 shows that the solid solution $Ag_{1,84}Cd_{0,08}Te$ possesses better thermoelectric properties and it is appropriate for practical application in the temperature range 250-350 K.

The investigated samples are of N- type conductivity.

The investigations of the thermoelectric properties of various solid solutions based on Ag_2Te or doped with different admixtures Ag_2Te are preliminary, but even this investigation shows that the thermoelectric efficiency coefficient of the solid solutions can increase significantly compared to the basis compound, in this case the Ag_2Te. On the other hand, the fact that the introduction of CdTe to Ag_2Te leads to significant increase of σ/λ is direct evidence [17], that the initial Ag_2Te ahs hidden reserves towards the zT factor, which gives optimism for the research of new Ag_2Te based solid solutions and improvement of the properties of the already obtained ($Ag_{1,84}Cd_{0,08}Te$) towards structure, purity of the initial components, additional thermal treatments, substitution in the tellurium sub-lattice, etc.

One of the possibilities for application of this semiconductor material ($Ag_{1,84}Cd_{0,08}Te$) is its usage as N-branch of a thermo element. For P-branch of this thermo element, a solid solution based on Sb_2Te_3 ($Bi_{0,5}Sb_{1,5}Te_3$) with basis characteristics at 300 K shown in Table 1, has been chosen. The thermo element is consisted by two semiconductor blocks – the one with N-type conductivity and the other – with P-type, which are connected in one of their ends with massive Cu-plate. The other two free ends of the blocks are also connected by soldering of two electrodes (copper plates). The mutual

copper plate is put at temperature $T_2 = T_{hot}$ and the other two are at temperature $T_1 = T_{cold}$ (T_1 is near to the room temperature).

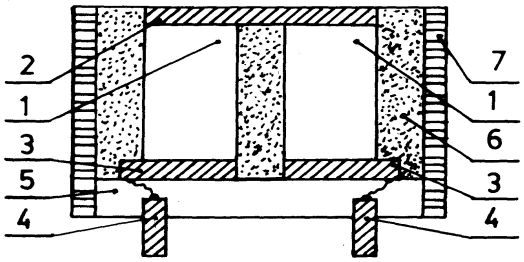

Fig. 1: Semiconductor thermo element: 1 – semiconductor blocks with N- and P-type conductivity; 2 – connecting Cu-plate; 3 – Cu-plates; 4 - leads; 5 – insulating plate (Teflon); 6 – polymer (epoxy raisin); 7 – plastic body.

The N- and P-branches of the thermo element as a rule are immovably connected in the circuit (by alloying) or movably (by pressing) using special rims. The used contact materials have to have low electrical resistivity, high heat conductivity and stability of these characteristics during the exploitation of the device.

The finding of appropriate commutation material is one of the hardest tasks during the development of thermoelectric devices, since a row of heavy requirements are claimed for them: to wet well the surface of the thermoelectric material, to have low electrical resistivity, which changes slightly during the temperature increase, to have linear expansion coefficient values near to these of the semiconductor thermoelectric material, to have high mechanical strength, not to have solid state transitions, etc.

Three compositions for commutation material (Tab. 2) were developed for the used system $Ag_{1,84}Cd_{0,08}Te/Bi_{0,5}Sb_{1,5}Te_3$. Commutation material III has been used for production of the thermo element.

Tab 2: Compositions of commutation alloys and their melting temperatures.

Composition, %	In	Cd	Zn	Sn	T_m, ºC
I	74,0	24,2	1,8	-	116
II	52,2	-	1,8	46	108
III	52,0	-	-	48	117

Thermo-electromotive tension appears in each branch of the thermo element, which is summed up for the whole thermo element. The maximum efficiency coefficient for this thermo element is [2]:

(1)

$$\eta_{max} = \frac{T_2 - T_1}{T_2} \cdot \frac{\sqrt{1 + z.\overline{T}} - 1}{\sqrt{1 + z.\overline{T}} + \frac{T_1}{T_2}}; \quad z = \frac{(\alpha_1 + \alpha_2)^2}{\left(\sqrt{\frac{\lambda_1}{\sigma_1}} + \sqrt{\frac{\lambda_2}{\sigma_2}}\right)^2};$$

where: α_1, α_2; λ_1, λ_2 and σ_1, σ_2 are the coefficients of thermal electromotive tension, the coefficients of heat conductivity and the specific electroconduc tivities of the N- and P-branches of the thermo element, respectively.

The efficiency coefficient depends on the consumed power. The condition for maximum extracted power from the thermo element is equalization of the consumer's and the thermo element's (thermo generator's) resistivities:

(2)
$$\eta_{(W=max)} = \frac{1}{2} \cdot \frac{T_2 - T_1}{T_2 + \frac{2}{z} - \frac{1}{4}(T_2 - T_1)}.$$

Using the parameters of the investigated thermoelectric materials (Tab. 1) at T_1 = 300 K, T_2 = 350 K, $\overline{T}$ =325 K, the efficiency coefficients have been determined by Eqs. (1) and (2): z = 1,32.10^{-3} K^{-1}; η_{max} = 1,36 %; $\eta_{(W=max)}$ = 1,35 %, i.e. the conditions, at which the investigations were led, correspond to work of the thermo element at full power regime. The obtained values of η seem low, but this is characteristic for all thermoelectric materials. The best thermo elements of the low-temperature materials group possess efficiency coefficient η = 2-3 % (values of 4-5 % have been reached in certain samples). These results give the reason to conclude that the solid solution $Ag_{1,84}Cd_{0,08}Te$ is appropriate for thermoelectric purposes: thermo-batteries, sensor for small gradients determination, thin film flow meters, structures for measurement of the thermo-electromotive tension coefficient of thin films, etc.

3.CONCLUSIONS

As a result of the performed investigations, the following conclusion can be made:

- the thermoelectric characteristics of Ag_2Te and the solid solution on its base ($Ag_{1,84}Cd_{0,08}Te$) have been investigated and analyzed;
- the main thermoelectric characteristics of the $Ag_{1,84}Cd_{0,08}Te$ solid solution α = 118 μV/K; σ = 2230 S/cm and λ = 2,45.10^{-2} W/(cm.K) ensure thermoelectric efficiency coefficient z = 1,27.10^{-3} K^{-1} (at 300 K), which surpasses this of the Ag_2Te;
- composition for commutation material, connecting the N- and P-branches of a single thermo element (52 wt. % In + 48 wt. % Sn) with T_m = 390 K, is developed;

-the possibility for application of the $Ag_{1,84}Cd_{0,08}Te$ solid solution as N-branch of a thermo element in combination with the solid solution $Bi_{0,5}Sb_{1,5}Te_3$ as a P-branch. The thermo element guarantees z values from $0,71.10^{-3}$ to $1,27.10^{-3}$ K^{-1} in the temperature range 250 -350 K. The maximum value of z is registered at 300 K (z = $1,27.10^{-3}$ K^{-1}).

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WATER AS AN UNIQUE LIQUID

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Abstract

The water is a liquid with a very big importance for the processes in the nature and living organism. An original method for investigation of the distribution on energy of the intermolecular bonds in water, so called water energy spectrum, has been presented. A new experimental semiautomatic setting for its measurement is performed. Applications of the method of the water energy spectrum for investigations of the solution of inorganic compounds, food supplements and medicines are given. They are possible thanks to the big variability of the water structure and respective the water energy spectrum influenced by different chemical and physical factors.

Keywords: *water, liquid, water energy spectrum.*

1. INTRODUCTION

The water is a unique liquid, thanks to the hydrogen bonds, connecting the water molecules. Every molecule is connected with 4 neighboring molecules, with such bonds and in a body make, a giant network similar to that between the neural cells of the human brain.

In our previous works [1-5] a method was created for determination the distribution on energy of the hydrogen bonds in water and water systems. The method is based on the measurement the alternation of the wetting angle of water drops, evaporating at standard conditions. For the distribution function on energy it was received:

$$(1)\quad f(E)=\frac{bf(\theta)}{[1-(1+bE)^2]^{1/2}}\ , \qquad b=14{,}33\ eV^{-1}\ ,$$

where f(Θ) is distribution function on wetting angle Θ, E is the energy of one hydrogen bond.

From numerous experiments it was found, that the distribution function on energy, called by us **water energy spectrum** depends on different chemical and physical actions on the water: dissolving organic

and inorganic compounds in it, influence of sound, vibrations and electromagnetic fields. The spectrum alters also under the action of generally speaking geophysical and cosmic processes. For determining only the influence of a given factor the so called **differential spectrum** is defined:

(2) $\Delta f(E) = f(probe) - f(control)$

For control deionized water is used.

The energy spectrum has N values:

(3) $f_i(E_i) = P_i / \Delta E,$ i = 1,2, … N

Received at probability P_i (ΔE is the energy interval in the spectrum). They can be considered as symbols recording some information. The common information H for the whole spectrum can be presented by the Shanon's formula:

(4) $H = -\sum_{i=1}^{N} P_i \, ld \, P_i$

where *ld* is logarithm to the base 2, and H is measured in *bit*.

We shall consider that the values $P_i \, ld \, P_i$, which are in the sum above, express the contribution of the single energies E_i in the common sum H.

We shall denote the value:

(5) $H_i(E_i) = -\sum_{i=1}^{Ni} P_i \, ld \, P_i \quad , \quad N_i = 1, 2, \ldots N$

as an information spectrum of the water. It expresses the information change, when the energy levels from E_1 to E_i are counted. The difference:

(6) $\Delta H_i (E_i) = H_i (probe) - H_i (control)$,

we shall call **differential information spectrum** of a given water probe. It can be considered as a new characteristic of the water to record and memorize by its spectrum the influence of different factors.

2. EXPERIMENTAL RESULTS

On the **figure 1** they are shown, the differential information spectra of solution of *KCl* and *NaCl*. Both compounds take place in the cell metabolism. We can see that the spectra are opposite.

Figure 2 represents the spectra of solution of *Vitamin C* and *aspirin* in healing dose.

Figure 3 demonstrates the differential information spectra of $CaCO_3$ solutions at different concentration. It can be established, that the big-sized concentration gives rise to a greater contribution of the deeper energy levels in the spectrum.

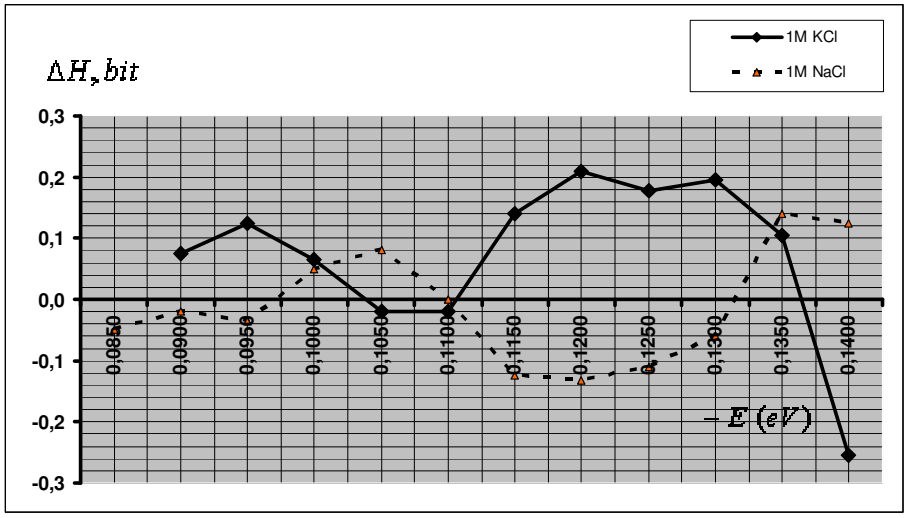

Fig.1. Differential information spectra of solution of *KCl* and *NaCl*.

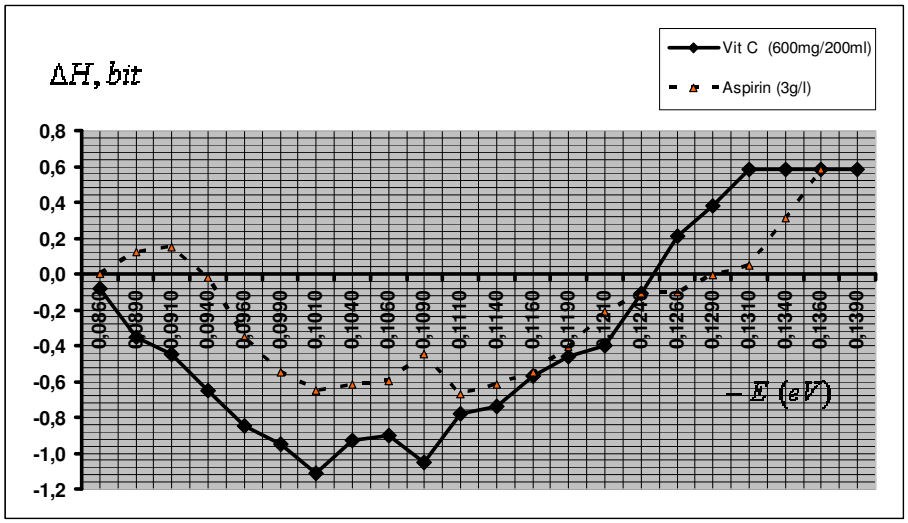

Fig.2. Differential information spectra of *Vitamin C* and *aspirin* in healing dose.

On the **figure 4** are shown the spectra of *1 mM/ℓ* solution of the antioxidants *putrescine (Pu), spermidine (Spd)* and *spermine (Sp).* The

spectra of first two, which have consequently 1 and 2 amino-groups NH_2 are close, but the spectrum of *Sp* (with 3 amino-groups) has wholly positive values.

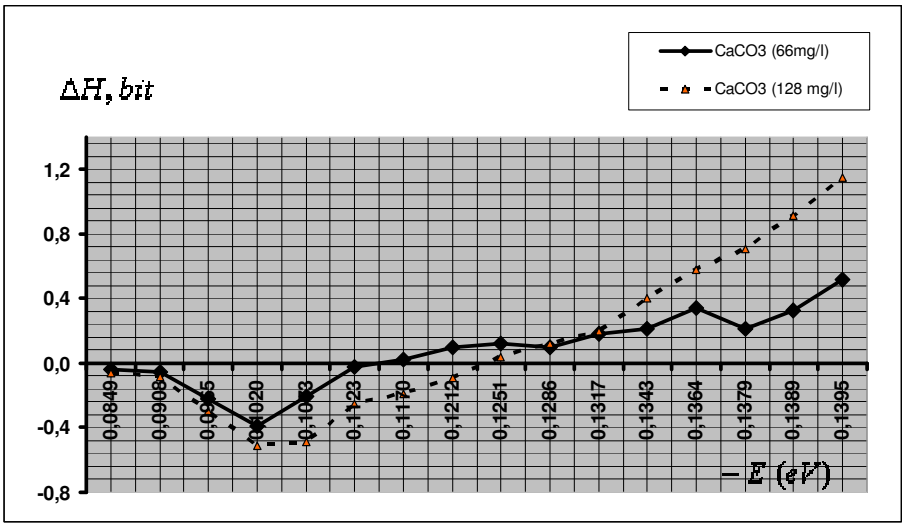

Fig.3. Differential information spectra of $CaCO_3$ solutions at different concentration.

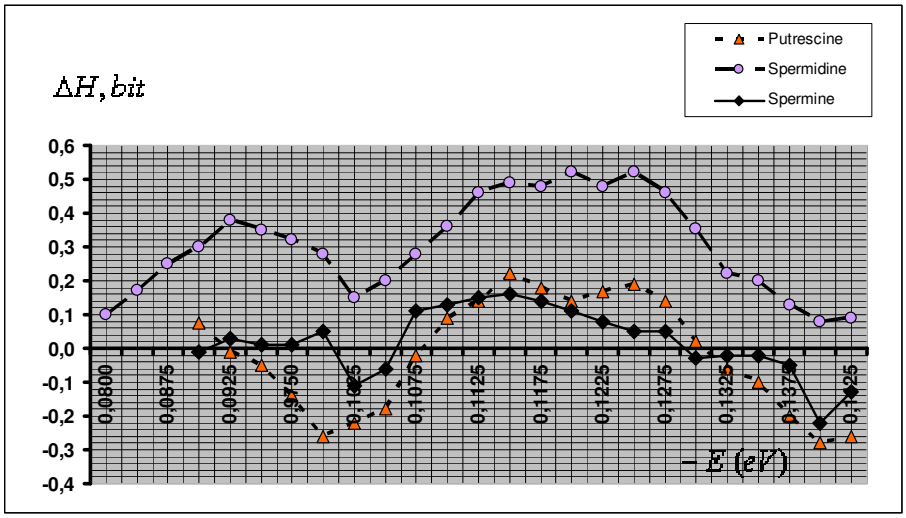

Fig.4. Spectra of *1 mM/ℓ* solution of the antioxidants *putrescine (Pu), spermidine (Spd)* and *spermine (Sp).*

For concrete applications of the method of the water energy spectrum the following parameters have been chosen:

-Alternation of the mean hydrogen bond energy

$\Delta E = E(probe) - E(control)$.

The latter are calculated from the energy distribution functions $f(probe)$ and $f(control)$.

-Alternation of the distribution function for single energies with peaks in the spectrum

$\Delta f_i = f_i\ (probe) - f_i\ (control)$ at energy E_i .

-Coefficient of linear regression $R(f_k\ ,\ \Delta f)$ between the differential and control spectra. When it is negative in sign and close to -1, it means that the given influence compensates the fluctuations in the control spectrum under the action of the environmental factors.

As an example the dates of investigation for solution from herb extracts are given in the **Table 1.** 10% solution in deionized water are investigated. As control deionized water is used.

In the first column the probes codes are shown. In the columns $4 \div 6$ they are given the alternations of the distribution functions:

Δf_1 - at energy - 0,1112 eV
Δf_2 - at energy - 0,1212 eV
Δf_3 - at energy - 0,1312 eV
Δf_4 - at energy - 0,1362 eV

The value Δf_1 corresponds to the so called peak of activity. It appears at activation of the water by magnetic field and electrolysis. The other peaks Δf_2 , Δf_3 and Δf_4 are typical for the herbs extracts. It is interesting to mark down, that all herbs extracts have negative in sigh changes of the mean bond energies, which means strengthening of the hydrogen bond and close to -1 coefficient of linear regression. The role of the peaks in the spectrum and of the linear regression coefficient can be explained after comparison with the extracts healing effect.

With a purpose to make the measurements of the energetic spectra easier a new semiautomatic setting has been performed. **Figure 5** shows the scheme of equipment.

Table 1. Summary results of the investigation

1	2	3	4	5	6	7
№ probe	$\bar{\Delta E}\,(10^{-3}, eV)$	R	$\Delta f_1(eV^{-1})$	$\Delta f_2(eV^{-1})$	$\Delta f_3(eV^{-1})$	$\Delta f_4(eV^{-1})$
1	- 10,2	- 0,90	10,5	13,8	28,5	19,1
2	- 11,2	- 0,84	24,4	8,1	25,1	18,7
3	- 9,6	- 0,86	7,7	10,4	23,7	44,1
4	- 7,6	- 0,85	12,4	9,1	14,1	22,1
5	- 12,3	- 0,80	37,3	3,7	16,9	47,5
6	- 13,9	- 0,88	31,6	15,1	21,1	42,3
7	- 9,1	- 0,72	11,2	20,9	24,4	24,5
8	- 9,4	- 0,78	22,7	19,0	14,6	33,5
9	- 14,3	- 0,90	20,9	31,9	28,1	23,6
10	- 9,2	- 0,84	17,9	23,6	18,4	17,9
11	- 9,3	- 0,84	6,1	25,5	18,2	32,7
12	- 17,1	- 0,90	28,6	38,4	38,4	38,4
13	-11,3	- 0,81	4,9	11,5	20,2	33,6
14	- 4,8	- 0,67	- 0,5	3,7	7,7	19,5
15	- 11,9	- 0,81	25,2	24,6	24,0	28,9
16	- 8,1	- 0,79	6,6	14,0	17,9	3,2
17	- 7,5	- 0,84	21,8	13,7	30,8	26,5
18	- 6,6	- 0,77	12,6	17,3	23,1	23,5
19	- 23,5	- 0,86	13,0	39,4	46,3	49,8
20	- 9,8	- 0,87	24,0	10,2	13,7	34,4

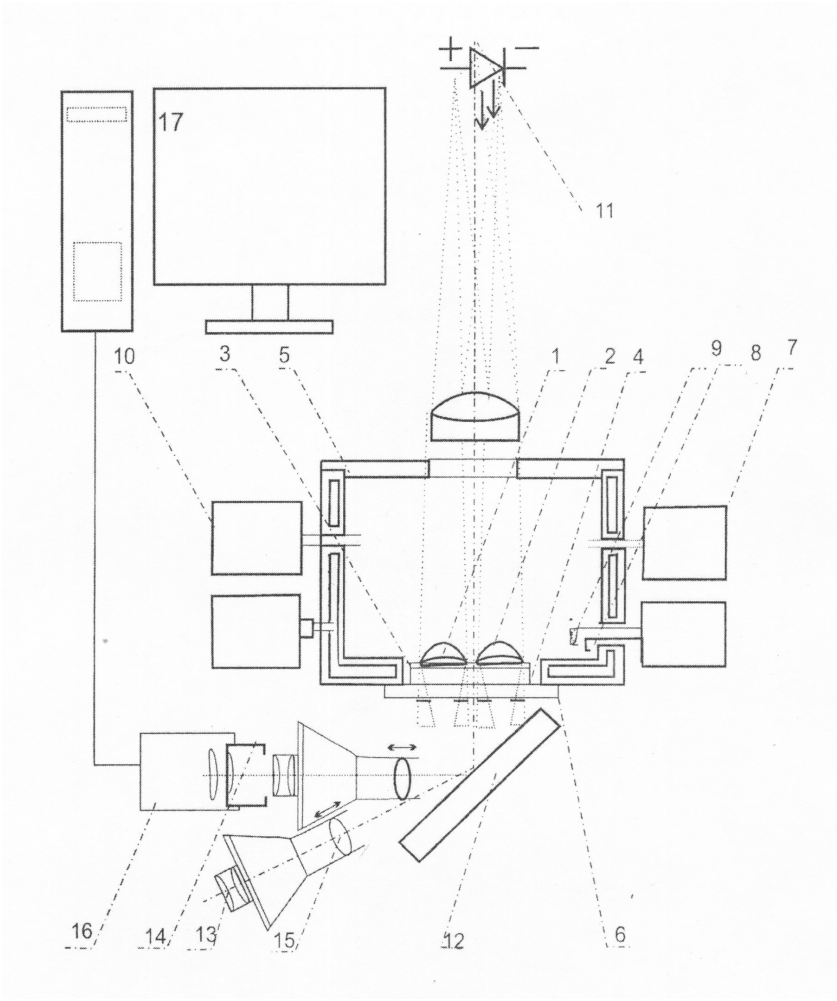

Fig.5. Scheme of equipment.

Legend:

1, 2 Water drops (probe and control).
3. Transparent folio of hydrophobic matter.
4. Glass plate.
5. Hermetic chamber.
6. Polymethylmethacrylate window.
7. Pump for air flux through the chamber.
8. Detector for temperature.
9. Detector for air flux.
11. Diode light source.
12. Flat mirror.
13. Microscope.
16. CCD camera.
17.Compute

Figure 6 shown the facsimile of a computer program for recording the information from the water drops evaporation.

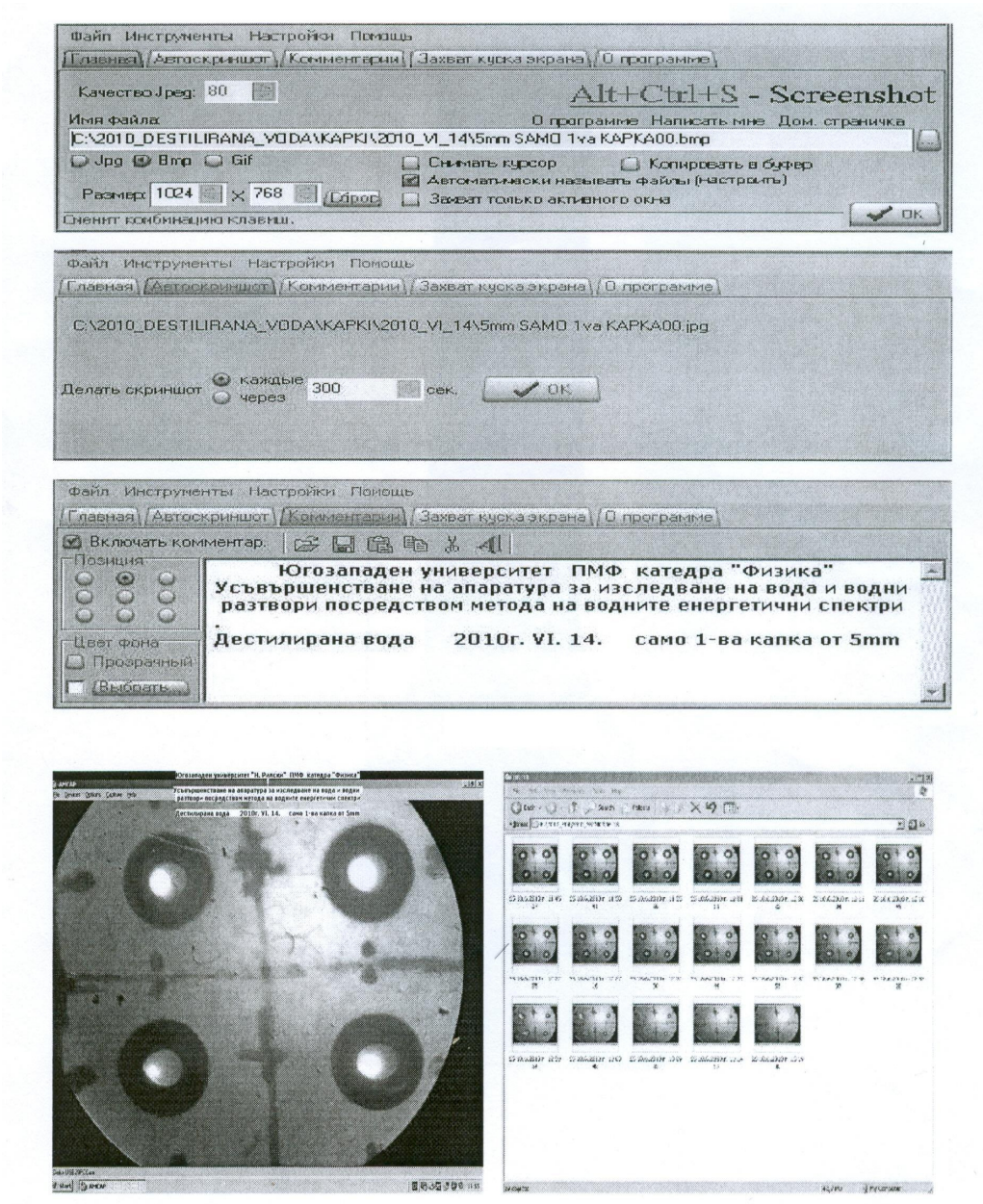

Fig.6 Facsimile of a computer program

3. CONCLUSIONS AND DISCUSSIONS

The new improved setting has been used for investigation of different methods for water activation by magnetic fields and electrolysis, of natural water and also of psychophysiological state of the brain in norm and pathology. The results received show that the water is really a unique liquid, which can record information for super weak physical and chemical influences.

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INVESTIGATIONS OF WINES BY THE METHOD OF THE WATER ENERGY SPECTRUM

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Abstract

The wines are composite water-spirituous mixtures with different organic and inorganic components. At evaporation of the wine drops the H-bonds between the water and water-ethanol molecules are destroyed and there fore it is possible to apply the method of the water energy spectrum. Different types of wines have been investigated and a new information about their quality and their conservation has been received.

Keywords: *wines, water energy spectrum.*

1. INTRODUCTION

Wine is one of the most ancient drinks which is entirely of biological origin. After the first mechanical treatment of the grape the gaind grape sap is liquid, which is mainly the inner cell mass of the berry. The main component of the juice is water in which are dissolved many organic and inorganic compounds- sugars, organic and inorganic acids, phenols, tannins and others. In the process of fermentation many complicated conjugation biochemical reactions take place, in which part of the sugars are transformed in to alcohols (mainly ethanol), CO_2 is released and the proportions of the others are changed. The main product has specific color, taste and aroma, which amounts can be measured by methods used in the organic chemistry, mainly chromatographic, spectral and also analytical. Nevertheless all self respected wine making companies use the subjective valuation of well trained taster specialists.

For balance-sheet we will accept, that the wine is a sophisticated water-alcohol mixture of soluble and eventually insoluble components. It's well known, that in water all molecules are connected with four neighboring molecules with hydrogen bonds [1]. In the spirit (ethanol C_2H_5OH) every single molecule is connected by hydrogen bonds with two other molecules. In water-spirit solutions, where water and spirit are mixed in arbitrary

proportions, according to Angelo’s model, water and spirit molecules form longer mixed linear chains of both components. This gives us ground to accept, that by the process of evaporation of the water-spirits mixture both the hydrogen bonds between water and water-spirit molecules get broken. At large the mixture goes poor on the spirit component.

Experiments show that drops of wine vaporize analogical to water drops, if dropped on a hydrophobic pad. So came out the idea for investigating wine using the water energy spectra method, which was developed in our former works [2÷6].This method is based on measuring of the wetting angle of water drops vaporizing in standard conditions in hermetic working chamber. This proved that by evaporation the wetting angle decreases stepwise to zero as for water as well for wine. From the measurements is declared the distribution functions on energy of the hydrogen bonds f(E) for which the following expression is found:

(1) $f(E) = \frac{b\ f(\theta)}{\sqrt{1-(1+bE)^2}}$, b = 14,33 eV^{-1} ,

where $F(\theta)$ is distribution functions on energy on wetting angle θ.

If we have a sample of particular water system, except it’s distribution function f(probe) we also measure the distribution function of a controlled water f(control). The measurements of the two functions, **also called energy spectra of probe and control** are taken simultaneously. A calculation is made of:

- Their difference, also called differential energy spectrum
- **Δf(E) = f(probe) – f(control)**.
- The average energy of the hydrogen bond between two molecules - **E(probe)** и **E(control).**
- Their difference - **ΔE = E(probe) – E(control)**.
- The coefficient of linear regression - **R(f_k, Δf).**

The last one has significant value, close to -1, when in the given probe the fluctuations in the controlled spectrum under the environmental factors are compensated.

In the standard spectrum of the control (deionized water), when concentrated from many measurements, some pikes of energy are presented by: -0,0937eV, -0,0987eV, -0.1037eV, -0.1112eV, -0,1212eV, -0,1312eV. The pike of energy by -0,1112eV, the so called **pike of activity** is increasing, if the water has been influenced by magnetic field or electrolysis trough membrane filter and also by homeopathic treatment. In the spectrum of wine as shown from the experiments, the first 4 pikes are missing, but the pikes by bigger (an absolute value) energies increase. And a new large pike appears by energy of -0,1362eV, which probably

corresponds to water which has hydrated the substances dissolved in the water-spirit solution.

Experiments with different types of wine where made, using a semi-automatic setting. Simultaneously where examined the summary energy spectra of 2 drops of wine and 2 drops of water-spirit solution (control) with concentration of ethanol equal to that in the wine.

2. EXPERIMENTAL RESULTS

Many experiments were conducted using several types of wine– home-made (”Bouquet”), red ”Mavrud” , white Muscat ”Menada” and red ”Terra Tangra”. The first two where examined with the bottle closed or opened for two weeks. Every measurement is accompanied with Passport, which contains the parameters of the meteorological conditions and the gathered spectra- energy spectrum of the control and differential energy spectrum of the investigated wine.

Figure 1 shows the obtained spectrum of the investigated home-made wine “Bouquet”, which has been preserved in closed container (alcohol content 12%). For control is used a 12% solution of ethyl alcohol in distilled water.

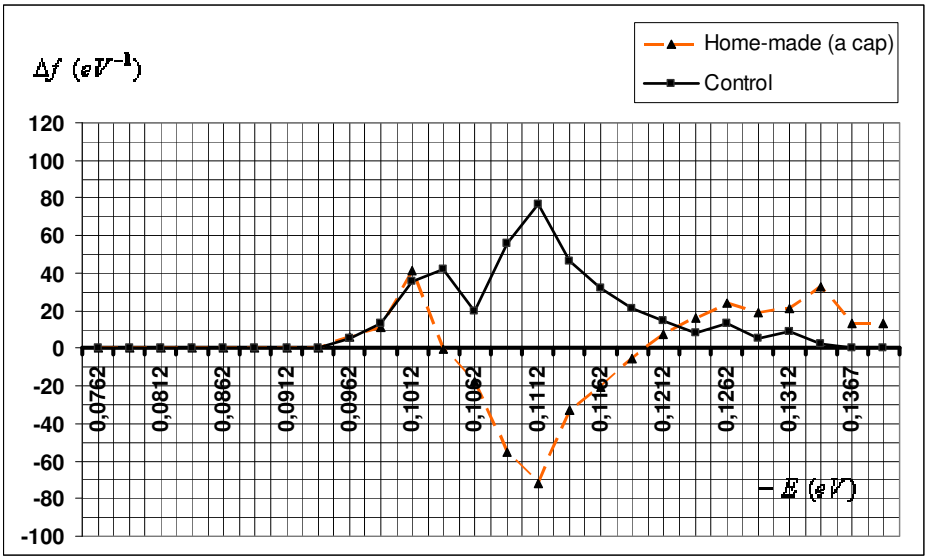

Fig.1. ***Experiment № 1.*** Home-made wine ”Bouquet” Start of the experiment.

The wine bottle is sealed with a cap.

Figure 2 shows the spectrum of the same wine remained open for 3 hours. For control is used a 12% solution of ethyl alcohol in distilled water.

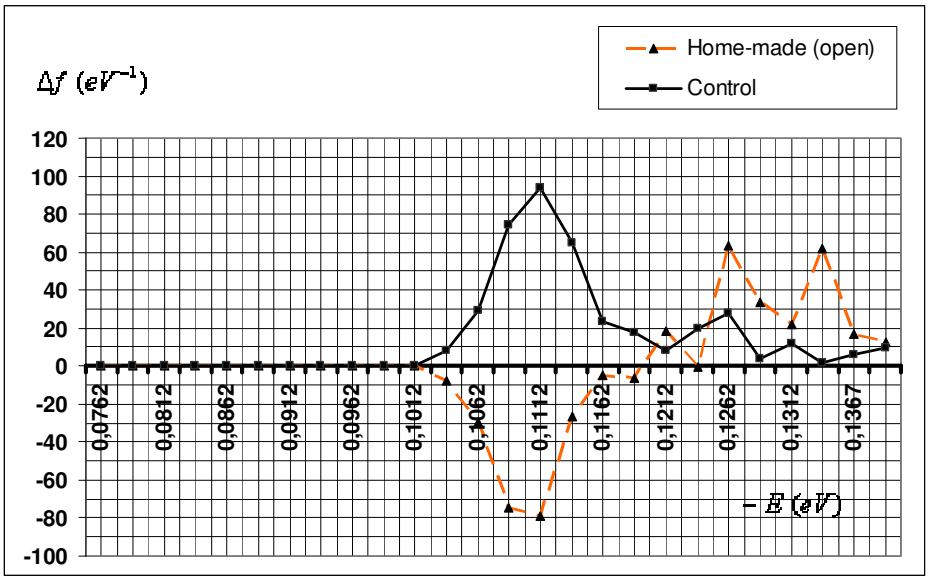

Fig. 2. ***Experiment №*** **2.** Home-made wine ”Bouquet” Start of the experiment. The wine has been kept open for 3 hours.

Figure 3 and **figure 4** shows the analogical spectra of wine “Mavroud”-Perushtitza-2006 with 12% alcohol content. For control is used a 12% solution of ethyl alcohol in distilled water.

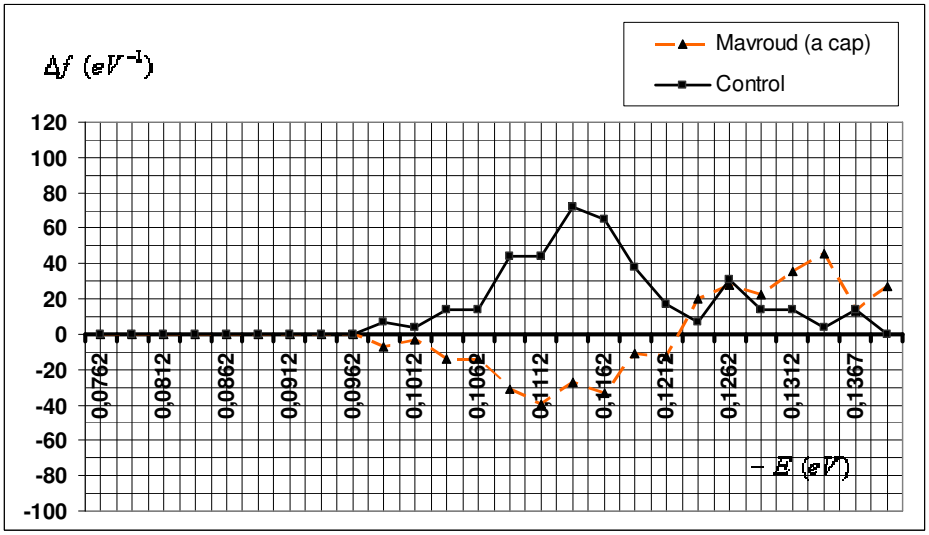

Fig. 3. ***Experiment № 15***. Wine ”Mavroud”-Perushtitza-2006. Start of the experiment. The wine bottle is sealed with a cap.

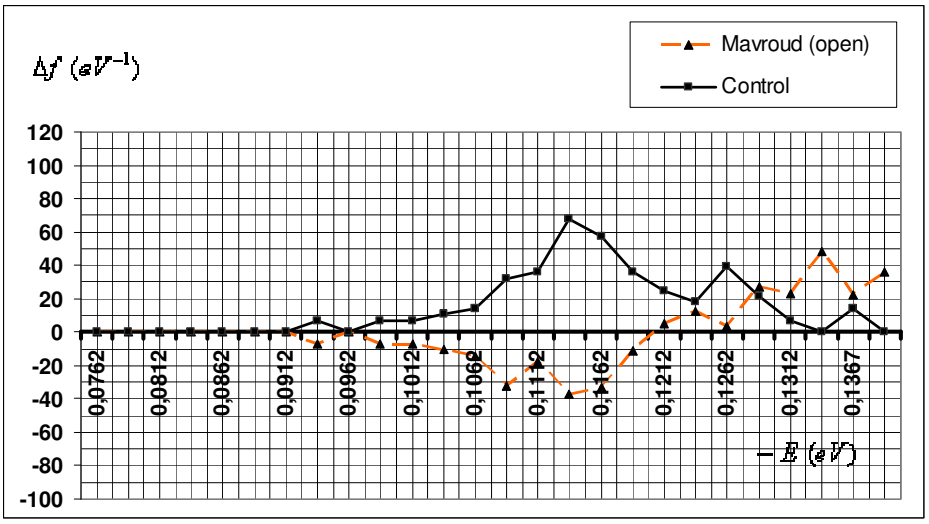

Fig. 4. ***Experiment № 16***. Wine "Mavroud"-Perushtitza-2006.
Start of the experiment. The wine has been kept open for 3 hours.

Figure 5 shows the obtained spectra of white wine "Muscat Menada" and red wine "Terra Tangra" (alcohol content 12%). For control is used a 12% solution of ethyl alcohol in distilled water (thick line).

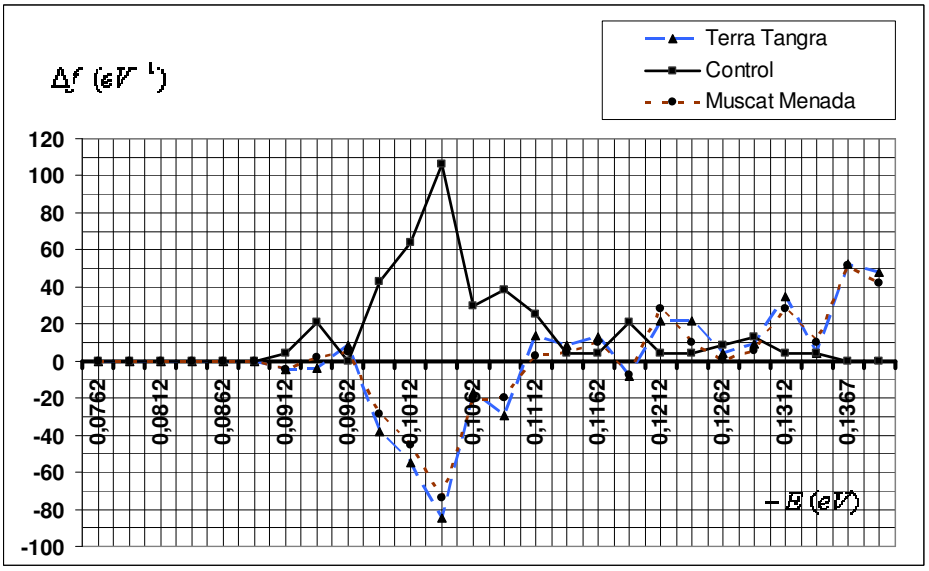

Fig. 5. Shows the obtained spectra of white wine "Muscat Menada" and red wine "Terra Tangra" (alcohol content 12%).

In **Table 1** are shown the summary results of the investigation Δ f=f’(probe)- f’$_K$ (control) at energy E= -0.1112 eV .

Table 1. Summary results of the investigation

№	Wine	$\Delta E=E-E_k$ [10^{-3} eV]	$\Delta f' = f'-f'_k$ [eV^{-1}]	$R(f_k; \Delta f)$	P
1	**“Muscat Menada” ,w.**	-7,6	2,4	-0,881	0,010
2	**"Terra Tangra" ,r.**	-15,0	13,6	-0,891	0,010
3	**Home-made “Bouquet",r. sealed**	-10,5	-58,7	-0,729	0,006
4	**"Mavroud"- Perushtitza ,r. sealed**	-10,2	-22,8	-0,422	0,140
5	**Home-made "Bouquet",r. opened**	-9,0	-37,5	-0,729	0,006
6	**"Mavroud"- Perushtitza ,r. opened**	-8,7	-37,5	-0,729	0,006
7	**Standard Deviation**	±1,0	±4,0		

3. CONCLUSIONS AND DISCUSSIONS

1.All the investigated wines show, in comparison with the spirit-water solution, a significant effect of increment of the hydrogen bonds energy($\Delta E<0$).

2.In most cases the investigated wines show a coefficient of linear regression which has a significant value, close to -1.

3.The investigated wines show distinctions beyond the margin of error for the parameters chosen for their characterization. This shows that the method of energy spectra can successfully be used for objective

characterization of the quality of wines and their alterations by different types of preservation.

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Spin-orbit interaction in aqueous solutions of $MCl_3.6H_2O$ (M = Fe^{3+}, Cr^{3+})

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***Abstract**: The aqueous solutions of $MCl_3.6H_2O$ (M = Fe^{3+}, Cr^{3+}) are investigated in this work. In this connection, the absorption spectra of these solutions are measured in the spectral region 1.6 – 2.5 eV. The exchange integrals for $Fe(H_2O)^{3+}_6$ and $Cr(H_2O)^{3+}_6$ complexes are calculated.*

***Keywords:** 3d cations, spin-orbit interaction, absorption spectra*

1. INTRODUCTION

The aqueous solutions of 3d ions salts manifest optical activity and interesting properties in magnetic field. This fact helped us when we decided to investigate these ionic liquids. In this work, the most important accent is on the existence and influence of aqueous complexes of Fe^{3+} and Cr^{3+} cations. Our analyses give answer of questions which are connected with the peculiarities of electron transitions in the complexes and with the stability in these complexes. Many authors have studied the absorption of the compounds $MCl_n.6H_2O$ (M = 3d transition metal ions, n = 2, 3), but they not give information about the exact number of d electron transitions there. This is the main aim in our work.

2. EXPERIMENTAL AND RESULTS

The experimental set up for measurement of absorption coefficient in visible spectral region has following parts: halogen lamp with stabilized rectifier 3H-7, monochromator SPM-2, system of quartz lenses, polarizer, sample holder and detector Hamamatsu S2281-01.

The concentration of the aqueous solutions of $MCl_3.6H_2O$ (M = Fe^{3+}, Cr^{3+}) is 1%. The thickness of the cuvette is d = 0.995 cm. The absorption spectra of iron and chromium undistorted octahedral complexes are measured. These complexes are high spin complexes in weak "crystal" field. The impurity absorption structures which are manifested in the spectral region 1.6 – 2.5 eV (figs. 1, 2) are compared. The calculation of first derivative of absorption coefficient determines the number of d electron transitions and the calculation of second derivative of absorption coefficient

defines exact energy position of d electron transitions in $Fe(H_2O)^{3+}_6$ and $Cr(H_2O)^{3+}_6$ complexes (figs. 1, 2). The energetic diagrams give us the real picture about spin-orbit interaction in our investigated complexes (figs. 3, 4).

3. DISCUSSION

The familiar colors of the transition metal ions in solutions are due to absorption bands which have their origins in electronic transitions within the 3d shell. The electric field of the nearest neigbour anions splits the energy levels of the unpaired d electrons and electronic transitions between these split energy levels give rise to the observed "crystal field" spectra [1].

The measurement of absorption spectrum of 3d metal ions solutions helps us to understand how many unpaired d electrons are in the different complex structures. In the case of $Fe(H_2O)^{3+}_6$, it is easy to determine the number of these unpaired d electrons. We can see that three absorption maxima manifest in the spectral region 1.6 – 2.5 eV. Therefore, we have three unpaired d electrons in the iron octahedral complex. The situation with the complex $Cr(H_2O)^{3+}_6$ is the other. Here, we observe more complicated absorption structure in the spectral region 1.6 – 2.5 eV (fig. 2). The Cr^{3+} maximum consists of some overlap structures. The calculation of the first derivative of absorption coefficient by the photon energy gives information about the number of d electron transitions in the complex $Cr(H_2O)^{3+}_6$. The exact position of 3d electronic states can be precisely determined only by calculation of the second derivative of absorption coefficient. In the end, the unpaired d electrons are three again in the chromium octahedral complex (fig. 2).

If the electron transitions are allowed by multiplicity then we can observe wide bands in the absorption spectrum [2]. The $t_{2g} \rightarrow e_g$ transitions which are allowed by multiplicity conduct to the excited state. In this state, the distance in equilibrium between the 3d ionic nucleus and the nucleus of ligand is bigger than this distance in the basic state. If the already mentioned distance hasn't change (principle of Frank-Kondon) the electronic excited molecules are in excited vibrated states. When the molecules are excited the bond lengths correspond to these in the basic state. The excited state interacts with the molecules of solvent that aren't located in the first coordination sphere. This interaction changes because the closest molecules of solvent are located at different distances from the 3d metal ion. The solvent can't reorganize during the transition. Therefore, the excited vibrated state of different molecules interacts with the molecules of solvent which are located at different distances from this state. The change of energy of solvation influences on the energy of excited vibrated state. The result is that the wide bands manifest in the absorption spectrum. The some transitions are spin forbidden and their reconstruction takes

place at a given level. For example, the transitions in Cr^{3+} complexes are carried out by the basic state (they are three unpaired electrons on the t_{2g} orbit) to the excited state (they are two paired and one unpaired electrons on the t_{2g} orbit).

The information from the literature [3] is that the bands around 15 000 cm^{-1} for aqueous solutions of Cr^{3+} are connected with the spin forbidden transitions $^4A_2 \rightarrow {}^2E$ and $^4A_2 \rightarrow {}^2T_1$. Hartmann and Schmidtke [4] explain the manifestation of doublets in Cr compounds with the splitting of state $^2T_1$ in the weak field. The two electron transitions $^6A_1 \rightarrow {}^4T_2$ are possible because of the splitting of state $^4T_2$. The spin-orbit interaction is the reason for the splitting of this state.

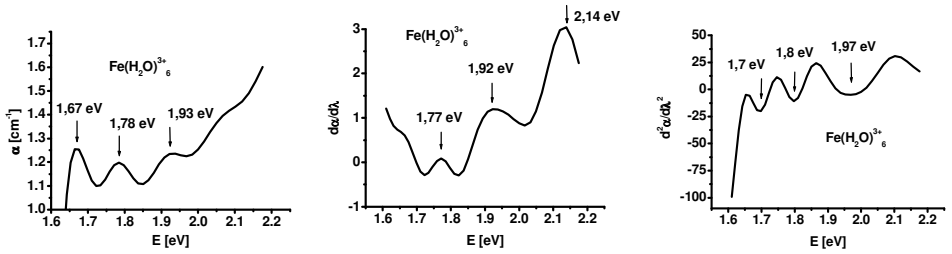

Fig. 1: Absorption spectrum of the complex $Fe(H_2O)^{3+}_6$ with calculated first and second derivative of absorption coefficient in the spectral region 1.6 – 2.2 eV.

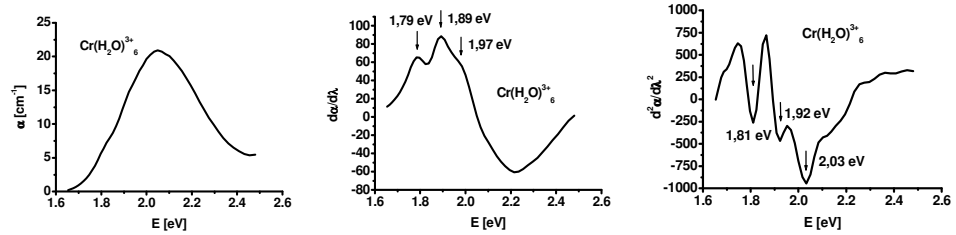

Fig. 2: Absorption spectrum of the complex $Cr(H_2O)^{3+}_6$ with calculated first and second derivative of absorption coefficient in the spectral region 1.6 – 2.5 eV.

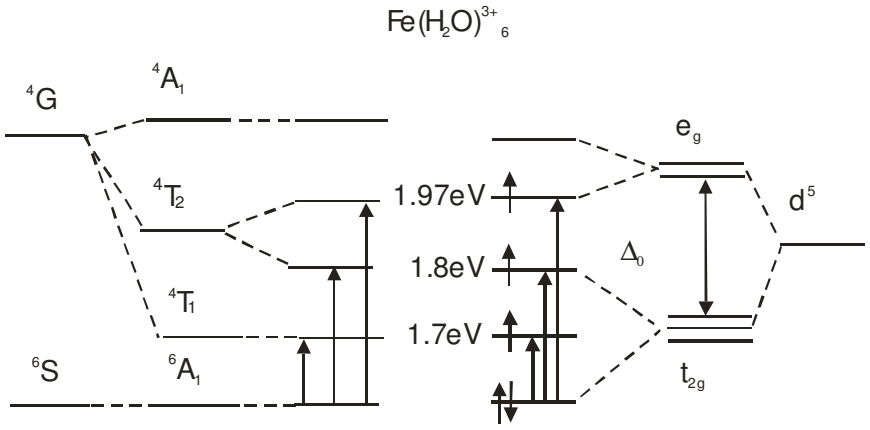

Fig. 3: Energetic diagram of the iron octahedral complex.

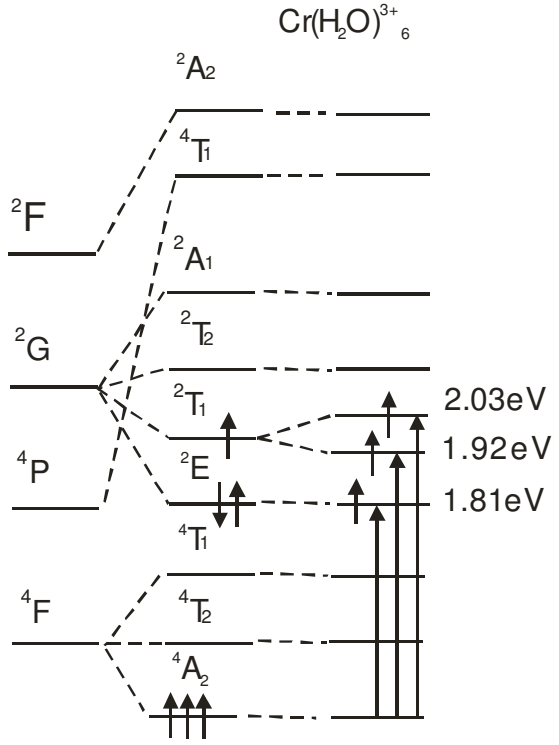

Fig. 4: Energetic diagram of the chromium octahedral complex.

The ionic radius of Cr^{3+} is 0.615 and this radius for Fe^{3+} cation is 0.58. The energy position of Fe and Cr absorption structures are compared. In

our opinion, the shifting of Cr absorption structure to the bigger energies is available because of the bigger ionic radius of this 3d cation. We assume that the bigger value of “crystal” field parameter Dq = 1637 cm^{-1} for $Cr(H_2O)^{3+}_6$ dues to the bigger Cr ionic radius. In comparison the value of this parameter Dq is 1590 cm^{-1} for the complex $Fe(H_2O)^{3+}_6$. In the opposite, the Racah parameter B = 93 cm^{-1} for iron octahedral complex is bigger than the same parameter B = 75 cm^{-1} for chromium octahedral complex. We decided also to apply the nephelauxetic ratio $\beta = B/B_0$ for $Fe(H_2O)^{3+}_6$ and $Cr(H_2O)^{3+}_6$ complexes. In this ratio, the parameter B is connected with the chemically bonded transition element and the parameter B_0 presents the field – free cation. The following inequality $\beta_{Fe} > \beta_{Cr}$ is satisfied in our case. β_{Fe} is equal to 0.15 and $\beta_{Cr} = 0.07$. The exchange integral $K(x^2 – y^2, xy)$ is calculated for the iron octahedral complex. Its value (13 377 cm^{-1}) corresponds to the electron transition at 1.7 eV (fig. 3). The value of exchange integrals $K(z^2, xz) = K(z^2, yz) = 15\,456$ cm^{-1} corresponds to the electron transition at 1.92 eV in the energetic diagram of chromium octahedral complex (fig. 4).

After all these analyses, we can say that we know what happens in the investigated Cr and Fe octahedral complexes. Next step of our experiments is connected with the investigation of optical activity and Faraday rotation of aqueous solutions of $MCl_3.6H_2O$ ($M = Fe^{3+}, Cr^{3+}$).

4. CONCLUSIONS

The spin-orbit interaction is the reason of splitting of the state $^2E(^2G)$ for the complex $Cr(H_2O)^{3+}_6$. The same reason is valid in the case of the complex $Fe(H_2O)^{3+}_6$, but here we observe the splitting of state $^4T_2$ (^4G).

If we compare the d electron transitions in iron and chromium octahedral complexes then we can see that they are three unpaired electrons in both cases.

The value of the exchange integral $K(x^2 – y^2, xy) = 13\,377$ cm^{-1} shows us that the e_g state $x^2 – y^2$ mixes with the t_{2g} state xy in the iron octahedral complex. The value of exchange integrals $K(z^2, xz) = K(z^2, yz) = 15\,456$ cm^{-1} shows that the e_g state z^2 mixes with the t_{2g} states xz and yz in the chromium octahedral complex.

ACNOWLEDGMENTS

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INTERRACTION BETWEEN TOBACCO SMOKE AND WATER

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Abstract

The particles of the tobacco smoke entering in the lung cells interact with the water round the cell membrane changing the water structure. This given rise to an exchange of the oxygen transport in the organism. An model of this process is supposed via aeration of the tobacco smoke through the water following by the investigation of the water energy spectrum. As a control the spectrum of a water aerated by the pure air is used. Both spectra have been measured simultaneously. Investigation have been performed with different tobacco ware and the results are analyzed.

Keywords: *wines, water, water energy spectrum.*

1. INTRODUCTION

Tobacco smoke is an air dispersion system with a spherical form of the aerosol particles, which are fluids (essential oils, tars) and solid components – products of the tobacco burning. It’s well known that the tobacco smoke has a noxious effect on the human health.

By smoking the tobacco smoke particles permeate deep in to the alveoli of the lungs. They interact with the water, which hydrates the cell membranes and alter it’s structure.

The main idea of the present work emerged few years ago. In order to study how the structure of the water alters when interacting with the particles of the tobacco smoke, samples of the water were aerated with tobacco smoke and their energy spectra was examined as for control was used pure water aerated with fresh air. The experiments show that the water energy spectra was also altered during the aeration process, in which the air was partially dissolved in the water.

2. EXPERIMENTAL RESULTS

Figure 1 shows the scheme of the setting used for airing water with tobacco smoke, in which 1 is the cigarette, 3-peristaltic pump, 4-aerated water (distilled water 70g).

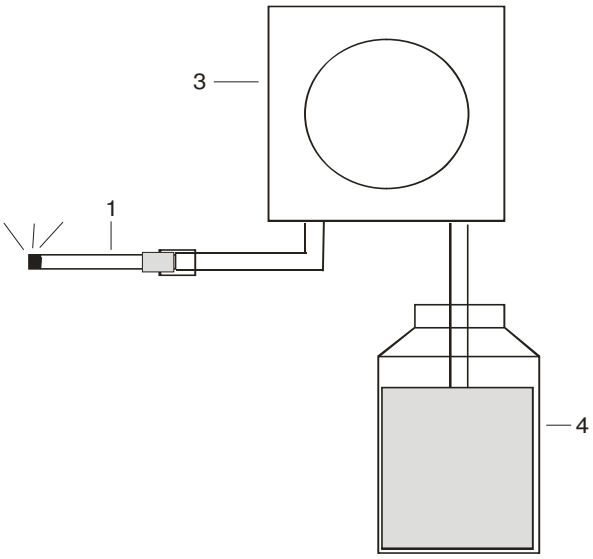

Fig.1. Scheme of the setting used for airing water with tobacco smoke.

For examination of the water spectra of the water was used a method, developed in works [1÷5]. It is based on the measuring of the wetting angle of water drops within their evaporation with standard conditions – temperature, atmospheric pressure, air humidity and its flux in the working chamber. Energy spectra of the water represent the distribution functions on energy of the hydrogen bonds between the water molecules. For the distribution function it was found the expression:

$$F(E) = \frac{bF(\theta)}{\sqrt{1-(1+bE)^2}} \quad , \text{ b = 14,33 eV}^{-1}$$

where $F(\theta)$ is the distribution function on wetting angle θ.

Since on the water, except for the studied factor (in our case- tobacco smoke) act many other processes with geophysical and cosmic origin, in order to eliminate their influence the differential spectra was used

$$\Delta F(E) = F(probe) - F(control) \quad .$$

Figure 2 shows the differential spectra of water, aerated with air (dashed line) and control (thick line) – water at rest. From the shown result we can determine, that the process of aeration leads to increasing the value of spectra of distribution of the aerated water by E=-0,1112 eV. This energy corresponds to the pike of activity in the standard spectra of water, which in former studies was found to respond to the activation of the latter by magnetic field, electrolysis of water trough membrane filter and turbulent flow of it , also by the solution in water of herbs which have immune stimulant effect.

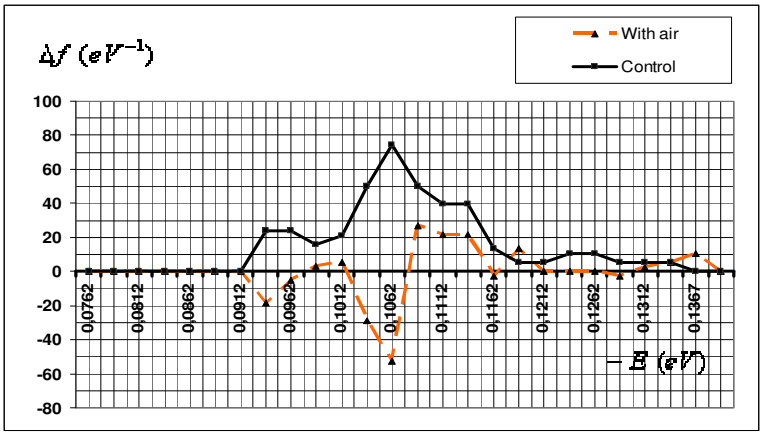

Fig.2. Differential spectra of water, aerated with air (dashed line) and control (thick line) – water at rest.

Figure 3 shows the differential spectra of water, aerated with tobacco smoke (dashed line), and the control spectra (thick line) of water aerated with air. Again we are convinced of the effect of bubbling – there is an increase in the pike of activity. Tobacco smoke, as we can see from this figure, decreases the latter.

26 examines were made, of which 13 by aeration of water with air (control), 7 by aeration of water with smoke from King (white) cigarettes and 6 by aeration of water with smoke from King (red) cigarettes. All the data collected from the experiments are shown in **Table 1** and **Table 2.**

From the energy spectra of the probe and the control are calculated the average energy of the hydrogen bond (E_1 and E_k), the difference between them ($\Delta E=E_1-E_k$) the values of the distribution function on energy (F_1’ and F_k’) and the difference between them ($\Delta F'=F_1'-F_k'$), at energy E= -0.1112 eV.

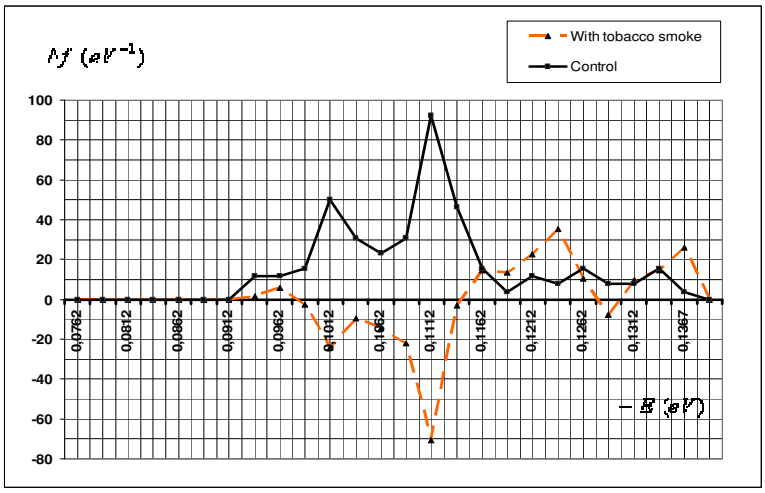

Fig.3. Differential spectra of water, aerated with tobacco smoke (dashed line), and the control spectra (thick line) of water aerated with air.

From the first series (cigarettes KING-white, Nicotine: 0,7 mg., Tar: 9 mg., Carbon monoxide: 10 mg.**)** averaged result from all measurements of the average hydrogen bond energy by aeration with air is:

$$\bar{\Delta E} = (-0{,}00039 \pm 0{,}00075)\ eV \quad .$$

This shows, that there is a tendency to increasing the bond energy (negative value), but the result is not statistically reliable. Respectively for the alteration of the pike of activity it comes out

$$\bar{\Delta F'} = (2{,}2 \pm 6{,}2)\ eV^{-1} \quad .$$

This alteration, which has a positive value in this case shows a tendency of increasing the activity of water by aeration with air but the result is not statistically reliable .

The second independent series (cigarettes KING-red, Nicotine: 0,8 mg., Tar: 10 mg., Carbon monoxide: 10 mg.**)** from the measurements of the water aerated with fresh air analogical results came out:

$$\bar{\Delta E} = (-0{,}0044 \pm 0{,}0006)\ eV$$

and $\bar{\Delta F'} = (15{,}2 \pm 6{,}9)\ eV^{-1}$.

Both results are statistically reliable.

By aeration of water with tobacco smoke, as for control probe the water aerated with air was, the following results came out:

Table 1. Results gathered from water aerated with air (control) and water aerated with smoke from King (white) cigarettes

	Date	Type of influence	Day after (treat-ment)	E_1 (eV)	$E_к$ (eV)	$\Delta E = E_1 - E_k$ (eV)	$F_1`$ (eV^{-1})	$F_k`$ (eV^{-1})	$\Delta F = F_1` - F_k`$ (eV^{-1})
1	22.10 2010	With air	1	-0,1114	-0,1082	-0,0032	61,3	39,7	21,6
2	22.10 2010	With tobacco smoke	1	-0,1170	-0,1110	-0,0060	21.5	92,3	-70,8
3	25.10 2010	With air	4	-0,1124	-0,1066	-0,0058	36,7	20,6	16,1
4	25.10 2010	With tobacco smoke	4	-0,1124	-0,1176	+0,0051	93,2	42,9	50,3
5	28.10 2010	With air	7	-0,1061	-0,1066	+0,0005	33,8	20,3	13,5
6	28.10 2010	With tobacco smoke	7	-0,1137	-0,1062	-0,0075	55	36,4	18,6
7	01.11 2010	With air	11	-0,1090	-0,1078	-0,0012	21,2	24,6	-3,4
8	01.11 2010	With tobacco smoke	11	-0,1154	-0,1061	-0,0093	13,1	28	-14,9
9	04.11 2010	With air	14	-0,1081	-0,1089	+0,0008	26,2	31,4	-5,2
10	04.11 2010	With tobacco smoke	14	-0,1125	-0,1071	-0,0054	64,6	37,7	26,9
11	09.11 2010	With air	19	-0,1084	-0,1173	+0,0089	28	58,5	-30,5
12	09.11 2010	With tobacco smoke	19	-0,1174	-0,1069	-0,0105	17,8	32,3	-14,5
13	18.11 2010	With air	28	-0,1103	-0,1076	-0,0027	23,3	19,5	3,8
14	18.11 2010	With tobacco smoke	28	-0,1134	-0,1070	-0,0064	14,3	30	-15,7
15		***SD***				*±0,0010*			*±4*

Table 2. Results gathered from water aerated with air (control) and water aerated with smoke from King (red) cigarettes

	Date	Type of influence	Day after treatment	E_1 (eV)	$E_к$ (eV)	$\Delta E = E_1 - E_k$ (eV)	F_1' $(eV)^{-1}$	$F_k`$ $(eV)^{-1}$	$\Delta F = F_1' - F_k`$ $(eV)^{-1}$
15	19.11 2010	With air	1	-0,1087	-0,1053	-0,0034	53	39,1	13,9
16	19.11 2010	With tobacco smoke	1	-0,1139	-0,1080	-0,0059	36,8	32	4,8
17	22.11 2010	With air	4	-0,1105	-0,1080	-0,0025	33,3	28,3	-15,3
18	22.11 2010	With tobacco smoke	4	-0,1177	-0,1069	-0,0108	13,2	48,6	-35,4
19	24.11 2010	With air	6	-0,1093	-0,1064	-0,0029	45,5	27,3	18,2
20	24.11 2010	With tobacco smoke	6	-0,1166	-0,1064	-0,0102	30,4	40,4	-10
21	30.11 2010	With air	12	-0,1104	-0,1099	-0,0005	27,8	40	-12,2
22	30.11 2010	With tobacco smoke	12	-0,1133	-0,1074	-0,0059	65,4	22,6	42,8
23	02.12 2010	With air	14	-0,1062	-0,0991	-0,0071	27,1	12,6	14,5
24	02.12 2010	With tobacco smoke	14	-0,1127	0,1070	-0,0057	55,2	43,3	11,8
25	06.12 2010	With air	19	-0,1090	-0,1042	-0,0048	43,5	26,4	17,1
26	06.12 2010	With tobacco smoke	19	-0,1180	-0,1077	-0,0103	32	39,1	-7,1
27		***SD***				*±0,0010*			*±4*

From the first series

$$\bar{\Delta E} = (-0{,}0057 \pm 0{,}0018)\ eV \quad , \quad \bar{\Delta F'} = (-2{,}9 \pm 13{,}8)\ eV^{-1}$$

From the second series

$$\bar{\Delta E} = (-0{,}0070 \pm 0{,}0017)\ eV \quad , \quad \bar{\Delta F'} = (1{,}2 \pm 9{,}7)\ eV^{-1} \quad .$$

From these results it’s clear that the pure effect of the influence of tobacco smoke on waters , are brought to reliable increase of the bonds between the water molecules, but the alteration of the pike of activity is within the mistake’s boundaries and is not reliable. In former researches (from 2005) of smoke from 12 cigarette brands, 2 brands of cigars, and also the influence of smoke from narghileh and 2 brands of cigarette holder the same results were gathered. For the alter value of the bond energy from all experiments the following was found

$$\bar{\Delta E} = (-0{,}0021 \pm 0{,}0011)\ eV \quad .$$

And for the alter of the pike of activity:

$$\bar{\Delta F'} = (0{,}64 \pm 4)\ eV^{-1} \quad .$$

3. CONCLUSIONS AND DISCUSSIONS

From all the given results the following conclusion can be made, that the tobacco smoke by influencing to the structure of the water does not statistically reliable alter the pike of activity, but reliably increases the energy of the hydrogen bonds between the water molecules. Probably around the aerosol particles a layer of water is formed with bond stronger than the bonds inside the volume. If we go back to the models of hydrated water around the cell membranes of the lung cells that we examined in the beginning than probably the increasing of the energy of the bonds between it’s water molecules hinders the receipt of oxygen in the human organism.

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The daily hour forecasting of the electrical energy production from renewable energy sources – a required condition for the operation of the new energy market model

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***Abstract**: The report presented the new energy market model in Bulgaria and the main attention is directed to a daily hour forecasting of the electrical energy production from renewable energy sources.*

The need of development of a methodology and the development of the most precise methods for predicting is reviewed and some of the used methods at the moment are presented.

An analysis of the problems related to the daily hour forecasting is done using data from the producers of electrical energy from renewable energy sources in the territory of western Bulgaria.

***Keywords:** Renewable energy sources, daily hour forecasting, electrical energy*.

New and current direction in the energy market is the forecasting of the electrical energy production from renewable energy sources (RES). The increase in the production of electrical energy from RES in Bulgaria imposes mandatory daily hourly forecasting, to work the energy system of Bulgaria efficient and flawless.

In developed new rules for trade in electrical energy, published in State Gazette issue 64 of 17.08.2010 [1], which will take effect from 01.07.2011, is introducing a new energy market model based on exchange hourly schedules of production and consumption of electrical energy between the coordinators of balancing groups (CBG) and the energy system operator (ESO). The main difference in the new and current rules is that all actors, whether buying or selling a regulated or freely negotiated prices, negotiate hourly electrical energy and prepare weekly and monthly final settlement. ESO prepares settlement to CBG, and CBG allocate calculating by ESO imbalances of its members depending on the individual participation of each member in the general imbalance. In the new rules, each participant draw hourly forecast profile for the purchase or sale of electrical energy per day

of physical delivery D, one day in advance D-1, this schedule shall be sent by members of balancing groups (BG) to their coordinator, and aggregate profile of all participants in the BG – by the relevant CBG to ESO. Participants who will buy or sell electrical energy at regulated prices formed the so-called coordinators of special balancing group (CSBG). In such special balancing groups are the customers of the public provider NEC, the customers end suppliers EON, EVN and CEZ, and the producers of electrical energy from RES. Up to the registering of CSBG of the producers of electrical energy from RES, its function will perform CSBG of the end supplier in whose licensing territory is connected producer of electrical energy from RES.

According to members of chapter 11 of the rules for trade in electrical energy [1], producers of electrical energy from RES are subject to balancing under special conditions, such all measured quantity of them produced electrical energy is charged at preferential prices by the relevant end supplier.

For RES with installed capacity over 30 kW, imbalances are due to crossing the border $\pm$ 20 % of the difference between the predicted and the measured profile and is in the direction of the general imbalance of his CSBG, such this quantity is valued at 50 % of current prices for energy shortage or surplus. These are the only preferential conditions for balancing in market model descriptions of electrical energy. With a not big investment, each producer of electrical energy from RES, with the exception of the wind generators, may be included in this tolerance. Although groups of end suppliers called special, in which at first time would be the producers of electrical energy from RES, for them not provided any preferences and they will be balanced by the ESO in the same way as standard BG. This means that CSBG can use the forecasts made by producers, only informative (because they will are too inaccurate $\pm$ 20 %) and to achieve least possible deviations of the aggregate forecast, as each kWh deviation from this forecast will pay to the ESO.

From the statement above becomes clear need to develop a methodology and develop of possible the most accurate methods for forecasting electrical energy produced from RES, of the licensed territory to end suppliers as CSBG.

As the authors have data from the producers of electrical energy from RES in the territory of western Bulgaria, the analysis of the problems for daily hour forecasting refers to that part of the country.

The group of RES, which has balanced in the March 2011, has the following structure:

- hydropower plants (HPP) under 10 MW – 100 objects with a total installed generating capacity 107,356 MW;

• photovoltaic power plants (PVPP) – 19 objects with a total installed generating capacity 7,674 MWp;

• wind power plants (WPP) – 6 objects with a total installed generating capacity 10,57 MW.

In western Bulgaria partition of wind power plants is 8,42 % of installed power of generation from RES, which are single wind generators located at remote distance. Forecasting of hourly electrical energy production from wind generators is successful only in so-called energy market on the day of delivery. Forecasts in this market are prepared on the day of trade and supply of electrical energy, which means that through measuring systems of wind and efficiency of work of the wind generator, can be draw accurate forecasts. In the model of the market day-ahead hourly forecasts of the wind generators are quite inaccurate, because they are based primarily on the meteorological forecast for wind speed and wind direction, which is not always sufficiently precise. Still at the National Institute of Meteorology and Hydrology (NIMH) are unable to draw hourly meteorological forecast for wind speed and wind direction. Therefore, for improving the accuracy of the forecast of total production of electrical energy from RES should be working in direction for improve accuracy of forecasting of the electrical energy production from HPP and PVPP.

The main part of HPP in the territory of western Bulgaria is built in the water catchments of the rivers: Mesta, Struma, Iskar, Ogosta, Vit, Black Vit and Osam. For these rivers, NIMH daily published in its website measured values of following physical variables: level measured H, cm; change of the level ΔH, cm; measured water quantity Q, m^3/s.

In order to draw accurate forecasts, HPP are divided into following groups according to their form of hourly profile of the electrical energy production and their dependence on certain attribute:

• Of flowing water (derivative) and below dams.

The profile of HPP of flowing water is directly related to the rainfall and the change of the levels of rivers and has seasonal character.

In the below dams HPP, work schedule depends on the agreed water quantities with Irrigation systems and the Ministry of environment and water. For them significantly influenced turns the function of the dam as an annual equalizer.

• Of geographical sign – HPP of the Iskar River, HPP on the northern slopes of Stara Planina, HPP at the foot of Rila and Pirin mountains.

Weekly aggregated forecast and measured profile of HPP in western Bulgaria (upper graph), is presented in fig. 1. At the bottom of the graph in fig. 1 are shown the forecast aggregate profiles of HPP, divided into groups depending on the shape profile and their relationship with meteorological data from the relevant stations of NIMH.

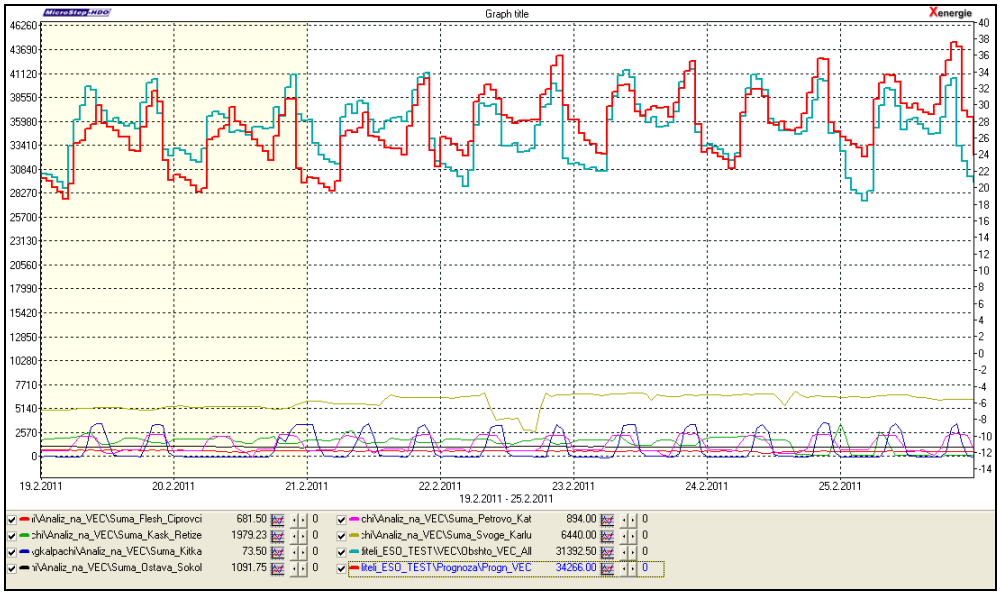

Fig. 1.

Daily aggregated forecast profile (red line) and measured profile (green line) for all HPP in considered territory are presented in fig. 2.

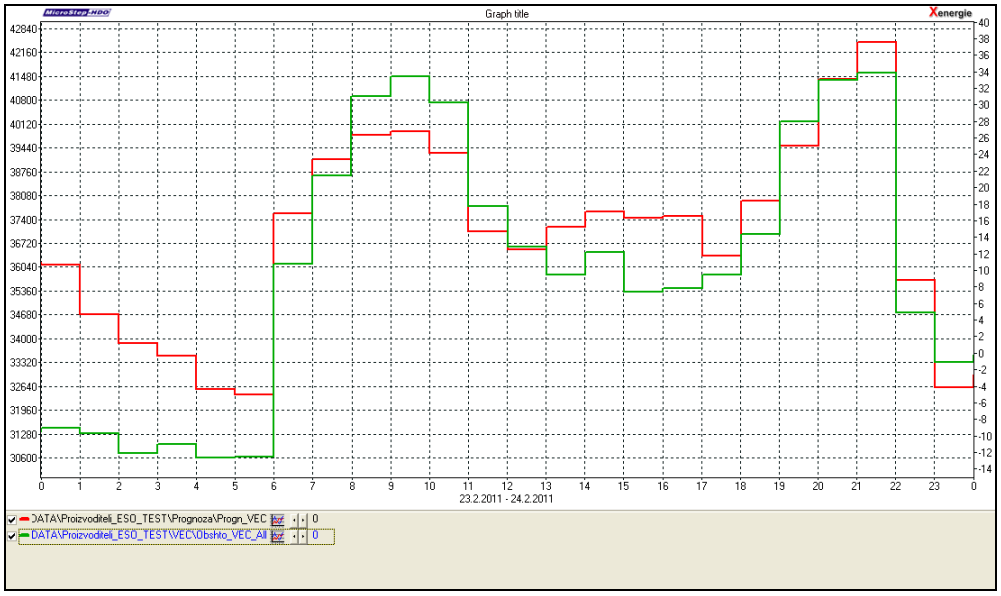

Fig. 2.

Daily forecast profiles for the different groups HPP, which constitute the total forecast for HPP in considered territory are presented in fig. 3.

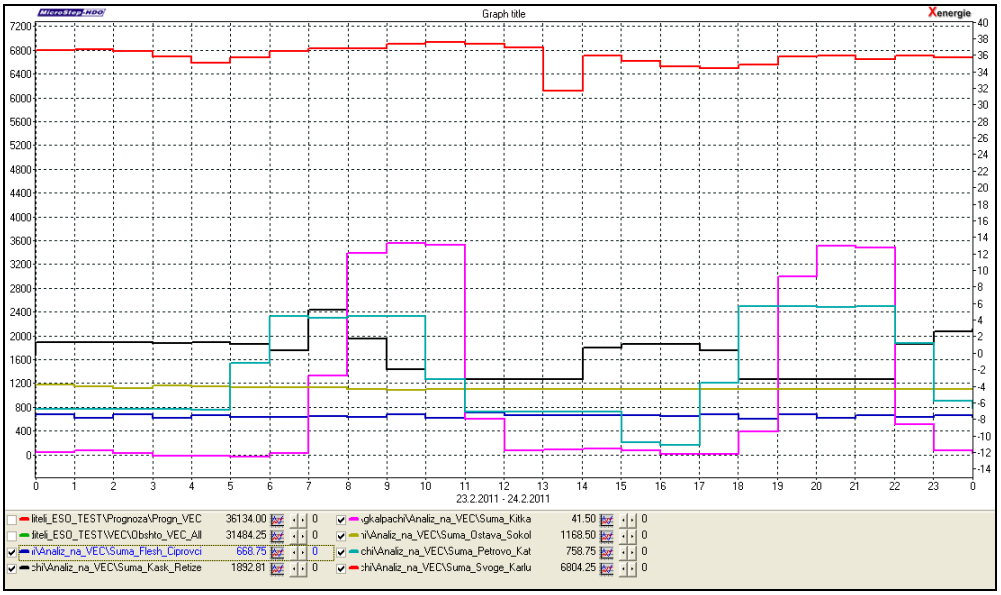

Fig. 3.

For drawing of successful forecasts, i.e. with an error less than 10 % have been developed different mathematical and experimental methods, in which compulsory involved:

- historical measured profile of production of electrical energy, received daily with current data D-2;
- historically measured meteorological variables that have direct connection with a RES with measured data to D-2 (quantity of rainfall, level of rivers, solar radiation, temperature);
- forecast meteorological data for these variables for day of production D.

Methods are selected of the base on minimizing the criterion $MAPE_2$, defined as:

$$MAPE_2\,[\%] = \frac{\sum_i abs(P_i - S_i)}{\sum_i abs(S_i)}.100, \tag{1}$$

where:

i is an index of the hour (0-23),

P_i is a forecast at the hour i,

S_i is a real value at the hour i.

The result was evaluated as a relative error of the produced electrical energy for the day:

(2) $$E\,[\%] = \frac{E_p - E_s}{E_s}.100,$$

where:

E_p is the forecast quantity of electrical energy for the day in a day of production D,

E_s is the measured quantity of electrical energy for the day in a day of production D.

The most accurate is the model of forecasting, in which the total hourly forecast for the production of electrical energy from HPP is the sum of individual forecasts for groups of HPP depending on the forecasted and measured meteorological data. In this model, the error for the period 01–03.2011, estimated by formula (1) is 6,23 %, but as energy by formula (2) is 1,23 %. A significant drawback of this method of forecasting is that it strongly depends on the reliability and the period of receipt of the actual measured load profiles, measured meteorological variables and forecast meteorological data.

PVPP for which shall be drawn hourly forecast of their production, have the following a territorial location and installed generating capacity:

- region Blagoevgrad, Sandanski, Petrich – 2,038 MWp;
- region Ihtiman, Sofia – 3,055 MWp;
- region Pleven, Vidin – 2,5805 MWp.

As the NIMH there is only one automatic meteorological station in Sofia, which measures hourly solar radiation in W/m^2, therefore, the developed methods is using for historical measured data, the data for solar radiation for Sofia and the forecasts for the relevant regions. It has been made experimental link between the forecast definitions of „considerable cloudiness“, „cloudiness“, „particulary cloudiness“, „smoke bomb“, „sunny“ and the hourly values of the solar radiation in W/m^2.

Thus in the model for the daily hourly forecasting of the electric energy production from PVPP are used for historical profiles the following data:

- measured hourly values of the produced electrical energy from PVPP, aggregated for the relevant region;
- measured hourly values of the solar radiation in Sofia;
- forecast hourly profile for the solar radiation to the relevant regions defined as a function of the definitions in the forecasts (sunny, considerable cloudiness etc.) as well as and on its dependence on the sunrise and the sunset in these geographic areas (longitude) according astronomical calendar for 2011.

In this model, the error for the period 01–03.2011, estimated by formula (1) is 8,5 %, but as energy by formula (2) is 2,18 %.

Weekly aggregated forecast profile (red line) and measured profile (green line) of PVPP in western Bulgaria are presented in fig. 4.

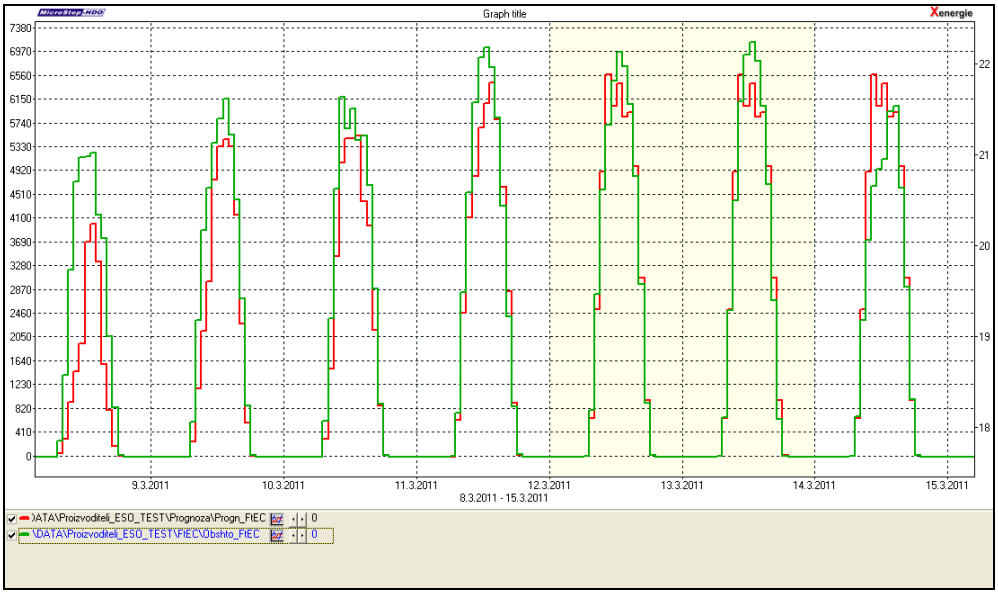

Fig. 4.

Daily aggregated forecast profile (red line) and measured profile (green line) for all PVPP in considered territory are presented in fig. 5.

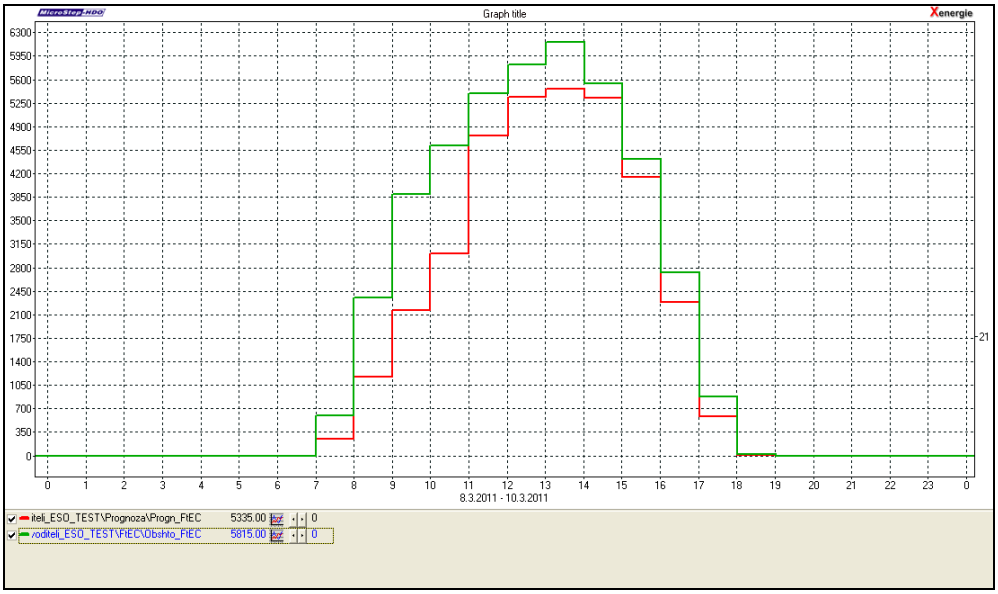

Fig. 5.

To improve the accuracy to drawing of the daily hourly forecasts should mainly relying on improving the accuracy of the used meteorological forecasts as well as on improving the accuracy of the measured data.

The measured meteorological and electrical variables must be measured hourly, i.e. as average values for interval of 60 min. The forecast meteorological variables through a mathematical model must also be presented exactly to an interval of 60 min.

The drawing of accurate daily hourly forecasts in the area of the electrical energy production from RES is required and sine qua non for the successful operation of the new energy market model, for the transition from centralized to decentralized generation of the energy sector and for the transition of the traditional energy system to intelligent Smart grid.

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State and possibilities for development of renewable energy in Bulgaria

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***Abstract**: After EU accession, Bulgaria adopted the following indicative goal: 16% of gross domestic energy consumption in 2020 to be produced from renewables. This has created favorable conditions and strong interest of Bulgarian and foreign business to invest in renewables. This interest is materialized in a boom in design and construction of the renewable energy installations. The paper examines the current state and opportunities for development of this sector in Bulgaria.*

***Keywords:** renewable energy, hydro power, wind power, solar power.*

1. INTRODUCTION

The Priorities in the energy sector of Bulgaria are in harmony with the requirements of EU directives and market mechanisms.

An important aspect is the policy of encouraging the use of renewable sources (RS) which aims to achieve sustainable energy development and improving the environment and is associated with the implementation of the undertaken commitments of the Republic of Bulgaria on:

- United Nations Framework Convention on Climate Change, adopted in June 1992 and ratified by Bulgaria on March 16, 1995.

- Kyoto Protocol ratified in 2002. Our country has an obligation to reduce greenhouse gas emissions in 2008-2012, with 8% of overall emissions compared to baseline in 1988.

- Directive 2009/28/EC on encouraging the use of energy from renewable sources (RS).

2. LEGAL REGULATIONS ON THE USE OF RENEWABLE SOURCES (RS) IN BULGARIA

After EU accession, Bulgaria adopted the following benchmark: 16% of gross domestic energy consumption in 2020 to be produced by RS.

Additional incentives for energy producers are bring in:

- The Energy Law adopted in 2003

- Energy Efficiency Act, 2008
- The Law on Energy from renewable sources, 2011

This has created favorable conditions and a strong interest of various entrepreneurs to invest in exploration and development of renewable energy installations(particularly after 2003). Constructed mainly small hydro, wind, photovoltaic stations, and extremely rare – installations for incineration of biomass and utilization of landfill gas and gas from wastewater.

2.1. The Law on Energy from renewable sources(Promulgated in the State Gazette No. 35 of 3 May 2011)

One of the main objectives of this Act is to promote production and consumption of energy produced from renewable energy sources by:

- guaranteed access, transmission and distribution of energy produced from renewable sources to the transmission and distribution networks;
- mandatory purchase of energy produced from renewable sources;
- preferential price for purchasing energy generated by RS, excluding energy produced by hydropower plants with capacity above 10 MW.

Regulatory authority - the State Energy and Water Regulatory Commission by 30 June each year determine the preferential prices for sale of energy generated from RS, excluding energy produced by hydropower plants with capacity exceeding 10 MW (Article 32).

According the law “Energy from renewable sources” includes: wind, solar; energy stored as heat in the air - aerothermal energy; energy stored in the form of heat beneath the surface of the solid earth - geothermal energy; energy stored as heat in surface waters - hydrothermal energy; ocean energy, hydropower, biomass; gas from renewable sources, landfill gas and gas from waste water treatment plants.

2.2. The Energy Law(Promulgated in the State Gazette No. 107 of 9 December 2003, last amended in the State Gazette No. 97 of 10 December 2010)

Introduces the requirements of European directives relating to encouraging the use of energy from renewable sources by obligation for setting an indicative target for electricity production from RS (Directive 2001/77 EC) and government regulation and licensing in the energy sector. According to the Energy law license to generate electricity or heat is needed when power plant is more than 5MW, (Article 39).

2.3. Energy Efficiency Act(Promulgated in the State Gazette No. 98 of 14 November 2008, last amended in the State Gazette No. 15 of 23 February 2010)

Associated with Directive 2006/32/EC on energy efficiency improvement in end-users. It provides sections and clauses for encouraging the use of RS for energy production, such as the creation of funds. Regulates the establishment of National Fund "Energy Efficiency and RS” which funding projects for development on energy efficiency in Bulgaria.

3. BULGARIA'S POTENTIAL FOR DEVELOPMENT OF ENERGY PRODUCTION FROM RENEWABLE SOURCES (RS)

3.1. Dynamics of installed power capacity in renewable energy

Legislative changes regarding the development of renewable energy sector in the country at the beginning of XXI century significantly increased investor interest. Initially, capital focused on the privatization of a significant part of small HPP (SHPP). Large HPP remained at the disposal of state, respectively NEC. This first wave of interest in ensuring the leading role of small hydropower plants in terms of installed capacity and the relative share of power in the renewable energy sector (Table 1). In practice, till the middle of the past decade, major investments were aimed at developing a "small" hydro potential. After 2005 there was rapid development of research and investment in wind power plants (generators) and only in the last 2-3 years - of photovoltaic systems for generating electricity and heat (Table 1 and Table 2).

Over the last 20 years the share in gross electricity renewables varies between 4 and 10% annually, and only in recent years has seen even minimal increase in this share (Fig. 1). A characteristic fact is that this increase and its variations are very closely linked to fluctuations of the annual production of electricity from small HPP. In future will be a gradual increase in the impact of wind turbines and photovoltaic systems.

Tab. 1: Dynamics of installed power capacity in renewable energy sources

Type RS	Мярка	2005	2006	2007	2008	2009	2010	2009(%)	2010(%)
HPP	MW	1 879	1 883	1 876	1 865	1 869	1 919	77,0	72,4
SHPP	MW	164	176	198	205	214	241	8,8	9,1
WPP	MW	8	26	41	113	335	465	13,8	17,6
PhPP	MW	0	0	0	0	6	21	0,2	0,8
BiogasPP	MW	0	0	0	0	4	4	0,1	0,1
installed sumed capacity of RS power plants	MW	2 051	2 085	2 115	2 183	2 428	2 650	100,0	100,0
PumpHPP "Chaira"	MW	864	864	864	864	864	864		

Tab. 2: Dynamics of electricity production from renewable energy sources

Type RS	Мярка	2005	2006	2007	2008	2009	2010	2009(%)	2010(%)
HPP	GWh	3 788	3 718	2 874	2 296	2 866	4 787	77,2	86,9
SHPP	GWh	548	520	504	527	604		16,3	
WPP	GWh	5	20	47	122	236	689	6,4	12,5
PhPP	GWh	0	0	0	0	3	17	0,1	0,3
BiogasPP	GWh	0	0	0	0	2	17	0,1	0,3
installed sumed capacity of RS power plants	GWh	4 341	4 258	3 426	2 946	3 711	5 509	100,0	100,0
PumpHPP "Chaira"	GWh	342	277	360	453	583			

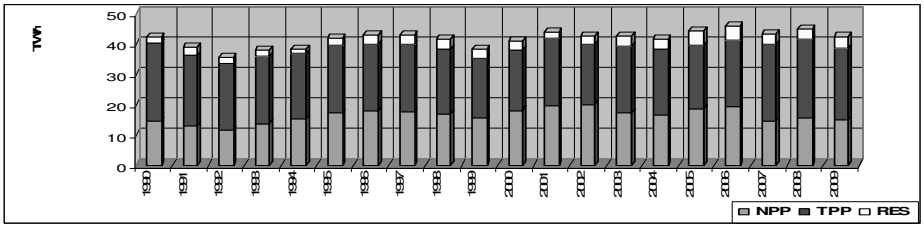

Fig. 1: Electricity generation by type

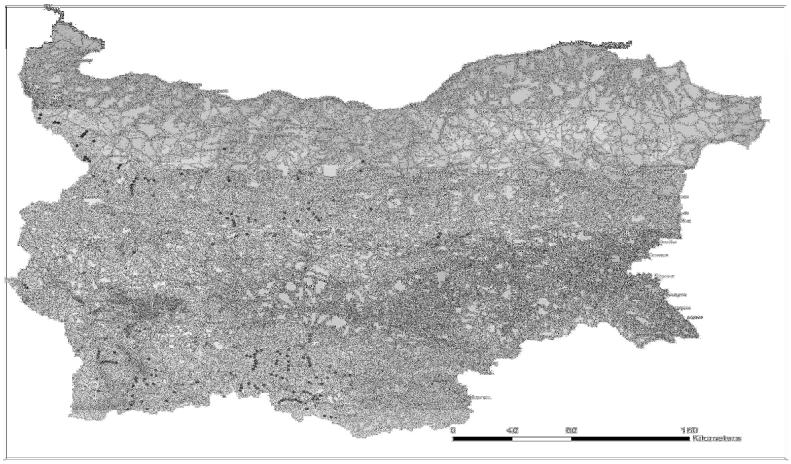

Fig. 2: Location of small hydro power plant (SHPP) along rivers till 2009

3.2. Geothermal energy

In Bulgaria there are over 150 geothermal springs with temperatures above 20℃. Most of them are shallow, as it ranges from 500 to1500 m in south Bulgaria and from 1000 to 5000 m in northern Bulgaria. According to reports by the European Bank and GEA geothermal potential of Bulgaria of electricity production with current technology options is estimated at 200 MW. In Bulgaria, the production of geothermal electricity is not developed

yet, but direct use finds applications in swimming pools, heating systems and spas.

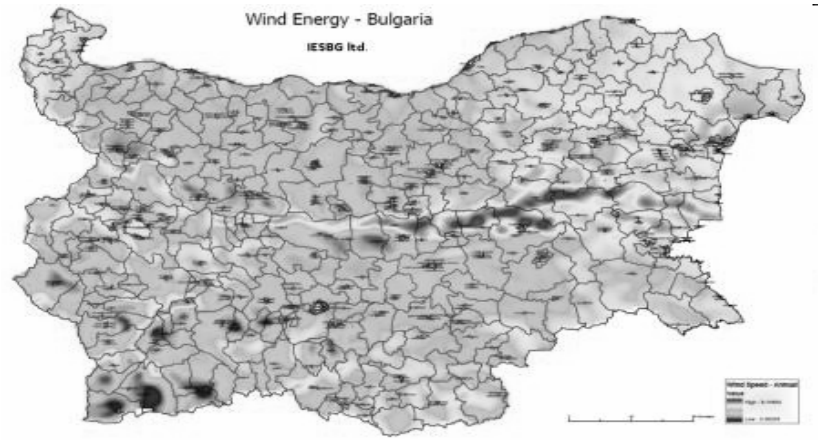

Fig. 3: Assessment of wind energy potential (reference period 1998-2008)

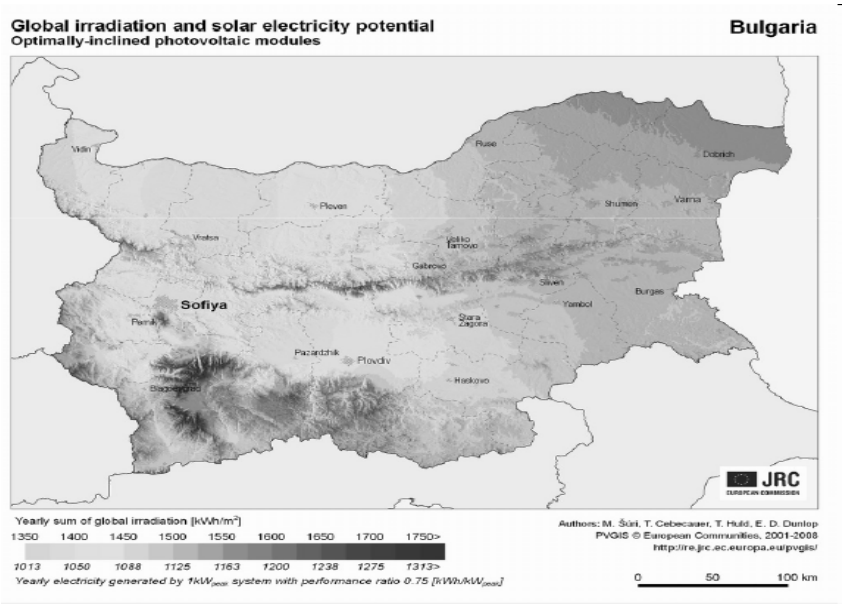

Fig. 4: Potential for solar energy

Tab. 3: Theoretical potential of biomass in Bulgaria

TEORETHICAL POTENTIAL OF BIOMASS IN BULGARIA, ktoe					
Energy crops	Agricultural solid waste	Urban solid waste	Firewood	Others	TOTAL
840	1 880	310	550	35	3 615

3.3. Development opportunities in the future

For the period 2003-2010 the State Energy and Water Regulatory Commission issued licenses for construction of power stations with the following power capacity for each type of technology:

-Wind power stations - 2017 MW;
-Photovoltaic power plants - 230 MW;
-Power plant running on biomass - 15 MW;
Total - 2262 MW.

To these we can add more than 840 permits for construction of small hydropower plants, of which only about 1 / 10 can be realized

4. CONCLUSIONS

Bulgaria has a substantial and diversified energy potential in renewable sources to be studied in depth. RS sector is developing dynamically only just the last 5-6 years, which explains the still low level of absorption (except to some extent on hydropower). Still legal regulations in the field of renewable energy are changing too frequently, which limits the active penetration of large investment in the sector. Bulgaria has the opportunity to meet the indicative target of 16% share of renewable energy in gross domestic final energy consumption in 2020 if deployment of wind energy and solar energy potential, especially if dynamically construct installations for utilization of biomass. We must not forget that the best intentions in this area should not conflict with the environment**.**

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Web based system for Renewable Energy Sources assessment

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Abstract: *The **RES_Assess** software is developing to assist in the preliminary assessment of potential renewable energy projects. First released include water pumping solar systems, passive solar systems, wind, and geothermal energy and biomass. The program guides the users in the design of their systems, by providing initial estimates. By changing the system's parameters, users are able to quickly screen an effective technology and system size depending on load, climatic conditions, and season of use. This paper describes scope of models (radiation, wind, geothermal, heat transfer) used to predict energy production from energy resource systems, climatic variables and system parameters and software technology for realising the project.*

Keywords: *Energy projects, Renewable energy, Web system*

1. INTRODUCTION

Many software tools have been developed for energy assessment of Renewable Energy Sources. The first group of these products is so called '*easy to use calculators'* [1] for different renewable technologies. These are simple software applications, which use suitable mathematical models for specified energy resource. These software tools are not suitable to make detailed energy and economical assessment for a project performance.

RETScreen Clean Energy Project Analysis Software [1,2] is the design tool, which is the world's leading clean energy decision-making software. It is provided completely free-of-charge by the Government of Canada as part of Canada's recognition of the need to take an integrated approach in addressing climate change and reducing pollution. The core of the tool consists of standardized and integrated renewable energy project analysis software that can be used worldwide to evaluate the energy production, life-cycle costs and greenhouse gas emission reductions for various types of renewable energy technologies (RETs). RETScreen is collection of static analytical models for different Renewable technologies. The software consists of easy-to-use Microsoft Excel spreadsheets.

The *Maui Solar Design Studio* is an advanced solar system design tool, suite of somewhat "Easy to use" tools, modules for both PV and solar thermal technologies [6,7]. It includes tutorials, hourly simulation results, system performance analysis, 30 year datasets for 237 US locations, financial analysis tools, load analysis optimization, hourly analysis e.t.c.

The *F-Chart* is the authoritative solar thermal system analysis & design tool [6,8]. Software includes modules for solar thermal and PV technologies, monthly performance results, system performance analysis, weather data for 300 locations, economic Analysis.

The *TOPFARM* project addresses optimization of wind farm topology and control strategy as based on detailed aero elastic modelling of loads and power production in a coherent manner [6]. The outcome of the TOPFARM project is a toolbox, consisting of advanced dynamic wake load models, power production models, cost models and control strategy models, and the synthesis of these models into an optimization tool.

Presented literature review shows, that available software tools are both static (excel spreadsheets) or dynamic models for specified renewable technologies only. There is not complete design tool for different renewable energy resources and dynamic (simulation) models.

A new project for software product for Renewable energy assessment – **RES_Assess** is presented in this paper. It could be an innovative and useful renewable energy awareness, decision-support and capacity-building tool. The core of the tool consists of standardised and integrated renewable energy project analysis software to evaluate the energy production, life-cycle costs and greenhouse gas emission reductions for various types of renewable energy technologies (RETs). The software consists of easy-to-use Web forms for collecting an initial project data. In addition to the software, the tool includes: product, weather and cost databases; an online manual; a website; project case studies. In complete design RES_Assess will provides a common platform for evaluating project proposals while significantly reducing the costs, associated with preparing preliminary feasibility studies. In addition, the tool will be suitable for educational and industry/market development purposes.

The Software is based on various models used to calculate, on a month-by-month simulation basis, the energy production of Renewable Energy Sources systems. They include models to compute solar, wind geothermal or other energy using daily distribution of climatic parameters and consumer demands. The models use the concept of utilizability to evaluate the interaction of the various components of the system and predict how much energy (or water, in the case of a pumping system) can be expected from the system on an annual basis.

RES_Assess allows decision-makers and professionals to determine whether or not a proposed renewable energy, energy efficiency, or

cogeneration project makes financial sense. If a project is viable — or if it is not — RES_Assess will help the decision-maker understand this: quickly, unequivocally, in a user-friendly format, and at relatively minimal cost.

2. WEB SITE OF RES_ASSESS SOFTWARE

The main Web page of *RES_Assess* Web site is presented in fig. 1. The initial version of this Web site is available on the address: http://www.renenergy2011/Ret_Assess/index.htm.

The technologies included in final release of RES_Assess’s project models will include renewable energy sources of clean energy as well as conventional energy sources and technologies. Project models ensure facilities for the next assessments: energy efficiency, heating and cooling (e.g., biomass, heat pumps, solar air/water heating, geothermal systems), power (including renewables like solar, wind, hydro, geothermal, etc.), and combined heat and power (or cogeneration).

Each model also will includes equipment characteristics, cost and weather databases and a detailed online user manual, all of which help to reduce the time and costs associated with preparing pre-feasibility studies. The RES_Assess Software can be used to evaluate industrial, commercial, institutional, community, residential and utility applications for the following technologies:

Wind Energy Project Model for central-grid and isolated-grid connected projects, ranging in size from large-scale multi-turbine wind farms to small-scale single-turbine wind-diesel hybrid systems, water pumping system etc. The mathematical model renders an account to the available meteorological data (monthly mean wind speed, wind speed distribution etc.) and turbine power curves.

Photovoltaic Project Model for on-grid (central-grid and isolated-grid PV systems), off-grid (stand-alone (PV-battery), hybrid and water pumping applications (PV-pump systems).

Solar Heating Project Model for ventilation air heating and process air heating applications of transpired-plate solar collectors, as well in the air-drying processes.

Solar Water Heating Project Model for domestic hot water; industrial process heat and swimming pools, heating in buildings with heat pumps ranging in size from small residential systems to large scale commercial, institutional and industrial systems.

Passive Solar Heating Project Model for passive solar designs, energy efficient windows use in residential and commercial building applications, massive walls, greenhouses, heating roofs etc.

Biomass Heating Project Model for biomass and waste heat recovery (WHR) heating projects. The model would be used to evaluate waste heat recovery, biomass, and biomass and waste heat recovery combined.

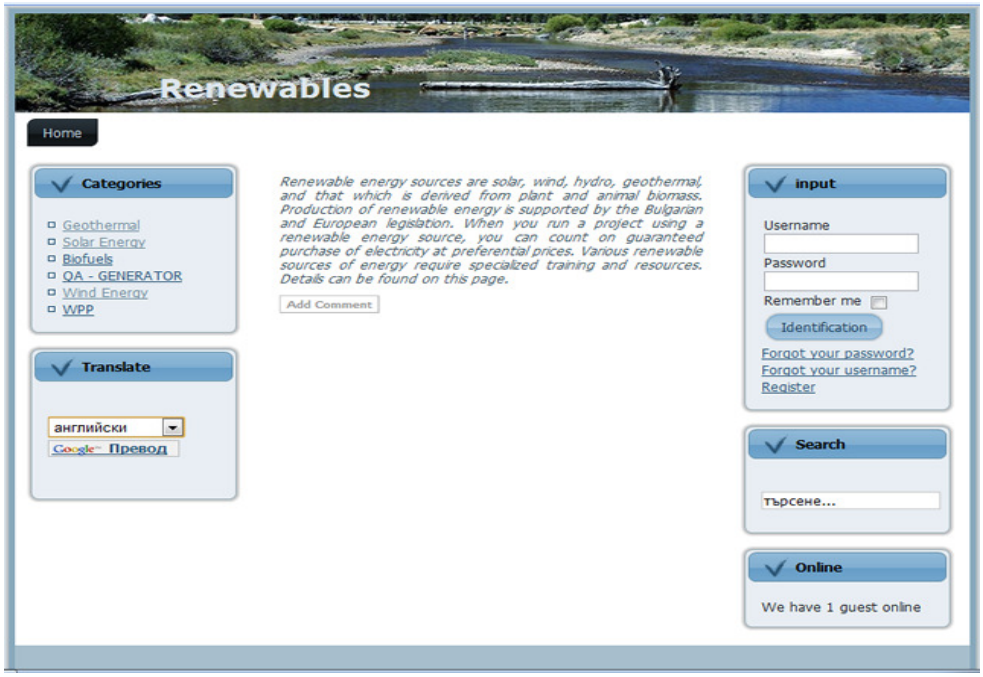

Fig. 1. Main Web Page of RES_Assess Web site

Geothermal and Ground-Source Heat Pump Project Model for heating and cooling of residential, commercial, institutional and industrial buildings using direct thermal systems, ground-coupled (horizontal and vertical closed loop) or groundwater heat pumps. Models use temperature distribution in earth layers and season accumulation effects.

Web site comprises client Web applications for communications with the users and server applications for solving the mathematical models and assessing procedures for renewable energy projects. Software is developing by well-known software developer tool Delphi (Embarcadero RAD Studio).

3. RES_ASSESS TECHNOLOGY

Software is developing by ***Embarcadero RAD Studio*** and ***Delphi for PHP*** software. These is an object-oriented, visual programming environment for rapid application development (RAD). Embarcadero RAD

Studio provides all the tools, needed to model applications, design user interfaces, automatically generate and edit code.

The Web part of Embarcadero RAD Studio is developed as a conceptual background for building ***WebSnap*** applications. WebSnap makes it easier to build Web server applications that deliver complex, data-driven Web pages. The base of WebSnap facilities in RAD Studio is ***IntraWeb*** technology.

IntraWeb is a new way to create web-based applications. Built upon *Web Solution Builder*, it extends the technology by providing an excellent tool for creating internet, intranet and extranet applications in a quick and easy to maintain manner.

IntraWeb works much like a normal executable application, with the exception that the user interface is a web browser instead of a window. After placing the application on a web server, a user can run an instance of the application by using a URL to start a session. The user's information will be tracked by the instance of the application in use, thus preventing data loss or accidental intermingling with another user's data. For each user, new session information is created and tracked automatically and is transparent to the developer. The overhead is low and the capacity of an IntraWeb application is similar to that of other web solutions such as ISAPI, CGI, or ASP.

IntraWeb allows developers to create applications in a true RAD manner by dragging and dropping components on an IW form, defining events and setting properties in a way that is similar to popular RAD environments like Delphi or Microsoft Visual Studio.

No HTML, CGI or JavaScript skills are required, all coding can be done with making use of Delphi or any other language you use on the .Net platform. Additionally, JavaScript may be used to implement custom client-side features (see Overview, Areas of Implementation).

The main technology scheme of IntraWeb is described in fig.2. When the Web application receives an HTTP request message, it creates a HTTPApp.TWebRequest object to represent the HTTP request message, and a HTTPApp.TWebResponse object to represent the response that should be returned. The application then passes these objects to the Web dispatcher (either the Web module or a *TWebDispatcher* component).

The Web Dispatcher controls the flow of the Web server application. The dispatcher maintains a collection of action items (*TWebActionItem*) that know how to handle certain types of HTTP request messages. The dispatcher identifies the appropriate action items or auto-dispatching components to handle the HTTP request message and passes the request and response objects to the identified handler so that it can perform any requested actions or formulate a response message.

The action items are responsible for reading the request and assembling a response message. The content producers can make use of other content producers or descendants of *THTMLTagAttributes*, to help them create the content of the response message.

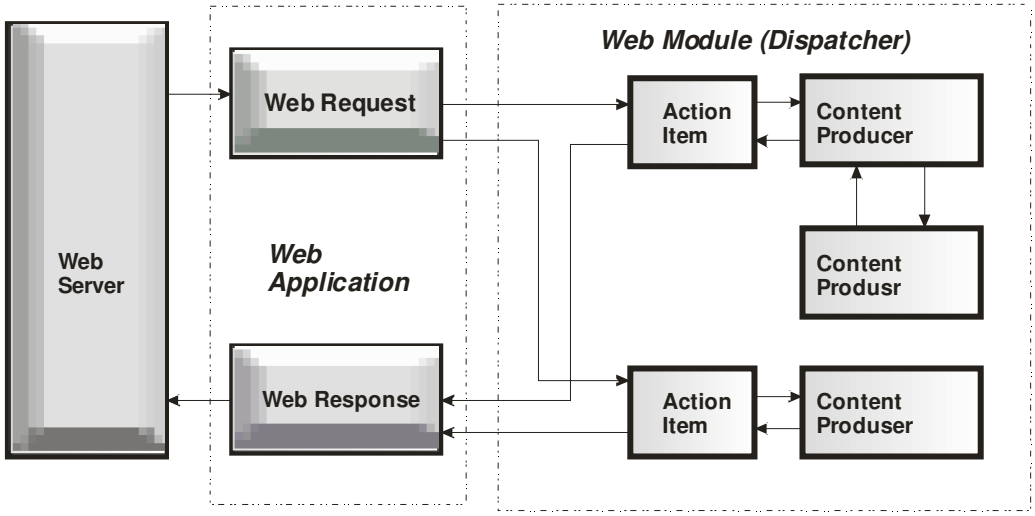

Fig.2 Schematic diagram of IntraWeb technology

If there is needed creating the Web Client in a multi-tiered database application, the Web server application may include additional, autodispatching components that represent database information encoded in XML and database manipulation classes encoded in javascript.

When all action items (or auto-dispatching components) have finished creating the response by filling out the *TWebResponse* object, the dispatcher passes the result back to the Web application. The application sends the response on to the client via the Web server.

4. CONCLUSION

Web based system RES_Assess would expand the public knowledge for renewable energy technologies, encouraging the implementation of energy efficiency measures, and contributing to a sustainable energy future. As the world moves towards addressing climate change and further protecting the environment, this project intends to encourage initiatives for RES energy developments and projects. The models included in this software project provide a set of equations that lend themselves well to an efficient simulation procedures and implementations. The incorporation of

these models into RES_Assess makes it possible to compare quickly the benefits of renewable energy systems to those of conventional energy sources. The models go into enough detail that meaningful physical phenomena are taken into account, while at the same time retaining enough simplicity to minimize data input requirements for users. The improvements in accuracy due to the use of hourly data, rather than monthly data used in most other renewable energy design models, are important.

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Instant Nature in Geography classes at High School

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***Abstract**: A practical guide about “How to make a school class in the open air with minimum preparation, time wasting and nerves”. In my eight-year practice as a school teacher I realized, that students and teachers adopt this method for variegate teaching with a great enthusiasm. Both sides are charged with positive energy and remember such lessons for a long time.*

The idea is recommended for high school students i.e. 14-19 years old, but it could also be applied in work with younger students – 1st to 7th grades with insignificant adaption concerning their age features. The exemplary school class was organized with 9th grade students (16 years old) from the Language High School “Acad. L. Stoyanov” – town of Blagoevgrad, Bulgaria..

***Keywords:** education, nature, high school, geography*

1. INTRODUCTION

“Instant Nature” emerged in the year 2005 in Language High School “Acad. L. Stoyanov” – Blagoevgrad. I was teaching, as usual, in the classroom. It was spring time and nature outdoor was awaking, the air was fresh and the plants were already turned green. The school process was intensive for both students and teachers. Sitting in the classroom I and my students felt somehow unnatural to be closed between four walls, instead of going outside, among green grass and fresh air.

So I thought: “Why don’t I organize my class outdoor on the plant landscape at the sunny weather?”

2. PERMISSIONS AND ORGANIZATION OF THE OUTDOOR CLASS

I asked and received permission from the school authorities. I don’t recommend to any teacher to organize outdoor classes without permission. There are several important things to beware of before that. You must be sure that the grass is treated against insects, weather is not too cold or hot

etc. Involve your students to help you with the preparation of this fast-organized, but very unusual school class.

In my case in this first outdoor class at school boys helped bringing a long desk for the girls, so they can feel as comfortable as possible outside the classroom (Fig. 1) Than they showed what man's solidarity is and sat on the grass as a separate group (Fig. 2).

All the students brought their notebooks and textbooks, some brought even their atlases.

Fig. 1 Girls sitting on a long desk, brought by boys, so they can feel comfortable outdoors.

The geographical map was attached on the fence. Then we proceeded with check out for absents and a brief review of the previous lesson. Important to say is that every teacher must be sure if he/she is in a good physical shape to sit down on the ground, to spend about 30-40 minutes there and then to be able to get up without having some health problems (Fig. 4). You must wear sunglasses if the sun is strong and to bring a bottle of water with you.

So after everything is done correctly it comes the time for examinations. Even suffering some objective limitations, such as lack of whiteboard and markers, you can use your imagination to bring comfort and uniqueness in the process of school exam in order to reduce stress in students.

Fig. 2 Boys sat down on the grass separately from the girl group.

Fig. 3 Geographical map attached on the fence

Some useful practical ideas are to ask the group to look at the clouds above. The teacher can examine them to make classification by type, shape, height and chance of precipitation. Together try to make a short-term weather forecast. This, of course, is not very precise, but your students will be very interested. Additional joy for them is to hope for fair weather in order not to be examined. If the teacher has information about the type and names of the surrounding plant species he could use it to make the class even more interesting. Another topic could be some information about the solar radiation (as you will experience its influence at the very same time), the air properties, the pollution and the importance of providing clean and fresh air for their organisms etc.

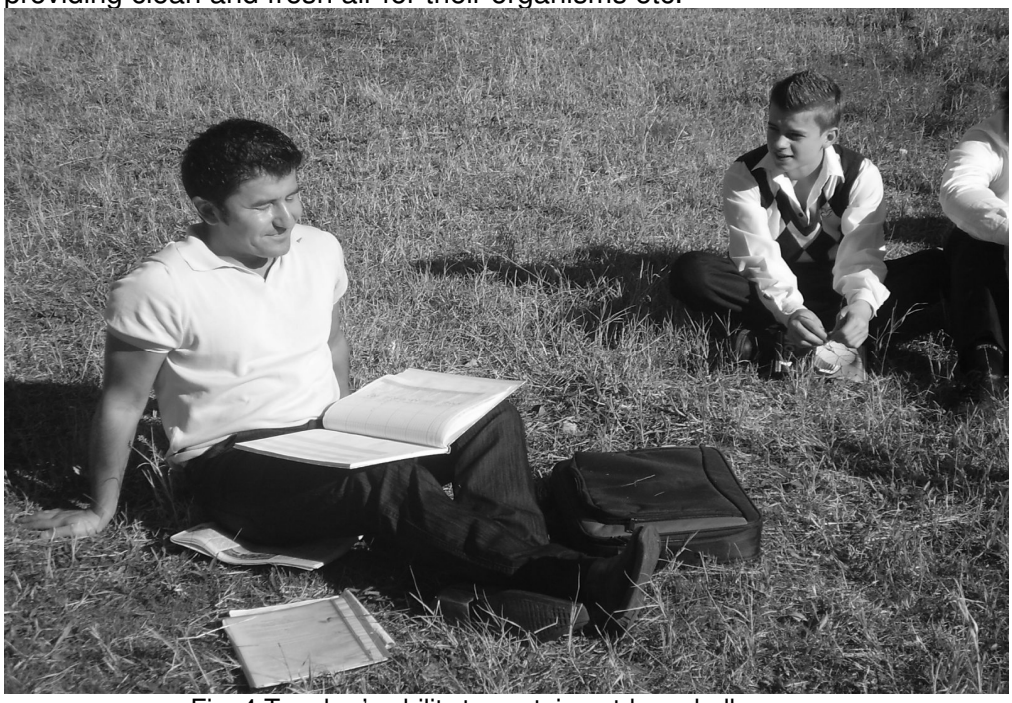

Fig. 4 Teacher's ability to sustain outdoor challenges

The new lesson can be presented easily with descriptive methods, such as speech, discussion, school map, atlases, textbooks and other helping materials. There are some difficulties for the students to write while sitting on the ground, so don't ask them to write long lesion plans during this lesson.

Fig. 5 During the exam

The last minutes of this lection are the most valuable and possess unusually big potential for the teacher to make impact on his students. The natural environment, sun light, fresh air and higher mood leaves a long and pleasant impressions. The teacher must not lack the opportunity to talk with his students about some intransient and educational topics. The discussion at the end of such a lesson will be remembered for a long time with a feeling of joy and satisfaction. This is the most important and valuable part of this uncommon class.

3. CONCLUSIONS AND ADVICES

To run everything smoothly the teacher needs some preparations.

- Chair (if you need one)
- Exercise covers for the students (from the school gym) and a bench if needed
- School map

The school must have a small green area in the school yard.

- You can ask school authorities for support. You can create such a place together with the students. It will be a good practical lesson for them

- It is important for you to remain inside the school area, behind the fence
- This will keep the world out of your business and no one will disturb you

Important advices:
- Grass in the green area must be treated against insects
- The weather must be not too hot and not too cold
- The most suitable time of the year is:
- In spring – May and June
- In autumn – September and October
- Involve your students to help you
- Carry sunglasses and a bottle of water
- Be in a cheerful mood

Useful topics:
- Examine students to make classification of the clouds they see by type, shape, height and risk of precipitation
- Together try to make a short-term weather forecast
- Prepare and explain your students about the plants surrounding you
- Tell them some interesting facts about the solar radiation that they feel at the moment, about the properties of clean air and how all natural conditions influence their health
- Create a loving attitude on nature in your students

If the teacher is capable of organizing such an uncommon school class, he will achieve a strong educational and perceptional effect upon his students. Both sides will be enthusiastic and emotionally satisfied at the end of the lesson. Such practices give great opportunities for teachers to create attitudes in students for loving and preserving nature. Originality and imagination of teachers are challenged and the results will be proportional to their efforts and charm. The natural landscape, surrounding the group, the sunlight and the fresh air will bring cheerful mood to everyone and this valuable lesson will never be forgotten. I can assure you – this worth all the risks of unknown and eventual discomforts. So, be initiative, and you will be fascinated by the results achieved!

4. ACKNOWLEDGEMENTS

Author thanks to the authorities of Language High School “Acad. L. Stoyanov” –Blagoevgrad, and in particular to Mrs. Tina Popova for her assistance. Thanks also to the students of 9A grade and all my students for their enthusiasm and support during this practice.

STATISTICAL ANALYSIS OF MONTHLY PRECIPITATION SUMS FOR THE 1982-2010 PERIOD

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Abstract: *The aim of the paper is to reveal variations of monthly precipitation sums for the 1982-2010 period. Official meteorological data for few stations in Bulgaria are put under investigation. For achievement of the above-mentioned aim the statistical methods for analysis of temporal (dynamic) ranges are applied. An estimation of trend and season changes of development is made.*

Keywords: *statistical analysis; temporal (dynamic) ranges; variations; trend of development; monthly precipitation sums*

1. DATA

The statistical records of 10 stations in Bulgaria, concerning monthly and annual precipitation sums for the 1982-2010 period are analyzed. For the first decade of this period (1982-1991) the data are gathered from official National statistical year-book. For the rest part of the period (1992-2010) data are gathered from national month’s hydro-meteorological bulletins. There are missing data in 3 stations (Plovdiv, Ruse and Vratsa) for two years (1990 and 1991). Due to the lack of uninterrupted strings for more stations the exploration was restricted within these narrow limits.

2. VARIATION OF ANNUAL PRECIPITATION SUMS WITHIN THE PERIOD

As is mentioned by many climatologists [4], in more stations in Bulgaria in the beginning of 80-s till the mid 90-s were registered abnormally low annual rainfalls. On this basis the hole period (1982-2010) provisionally was divided in two sub periods (1982-1994 and 1995-2010), the second one of which was distinguished by normal and higher annual precipitation sums. The goal of the paper is to corroborate or reject this provisional division and to investigate for which months we have the statistical significant variation

of rainfalls, similar to the yearly one, and could they be used for explanation of fluctuations of the annual precipitation sums.

3. STATISTICAL METHODS

The Curve Estimation procedure in SPSS 16.0, which produces curve estimation regression statistics and related plots for 11 different curve estimation regression models, is used to determine whether the time-series exhibit a tendency either to grow or to decrease fairly steadily over time. If you select Time instead of a variable from the working data file as the independent variable, the Curve Estimation procedure generates a time variable where the length of time between cases is uniform. If Time is selected, the dependent variable should be a time-series measure. Time-series analysis requires a data file structure in which each case (row) represents a set of observations at a different time and the length of time between cases is uniform. Appling the Curve Estimation procedure for the annual data shows that the time-series have no tendency to grow or decrease, so the simple average method is used for finding the characteristics of seasonality.

Absolute size of seasonality, relative size of seasonality and seasonal indexes are calculated. In order to analyze the seasonal indexes, the following should be taken into consideration: if we accept that the typical amount of rain is 100%, then the bigger than 100% values (A%) show increasing of (A-100)%, and the smaller (B%) show decreasing of (B-100)% for each month [3].

Additionally, the Mann-Whitney U test is applied. The Mann-Whitney U test is the most popular of the two-independent-samples tests. Mann-Whitney tests that two sampled populations are equivalent in location. The observations from both groups are combined and ranked, with the average rank assigned in the case of ties. The number of ties should be small relative to the total number of observations. If the populations are identical in location, the ranks should be randomly mixed between the two samples. The number of times a score from group 1 precedes a score from group 2 and the number of times a score from group 2 precedes a score from group 1 are calculated. The Mann-Whitney U statistic is the smaller of these two numbers. In our case, the comparison is between the months with different average amount of rain for the periods 1982-1994 and 1995-2010. These months are usually January, June and September. Determining the presence of statistically significant differences is based on the p-value (the smallest significance level at which a null-hypothesis can be rejected) and the significant level (α).

4. SOME PECULIARITIES OF PRECIPITATION REGIME FOR THE PERIOD

In prevailing number of station there are no remarkable differences in mean precipitation sums for most of the months for two sub periods. The exception for almost all of the stations is September, with great increase of average rainfalls during the 1995-2010 period [1, 2]. In all cases, according the Mann-Whitney U test this growth is statistically significant (Tab. 1).

Tab. 1. Mann-Whitney U test p-value significance level

station/month	January	September
Sandanski	0,050	0,0001
Kyustendil	0,144	0,0280
Plovdiv	0,011	0,0003
Vidin	0,036	0,0010
Sofia	0,036	0,0010
Vratsa	0,050	0,0030
Pleven		0,0002
Veliko Tarnovo		0,0003
Ruse	0,030	0,0003
Varna	0,008	0,0040

In some stations there are considerable changes in mean precipitation sums in January, June, July, October, November and December. Only for the January, in five stations (Varna, Plovdiv, Ruse, Vidin and Sofia), statistically significant growth (p-value smaller than 0,05) is observed (Tab. 1). For another two stations (Sandanski and Vratsa) the p-value is at boundary level.

5. TRENDS IN PRECIPITATION REGIME

For two months with statistically significant growth – September and January are established different trends. In most stations September’s trends (in cubic function) have similar graphics with almost regular sine shape (Fig.1 and Fig.2). January’s precipitation trends (for the stations with established statistically significant growth) are linear in prevailing number of cases (Fig.3 and Fig.4).

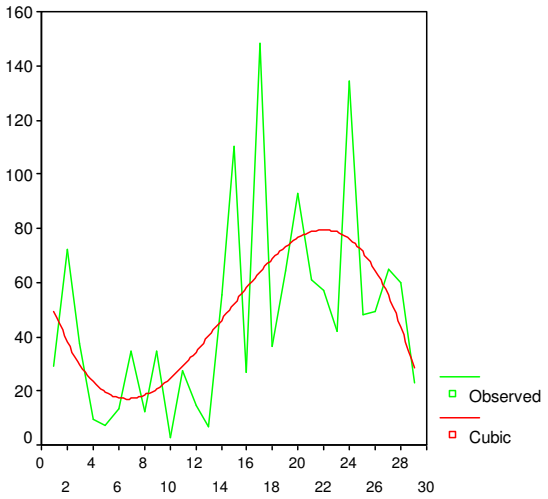

Fig. 1. September's precipitation trends - Pleven

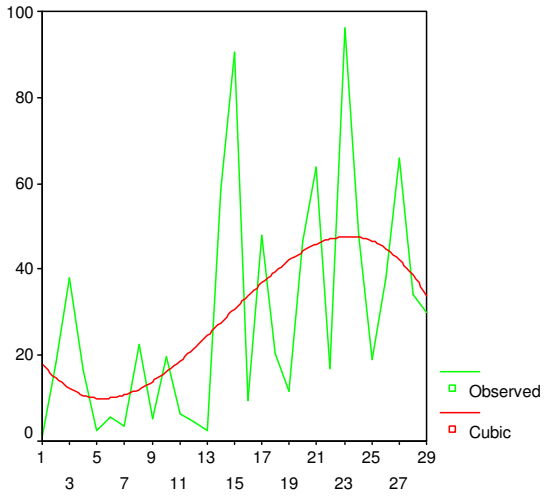

Fig. 2. September's precipitation trends - Sandanski

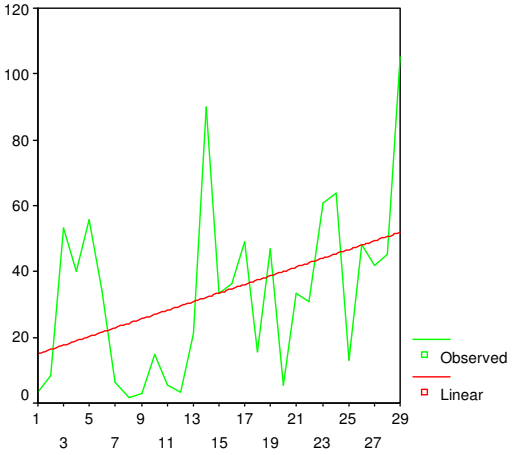

Fig. 3. January's precipitation trends -Varna

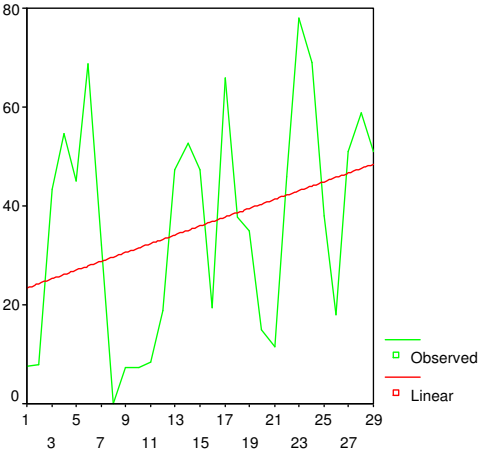

Fig. 4. January's precipitation trends - Vidin

It's very important to record that the annual rainfall's trends (in cubic function) in some stations are nearly identical with September's trends as is shown in Fig.5.

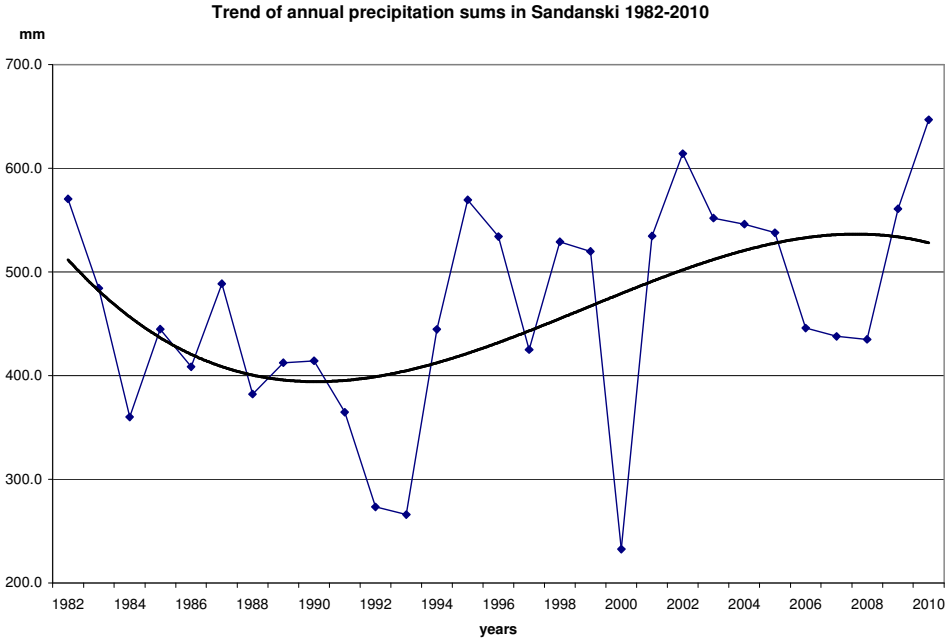

Fig.5. Observed sums and trend of annual rainfalls in Sandanski

We may clearly define descending line for the first sub period (1982-1994) and ascending one for the second sub period (1995-2010). This is valid for station Sandanski with Mediterranean precipitation pattern and for almost all stations in Tempered Continental climate zone in Bulgaria. Station Sofia make an exception, where the graphics of trends are similar, but in linear function with gradually increasing. In stations with transitional features in precipitation regime (Kyustendil, Vidin, Varna) there is no coincidence of graphics of annual rainfall’s trends and September’s trends.

Respectively, ascending graphics of January’s precipitation linear trends are like graphics of annual rainfall’s trends in stations with transitional features in climate (Vidin, Varna), as is shown in Fig.6

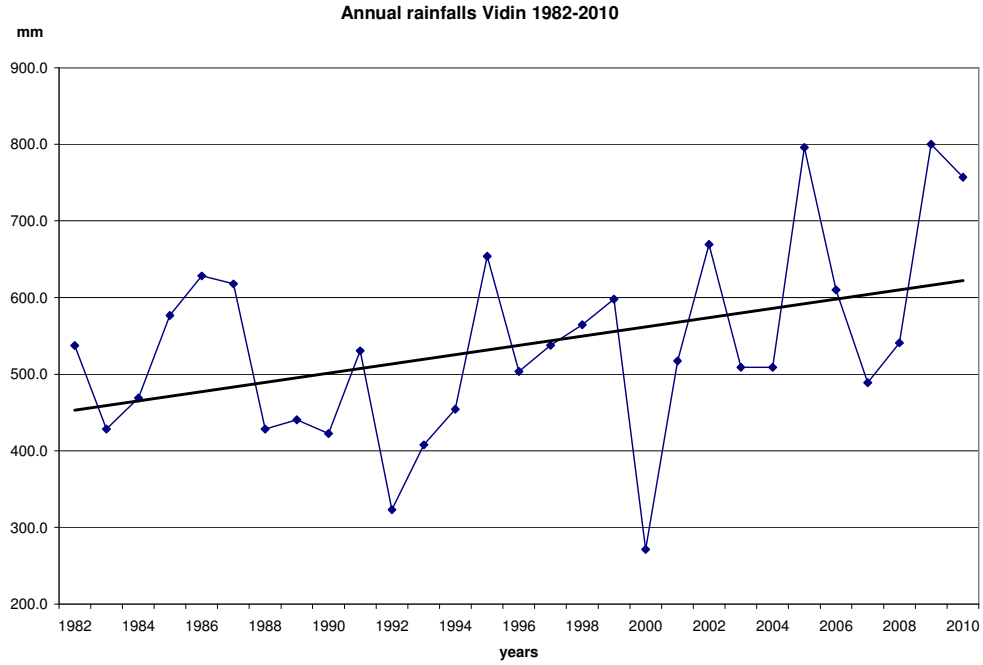

Fig.6. Observed sums and trend of annual precipitation sums in Vidin

6. CONCLUSIONS

Obtained results proves suggested null hypothesis. Established statistical significant variation of September's and January's rainfalls gives all reasons to divide investigated period (1982-2010) to two sub periods (1982-1994 and 1995-2010). In different climate zones in Bulgaria graphics of annual precipitation trends are similar with September's or January's ones. Analyzing variations of September's rainfalls a fluctuation with almost regular sine shape is determined. Previously reported increase of precipitation in September [1,2] reaches his peak 5-6 years ago and now descending trend is observed.

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Мониторинг на свлачището при г. Симитли през последните 2 години

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Абстракт*: В доклада са представени резултатите от двугодишен мониторинг на най-активното свлачище в Благоевградска област, разположено над квартал Ораново, град Симитли. За целта са регистрирани деформациите чрез многократни GPS измервания на репери, разположени в различни части на свлачището. Анализирана е връзката на скоростта на свличане с валежите, измерени в близки станции. Дискутират се динамиката на това свлачище и рискът, който то представлява за къщите в Ораново и местното население.*

Ключови думи: *Свлачище, GPS мониторинг, Симитли*

1. ВЪВЕДЕНИЕ

Свлачищата са естествени природни явления, които обаче едновременно представляват и сериозен георизк. Процесът на свличане е възможно да доведе до повреждане или пълно разрушаване на сгради, пътища и други инженерни съоръжения.

Обект на изследване е свлачището, разположено в непосредствена близост до квартал Ораново, град Симитли. В обхвата на Симитлийската котловина са описани над 50 различни по размери свлачища. Повечето от тях са консистентен тип [1]. Районът се характеризира и с висока сеизмичната активност. Тук се намира епицентърът на земетресението с най-голям магнитут, регистрирано на територията на България през 1904 г.

През пролетта на 2009 г. свлачището над Ораново значително се активизира. То е разположено на южния склон на Натин рид. Формата на свлачището в план е продълговата, като размерът на по-дългата ос с направление ССИ-ЮЮЗ е около 400 m. Ширината му в горната част е 140 m, в средната – 70 m, а в долната част до 200 m. В план площта му е около 46-47 ha, а реалната площ на повърхността е със 7-8% повече. В горната си част близо до Натин рид склонът има наклон

около 20°, но по-надолу нараства на около 25 °, след което в близост до Буков дол отново намалява.

Геоложките проучвания показват, че целият район между Буков дол и Духарски дол е изграден от неогенски седиментни скали (меот). Те са представени от пясъчници, алевролити и песъчливи глини в неравномерна алтернация помежду си. Пластовете имат генерален наклон на юг до 25°. Съвпадението на наклона на склона южно от Натин рид с наклона на пластовете заедно с наличието на глинести пластове са условия, благоприятстващи възникването на свлачищен процес [2].

Всъщност активизираното през 2009 г. свлачище е част от един значителен свлачищен комплекс, разположен между Духарски и Буков дол. Той включва общо 16 свлачища, образувани в една или друга степен вследствие на подземния добив на въглища [2]. В горната част на активното свлачище е формиран циркус, където движението става на отделни блокове, по надолу те се раздробяват и се формира свлачищен език, съставен от консистентна маса. В дъното на циркуса наклонът е малък и тук са се образували две свлачищни тераси, на които има няколко плитки свлачищни езерца. По-постоянно е езерото на втората тераса, което е дълго 35 m и има площ около половин декар. Под циркусния праг наклонът е значително по-голям – около 25°. Свлачищният език е формирал мощен свлачищен вал, който е преградил Буков дол. Зад него пролетно време се формира свлачищно езеро, което през лятото пресъхва. Поради натрупването на значително количество консистентна маса при петата на свлачището теренът е заравнен и тук е оформена третата свлачищна тераса.

За свлачището под Натин рид се знае, че периодично се активира, след което има период на затихване на движенията и стабилизация. Според местните жители под Натин рид е имало постройки, които са се напукали още през 50-те години на XX в и са били изоставени. Има и други данни за свлачищна активност преди започване на въгледобива в началото на 70-те години – през периода 1968 – 1970 г. [2]. По-късните документирани активизации са през 1992, 1994 и 1998 г. Посочени са засегнатите площи и височината на главните свлачищни откоси. Няма обаче информация за параметрите на хоризонталните премествания, а още по-малко за интензивността на движенията.

Последната съществена активизация на това свлачище започва в началото на 2009 г. От средата на същата година се провежда мониторинг на свлачището, като с помощта на GPS апаратура се определят параметрите на свлачищните деформации. **Целта** на доклада е да се представят резултатите от този двугодишен мониторинг.

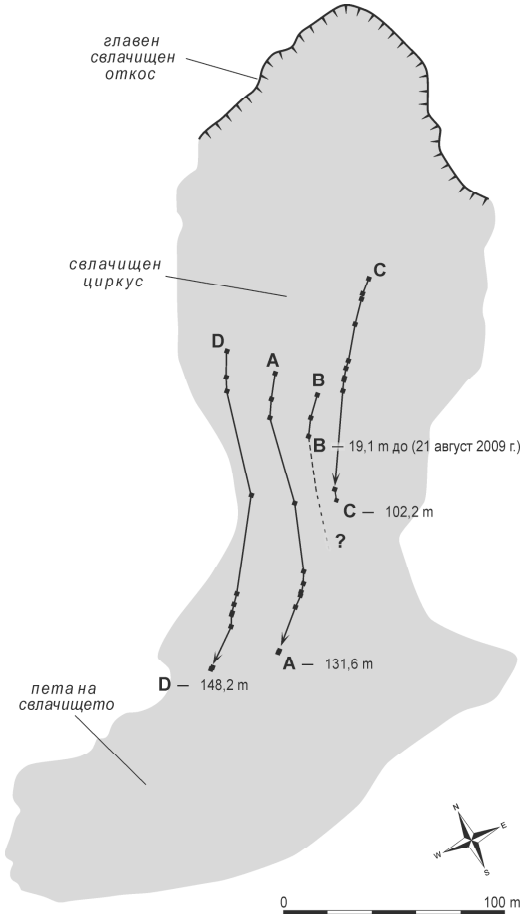
2. МЕТОДИКА НА ИЗСЛЕДВАНЕТО И ПОЛУЧЕНИ РЕЗУЛТАТИ

В световен мащаб GPS технологиите се наложиха като надежден метод за проследяване на разнообразни деформации и придвижвания. Повторните GPS измервания в определени пунктове позволиха успешно да се установят скоростите на динамични природни процеси, като движението на ледниците и дори дрейфа на континенталните плочи. Заедно с това през последното десетилетие GPS мониторингът на свлачища се утвърди и замени традиционните геодезически методи [3,4,5,6].

Периодът на наблюдение обхваща точно две години – от 6 юни 2009 г. до 6 юни 2011 г. През този период са направени общо 11 измервания: 6 юни, 17 юли, 21 август и 20 ноември през 2009 г.; 26 март, 14 май, 15 юли 28 август и 31 октомври през 2010 г.; 5 април и 6 юни през 2011 г. Подробен анализ на скоростите на движение по периоди може да се открие в публикациите, посветени на темата [7, 8]. При първите 6 измервания за определяне на координатите на реперите е използван едночестотен GPS приемник Magellan Mobile Mapper 6. За подобряване на точността на суровите данни са използвани корекции в RINEX формат от най-близката перманентна станция в Сандански. На всеки репер са направени по няколко измервания за по-голяма сигурност на резултатите. След май месец 2010 г. измерванията се извършват с GPS апаратура, включваща двучестотна антена. Конфигурацията се състои от приемник Topcon GRS-1 и антена PG-A1. С тази апаратура при използване на RTK корекции от мрежата с перманентни станции на фирма Булипос (сега SmartNet) се осигурава точност в рамките на 10-20 mm в позиция и 15-30 mm във височина.

При първото измерване бяха поставени четири репера, означени с латински букви – „**A**”, „**B**”, „**C**” и „**D**”. Три от тях са разположени на втората свлачищна тераса в линия перпендикулярна на дългата ос на свлачището, а четвъртият по-високо на първата тераса. За репери „**A**” и „**D**” са използвани дънери, а за репери „**B**” и „**C**” едри гранитни камъни. Всички репери са маркирани с боя, за да се разпознават лесно. Използването на дънери като репери се оказа значително по-удачно в това консистентно свлачище. При движението си надолу те се задържат на повърхността, докато камъните лесно може да потънат в консистентната маса и да се изгубят. Така например репер „**B**” по време на интензивните свличания през есента на 2009 г. беше изгубен и затова за него има само три измервания. По-късно в тази зона на свлачището беше установен нов репер „**E**”, като за целта беше използван сух дънер.

За целия двугодишен период на наблюдение на най-голямо разстояние се е преместил репер „**D**” (фиг.1). Неговият път, измерен по хоризонтала, е 148,2 m, а по вертикала около 47 m (при измерване с едночестотен приемник грешката по ***Z*** е значителна). Като се има предвид и движението му надолу по повърхността на склона, сумарният вектор на преместването му е с около 10 m повече. Значително хоризонтално преместване се отбелязва и при репер „**A**” – 131 m, а „**C**” изминава 102,2 m. Техният реален път също е с 6-7% повече.

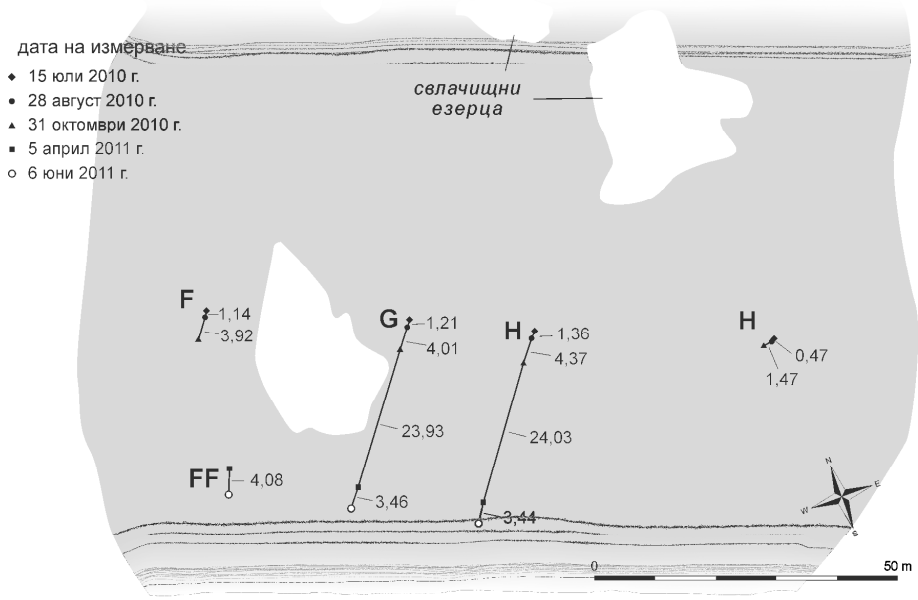


Фиг. 1. Карта с началната и крайната позиция на четирите репера, поставени на 6 юни 2009 г. и пътят, изминат от тях. Пътят на репер „**B**” е само за периода от 6 юни до 21 август 2009 г. С черни ромбчета са представени местата на реперите по време на всичките 11 измервания.

Както беше отбелязано, след третото измерване репер „**B**” потъна в свлачищната маса. За периода на измерване от 6 юни до 21 август 2009 г., обхващащ 76 дни, този репер изминава 19,1 m. За да може да се продължи мониторингът в тази зона на свлачището, от следващото измерване на 20 ноември 2009 г. се провеждат редовни измервания на репер „**E**”. Периодът продължава 563 дни и през това време реперът е изминал 103,6 м.

След изтичане на първата година на наблюдение повечето от реперите (с изключение на „**C**”) се бяха свлекли в долната част на свлачището. Следенето на свлачищния процес в циркуса и склона под него от средата на месец юли 2010 продължи с нови четири репера, означени със следващите букви от латинската азбука - „**F**”, „**G**”, „**H**” и „**I**” (фиг.2). Направени са от дървени дъски, боядисани в бяло и червено. Разположени са в права линия, перпендикулярна на

дългата ос на свлачището през около 30 m разстояние. Поставени са в горната част на свлачището на втората свлачищна тераса. Целта е при движението си надолу да се установят евентуални различия в динамиката на придвижване между източната и западната част на свлачищния език.



Фиг. 2. Пътят, изминат от новите репери поставени в средата на юли 2010 г. Отдясно е посочен размерът на хоризонталния вектор за всеки от периодите в метри.

За съжаление по различни причини и на новите репери наблюдението не можа да се извърши през целия период. При четвъртото измерване в началото на април два от тях не бяха открити. Поставеният в най-източната част на свлачището репер „**I**" вероятно е потънал в консистентната маса, противоположният „**F**" беше открит изваден извън свлачището. За този период от 13 юли до 31 октомври 2010 г. (111 дни) репер „**F**" се е преместил с 506 cm, а „**I**" с 194 cm. През същия период другите два нови репера „**G**" и „**H**" са се преместили съответно на 521 cm и 573 cm.

Целият период на наблюдение на новите репери от 13 юли 2010 г. до 6 юни 2011 продължава почти 1 година – общо 328 дни. За това време репер „**G**" се е изместил с 32,6 m в югозападна посока, а „**H**" с 33,2 m в същата посока. Наклонът в тази част е малък – 5-6 ^{o}, така че реалният тримерен път е с около метър повече.

За да не се прекъсва мониторингът в най-западната част на свлачищния циркус на мястото, където би могъл да се намира репер „**F**" в началото на април 2011 г. беше поставен отново репер, но тъй

като това вече е нов репер той беше означен като „**FF**”. От 5 април до 6 юни 2011 г. той е изминал хоризонтално разстояние от 408 cm.

Единайсетте измервания разделят двугодишното наблюдение на десет периода с различна продължителност. Ако се проследи движението на реперите през тези периоди се вижда, че на най-голямо разстояние (48,4 m) се е преместил репер „**D**” през третия период – между 21 август и 20 ноември 2009 г. Като се знае, че продължителността му е 91 дни се вижда, че средната скорост на придвижване в хоризонтално направление е била 53 cm на ден.

Когато се говори за средна скорост не трябва да се разбира, че реперът през цялото време се е движел с постоянна скорост. По всяка вероятност движението е във вид на пулсации, които са свързани със различната степен на овлажняване на свлачищната маса, което пък е свързано с количеството на валежите. За характеризиране на техния режим са използвани станциите Рилци и Сандански. Данните са достъпни чрез интернет страницата Stringmeteo [9]. В друг раздел на същата страница има и графични данни от автоматична станция в Симитли, но за съжаление данните са непълни и ненадеждни затова се използват станциите, разположени съответно на 18 и 39 km. Ежедневните данни са сумирани за всеки период. Понеже периодите са с различна продължителност, сумарните количества са разделени на броя на дните за да се получи средна стойност. Това разбира се в голяма степен е условно, тъй като различните валежи влияят по различен начин на динамиката на свлачището. Например интензивните еднократни валежи ще имат значително по-малко влияние, отколкото неколкодневен период с не много интензивни, но продължителни валежи, които в много по-голяма степен ще проникнат в почвата и така ще подхранят грунтовите води. Въпреки това, средният валеж за периода дава представа за метеорологичната обстановка през него и дава възможност за съпоставка на валежите в различните периоди.

В станция Рилци най-голямата сума на валежите е измерена през деветия период от 31 октомври 2010 г. до 5 април 2011 г. – 222,5 mm. Този период обаче е и най-продължителният – 156 дни. Като се раздели валежната сума на броя на дните, се получава 1,43 mm среднодневно. Въпреки, че този период е най-дълъг в съседната станция Сандански най-голямата валежна сума се отбелязва при предишния осми период от 28 август до 31 октомври 2010 г. – 179,9 mm, който има само 64 дни. Затова и среднодневния валеж е два пъти по-голям – 2,81 mm, което е и пикът по този показател за времето на цялото двугодишно наблюдение. Среднодневният валеж е най-голям през същия осми период и в станция Рилци – 2,78 mm. Най-сухият период и в двете станции е вторият – от 17 юли до 21 август 2009 г.

Сумата на валежите в станция Рилци е само 26,6 mm, а в Сандански – 27,7 mm, като среднодневните валежи са съответно 0,75 mm и 0,79 mm.

Ако се съпоставят среднодневните скорости на свличане със среднодневните валежи се вижда, че най-големите скорости на свличане имат реперите „**D**" (53 cm/ден) и „**A**" (44 cm/ден) през третия период, без той да се отличава с най-високите среднодневни валежи – 1,45 mm за Рилци и 1,65 mm за Сандански. Също значителна средна скорост от 36 cm/ден отбелязва „**D**" през четвъртия период при среднодневен валеж от 1,57 mm за Рилци и 1,35 mm за Сандански, а също „**A**" (30 cm/ден) и „**D**" (29 cm/ден) през първия период, когато среднодневният валеж в станция Рилци е бил 2,49 mm, а в Сандански със съответно 1,65 mm.

Най-малките средни скорости от 1 см на ден се отбелязват при същите репери „**A**" и „**D**", но в последния десети период от 5 април до 6 юни 2011 г. През този период действително се отбелязват и едни от най-ниските стойности на средните ежедневни валежи в станция Рилци – 0,79 mm. В другата станция обаче тази стойност е почти два пъти по-висока – 1,27 mm, но трябва да се отчита, че тя значително по-отдалечена. За малките средни скорости на реперите „**A**" и „**D**" освен по-малките валежи голямо значение има и това, че те тогава се намират в петата на свлачището, където наклонът е малък. Доказателство за това, че мястото има решаващо значение за скоростта на свличане са представените по-горе високи средни скорости на същите репери през третия и четвъртия период, когато те се спускат по стръмния склон под свлачищния циркус.

Другите репери също отбелязват своя пик в средните скорости на свличане, когато преминават през стръмния участък. Репер „**C",** докато се намира в свлачищния циркус през различните периоди, се придвижва със средни скорости между 3 и 13 cm на ден. При навлизането си в стръмния участък през деветия период от 31 октомври 2010 г. до 5 март 2011 г. този репер увеличава скоростта си до 29 cm на ден. Репер „E" има повече измервания по време преминаването му през стръмния участък. През четвъртия и петия период скоростта на свличане е 23 cm/ден. През шестия период между 14 май и 15 юли 2010 г. тя намалява на 14 cm/ден, а през следващия седми, продължаващ до края на лятото (до 28 август), скоростта намалява до 6 cm/ден. През осмия период тя се увеличава на 17 cm/ден, но максимумът за този репер се отбелязва през деветия период от 31 октомври до 5 април, когато тя е била 27 cm/ден. Анализът на данните показва, че свличането се редуцира съществено през летните месеци юли и август, докато през зимата скоростта е много по-голяма.

Същата закономерност се забелязва и при анализ на скоростите през различните периоди на новите репери. През седмия период (който се явява пръв за тяхното наблюдение) реперите „**G**” и „**H**” имат еднаква скорост – само 3 cm/ден. През осмия период скоростта нараства на 6 cm/ден за репер „**G**” и 7 cm/ден за „**H**”. През следващия период – зимата на 2010 – 2011 г. и двата репера се придвижват средно с 15 cm /ден. Скоростта им намалява отново синхронно през последния десети период на 6 cm/ден. Трябва да се има предвид, че и през четирите периода двата репера се придвижват в горната част на свлачището преди стръмния участък.

3. ЗАКЛЮЧЕНИЕ

Най-голямо влияние върху скоростта на свличане има наклонът на склона. Това се доказва от факта, че всички репери, когато преминават през стръмната част между свлачищния циркус и петата на свлачището увеличават скоростта си. Валежите също имат значение, но то по-ясно се изразява когато реперът се намира в зона от свлачището с еднороден наклон. Други климатични елементи, които имат влияние са температурите и влажността на въздуха. Придвижването на реперите значително се намалява през втората половина на лятото, когато температурите са високи, влажността малка, което води до съществено изсушаване на свлачищната маса. През студеното полугодие свличането е по-интензивно, дори когато валежите не са толкова високи. Тогава влажността на въздуха е значително по-голяма, изпарението е малко и свлачищната маса е силно овлажнена, което благоприятства свличането.

Засега свлачището не е засегнало пряко къщи от квартал Ораново. Опасността обаче не е само пряка, но и косвена. Сериозен риск представлява образуваното езеро при преграждането на Буков дол. По време на проливен дъжд, то би могло внезапно да прелее и ерозионно да прореже неспоената свлачищна маса, като се образува мощен кално-каменен поток, който да причини сериозни разрушения и жертви.

Идея за това какъв риск представляват водните обекти в свлачището дават последствията от внезапното свличане на 14 март 2010 г. на част от основния откос в по-голямото езеро, намиращо на първата свлачищна тераса. В резултат на това голяма част от водата беше изтласкана надолу по склона, което предизвика паника сред населението на квартал Ораново. По това време езерцето е имало площ не повече от половин декар, а дълбочината му под един метър. Завиряването на Буков дол е възможно да доведе до образуването на значително по-голямо езеро.

За ограничаване на свличането и предотвратяване на такива инциденти в средата на август 2010 г. община Симитли изгради канал, който отводнява голямото езеро на първа тераса и езерото на втора тераса, а под него водата се извежда извън територията на активното свлачище с PVC тръби. Тази мярка е временна, защото при постоянното движение тръбите се разглобяват и водата изтича отново в свлачището. Това прави дренажната система неефективна Доказателство за това са сходните средни скорости през студеното полугодие (когато би трябвало да се почувства ефекта по-силно) на реперите, намиращи се в свлачищния циркус. През третия период преди прокопаването на канала репер „**C**" има средна скорост от 13 cm/ден, която дори е по-малка от тази на „**G**" и „**H**" – 15 cm/ден през деветия период. За ограничаване на риска, свързан със свлачището е необходимо да се потърси трайно решение, като специално внимание трябва да се обърне на езерото, образувано при преграждането на Буков дол със свлачищна маса.

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Background contamination of trace elements in soils of Strandzha's reserves Tisovitsa and Sredoka

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***Abstract**: The paper presents the results of the landscape-geochemical investigation carried out in two reserves that are part of nature park "Strandzha". These areas are considered as intact and the results can be treated as background for the concentrations of trace elements. The radial geochemical differentiation of some trace elements such as copper, lead, zinc, cadmium, cobalt and nickel in the soil layers and the vegetation cover has been studied. A comparison of other background areas in Bulgaria has been made.*

***Keywords:** Geochemistry, Landscapes, Background monitoring, Strandja*

1. INTRODUCTION

The ecological-geochemical studies in nonanthropogenic areas such as natural parks and reserves are necessary for determination of technogenic impact. One of the main characteristics in forecasting of the impact of environmental pollution is the determination of background concentration of the elements in nature landscapes. This is a leading geochemical standard for quality of environment in ecological-geochemical evaluations.

The regional geochemical background is a basis for establishing standards of hygiene for quality of the environment. The local geochemical background is a basis for evaluation of particular geochemical anomalies – natural and anthropogenic [1].

When background rates for evaluation of ecological hazard for heavy metal pollution are missing, the average concentration of the elements in the environmental element like soil, water, vegetation, rocks in the world or in Bulgaria and standards of hygiene (limited concentrations) are used. They are determined experimentally and the parameters are not correct.

The researches proved that the diversity of soil formation conditions determinate the formation on different levels of concentration of heavy metals in the soils in similar genetic groups [2, 3]. The process is similar for the other landscapes elements. The determination of local background levels of concentration of heavy metals in soils in a given region is more important, than using of average concentration or hygienic rates.

For the goal of landscape-geochemical investigations in background territories priority must be the typicalness. It determines the key peculiarities of the geochemical state in wide regions.

The main objective of the present study is to determine the concentration and radial differentiation of the chemical elements Cu, Pb, Zn, Co, Ni, Mn in the soil and parts of the forest vegetation in typical intact reserve territories in Nature Park “Strandzha”. The results will be compared with similar studies from Bulgaria and the world.

2. STUDY AREA AND METHODS

The reserves “Tisovitsa” and “Sredoka” are situated in northeastern and southwestern part of Nature Park “Strandzha”. They have been created for protection of valuable forest landscapes with domination of oriental durmast (*Quercus polycarpa)* and oriental beech (*Fagus orientalis*). The protected area of “Tisovitsa” reserve is 749,3 ha while “Sredoka” reserve has 607,8 ha. They are situated at elevation ranging from 250 to 350 m on the slopes of Bosna ridge and the water divide ridge between the rivers Veleka and Rezovska.

The rocks in the study area are represented by the volcanic-sediment complex of senon, that imclude tuffs, tuffits, sands, conglomerates, alevrolites etc [4, 5]. There are outcrops of metamorphic rocks in the “Sredoka” reserve– methapelites, metaalevrolites with thin lines of marble with Plaeozoic - Lower Triasssic age.

The region is part of the area with Mediterranean climate characterized by autumn-winter maximum of rainfalls, low annual temperature amplitudes and longer period of transitional seasons [6]. The rainfalls are above the average quantities of the country and increase from the seacoast to the interior part. The station Tsarevo, located on the coast, has 650 mm, while the station Gramatikovo has 857 mm and station Malko Turnovo 969 mm. The average annual relative humidity of the air is high (75-78 %) as a result of the breezes in the valleys of the rivers Veleka and Rezovska.

The soils determined transition between cinnamon soils and yellow soils (*Alisols*) in the reserves.

The forests cover 95-98 % of the study area. The forests of *Fagus orientalis* formed on shallow cinnamon soils (ph 5,0-5,5) cover negative relief forms. The wide water divide ridges are covered by oak forests

(dominated by *Quercus polycarpa*, *Quercus fraineto*), in some places with beech forests developed on leached cinnamon soils (ph 5,0-5,6). The specific formations for Strandzha Mountain such as *Rhododendron ponticum, Laurocerasus oficinalis, Daphne ponticum, Ilex aquifolium, Taxus baccata, Vaccinium arctosaphylos, Pyracantha coccinea, Mespilus germanica, Sorbus torminalis, Sorbus domestica* etc. are distributed in wet valley areas [7].

The goal of the field and laboratory investigations is to reveal the spatial specificity of heavy metals concentration in the soil and vegetation cover. The soil samples from all genetic layers and leaves from oriental durmast and oriental beech are collected for chemical analysis.

The Chemical analysis has been carried out in Central laboratory of general ecology of Bulgarian Academy of Sciences using by the method of atom absorption with spectrophotometer (AAS) – Perkin-Elmer 3030B.

The coefficient for Radial differentiation (R), which is a ratio between the content of the elements in soil horizons, or vegetation and their concentration in the bedrock, is used to determine the migration of elements in the system soil-rock. Using this coefficient we can follow the migration flows in vertical direction (upward and downward) and the concentration in different geochemical barriers.

To achieve this goal, two profiles have been sampled in both reserves. The first one is in the “Tisovitsa” reserve and represents typical environment for Strandzha Mountain. It is situated on the degrade ridge of Murzevsko kale peak (288,9 m) in mixed oak forests with shallow cinnamon soils on metamorphic rock – quartzite.

The second profile is situated on rectilinear slope of Gradevski hill (310 m) in oriental durmast forest and cinnamon soils in “Sredoka reserve”.

3. RESULTS AND DISCUSSION

The concentrations of the investigated microelements in the soils have higher values in the genetic horizons of “Sredoka” Reserve. The accumulation of biophilia elements as zinc, lead, cadmium and manganese in the uppermost “A” horizon is typical for both profiles. Only the copper is not accumulated in uppermost horizon. Its values for “Tisovitsa” reserve are even lower than background values for cinnamon soils in Bulgaria. The concentration of cobalt in the soils of the “Tisovitsa” reserve is one of the lowest in Bulgaria. The values are comparable to the lowest concentration of cobalt (1,7 -3,9 mg\kg) in yellow soils sampled near the village of Bulgari, which is located near the study are [8].

Table 1 Concentration of heavy metals (mg/kg) in genetic horizons in soils of the reserves Tisovitsa and Sredoka

oil horizons – depth (cm)	Cu	Pb	Zn	Cd	Co	Ni	Mn	pH
A (0-12) "Tisovitsa"	7.33	22.79	69.37	0.390	1.58	2.77	495.70	5.02
B (12-32) " Tisovitsa"	17.23	19.16	51.69	0.210	2.80	4.30	548.59	5.07
C (32-33) "Tisovitsa "	23.32	14.55	52.42	0.190	3.18	11.36	211.29	5.50
A (0-15) " Sredoka "	37.34	19.97	108.28	0.280	10.13	27.21	651.99	5.50
B (15-20) " Sredoka"	45.66	15.76	62.88	-	12.68	32.98	457.59	5.60
C (30), " Sredoka"	64.28	12.98	55.62	-	13.85	41.55	523.59	5.60

The analysis of the data from Table 1 and Table 2 are showed correlations between concentrations of the element in investigated region with the data from background regions in Bulgaria. The acid metamorphic rocks dominated in the region. Concentrations of the researched microelements for Bulgaria are comparative with these in investigated region.

The concentration of cadmium in acid metamorphic rocks is higher than the average concentration in the lithosphere. As it is typical catiogenic halkophillic element it actively migrates in acid environment. This explains the double greatest concentration in the horizon “A” in the soils of the “Tisovitsa” reserve in comparison with “C” horizon. Its mobility in acid soils facilitates hundred thousand times more effective extraction absorption by the vegetation.

Only the concentrations of zinc in reserve “Sredoka” is higher then all concentrations in Table 2. The concentration in surface horizon “A” is over limited concentrations. This is result of bioecological activity of this element in “A” horizon. It is proofed of radial differentiation of this element in both soil profiles.

The average concentrations are below the limit concentrations in acid pH environment, concerning of hygienic standards for background concentrations in soils for Bulgaria.

Mn and Cd (2,35 and 2,05) have average state of radial differentiation in “Tisovitsa” reserve, while Pb and Zn (1,57 and 1,32) have poor (Fig. 1). The accumulation of these elements in uppermost horizon is as a result of its high biophilic and alkalis-acid environment conditions. All these elements have which active migration in more acid environment and have important function in the metabolism of the vegetations. The concentration of

manganese in the uppermost horizon is determined by its high concentration in the litter, which transformed into humus in the future.

Table 2 Concentration of heavy metals (mg/kg) in the rocks [9], soils in world [10], soils in Bulgaria [11,12], soils in background regions in Bulgaria [13], cinnamon soils [14] and Limited concentrations of soils in Bulgaria [15]

	Cu	***Pb***	***Zn***	***Cd***	***Co***	***Ni***	***Mn***
Acid metamorphic rocks	20	20	50	2.4	11	10	387
Soils in world	20	10	50	0.5	8	40	900
Soils in Bulgaria	30	35	75	0.06-0.7	15-25	36	1000
Soils in background regions in Bulgaria	24	25	67	0.03	17	28	695
Cinnamon soil in Bulgaria	21.8	19.7	65.6	0.19	14.7	24.1	729.6
Limited concentration in pH $\leq$ 6 in soils Background concentrations	34	26	88	0.4	20	46	850

Cadmium is the only element which is not important for the vegetation, but it is absorbed by roots system and leaves [16]

it is noteworthy the higher concentration of catiogenic element Co in the leaves of east oak in spate of registered lower concentrations in the soil. It is as a result of the active absorption of the tree vegetation. The trees, especially oak, actively absorb cobalt in comparison to the bush and grass vegetation [17].

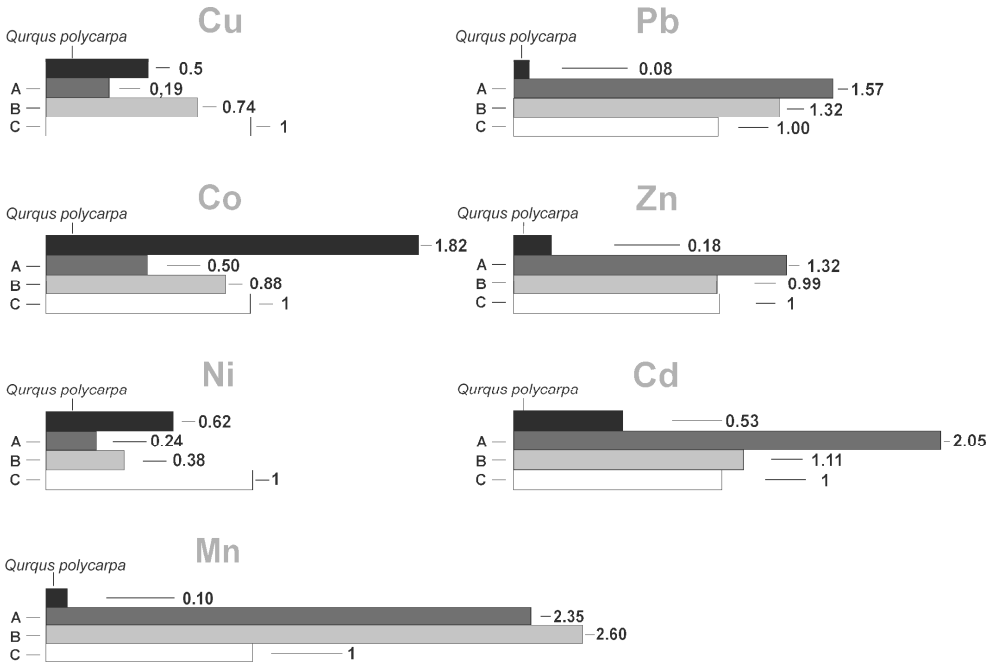

Fig. 1 Vertical differentiation of heavy metals in soils horizons of Chromic cambisols and oriental durmast (*Quercus policarpa*) in reserve “Tisovitsa”

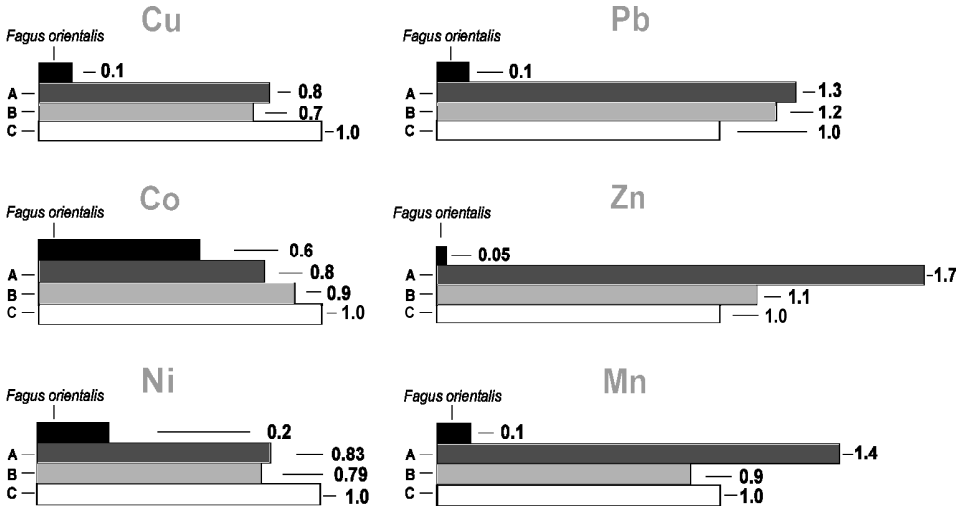

Fig. 2 Vertical differentiation of heavy metals in soils horizons of Chromic cambisols and oriental beech (*Fagus orientalis*) in reserve “Sredoka”

The results are comparable with the values of heavy metals concentration in leaves of *Quercus pubescens*, formed on andesite in Eastern Stara planina [18]. There are more differences in the

concentrations of zinc, nickel, manganese and especially cobalt. The zinc is 2-3 times lower and the nickel is 3-5 times higher. The most interesting are the differences in the concentrations of the cobalt. In leaves of oriental durmast in “Tisovitsa reserve” it is 80 times higher [19].

The profile of “Sredoka” reserve (Fig. 2) shows higher concentrations of zinc, manganese and lead in the horizon “A” in comparison with the horizon “C”, while there is no data for cadmium. The higher concentration is due to the biophilic character of these elements and similar alkali-acid conditions as in the precede profile. At the same time the copper, which has phitotoxic effect, decreases its concentration from the uppermost horizon of the soil. This can be explained with the lythogeochemical basis, where the concentrations of these elements are low. The type and substrate of soil formation rocks are among the main factors that determine the basic geogenic concentration of heavy metals and metalloids in the soils [9].

The cobalt is the element with the highest concentration in the leaves of the oriental beech, as in the precede profile. The concentration of zinc is lowest. Probably, the zinc is concentrated or blocked in the roofs of the vegetation. It is the element with the highest concentration in the radial differentiation in horizon A of the soil profile.

4. CONCLUSION

The geochemistry of every one of the investigated elements has specific peculiarities in their migration and concentration in the soils horizons and in the vegetation. Taking into account the fact that we assume the region as background (without significant anthropogenic influence), the leading elements for organization of background monitoring of nature environment, are zinc, copper, lead, cadmium and manganese.

The zinc has higher concentration in the study area in comparison with the background values, which is as a result of lythogeochemical peculiarities in the region. In the “A” horizon of the soils its concentration is higher than average values in Bulgaria in both profiles.

The geochemistry of copper shows specific peculiarities connected with the low level of radial differentiation, which determines its poor mobility in profile and the three times higher concentrations than the average concentrations for the world and Bulgaria in “C” horizon of cinnamon soils (*Chromic cambisols*) in reserve “Sredoka”. Although, it is one of most mobile elements in hypergenic processes the copper can form compounds with poor mobility, which stay prolonged time in the soil profile. Lythogeochemical peculiarities are also decisive for the higher background. Malko Turnovo region is a copper ore producing region.

The lead has an average level of radial differentiation in the soil profile, which determines low accumulation in “A” horizon. Its concentration is

background and comparable with the concentration in the other regions of Bulgaria and the world.

The concentration of manganese in the uppermost soil horizons is a result of accumulation of organic substances in the soils. They are result of degradation of thick layer of litter, formed under oak and beech forests in the both reserves. The concentrations are lower than the background concentrations for Bulgaria and the world.

The bedrock, tree vegetation and alkali-acid conditions determine the higher concentration of cadmium in the surface soil horizon of the Tisovitsa reserve. Its concentration is higher than the concentration in the other background regions in Bulgaria and also for cinnamon soils. They are comparable with the average concentrations in the soils of Bulgaria.

The distribution of the cobalt in the profile rock-soil-vegetation shows strong migration in radial direction and concentration in the vegetation. The concentrations in the soils are among of the lowest in Bulgaria.

The nickel shows relatively low rate of migration in radial direction. Its concentration is comparable with the background concentrations of this type of soil in Bulgaria and the world.

We consider that the final results of the study are representative for the background landscape-geochemical structure of the Nature Park “Strandzha”. Taking into account the complexity and diversity of the factors in the region it is necessary to conduct more detailed and complex investigations in different hypsometric levels in the area.

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PROBLEMS FOR THE ENVIRONMENT CAUSED BY THE CONTAINERS FOR STORAGE OF WASTE

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Annotation: *With bringing into use of the plastic containers for waste in the places of residence, it was found that they are not appropriate because of the following reasons: in the places of residence people use solid fuel (coals and wood); they are unstable at mechanical hit – they break easily, they ignite from the thrown away waste (ash and cinder); because of their fragility the lids are missing or are open all the time; the containers that are out of use are being heaped in storages, where they take a lot of place and are an unpleasant view.*

Key words: *Containers, fire, pollution, waste, environment.*

1. INTRODUCTION

The researches of the condition of containers for waste located in the places of residence show that many of the containers for separate collecting, as well as these for daily waste made of plastic, are damaged, broken and in many cases burnt.

The practice shows that after the commissioning of the plastic containers many of them have been burnt as a result of throwing away ash and cinder that were not extinguished, deliberate fire-raising by unconscionable citizens, as well as, self-ignition of greasy threads thrown by service - stations and textile materials and others. This contributes for the pollution of the surrounding air space with products for burning.

In practice it was found that the plastic containers are unsuitable for places of residence where there are no central steam heating, and local heating installations with solid fuel (wood and coals) are used. It should be taken into consideration that in these containers people

throw away waste that during burning releases highly toxic substances – these are animal and vegetable fats, wool, cotton fabrics, threads, greasy threads from service-stations.

From financial point of view the price of a plastic container is lower than the price of a metal one. But they are unsuitable because of the fact that when the waste in them burns they burn too and in this way they go out of use. Thus they are an additional problem for the environment. The balance shows that not only the expenses for their replacement are higher but the burning of these containers contributes for the pollution of the surrounding air space.

The cases, when containers that are out of use are being heaped in big amounts and take a lot of space, are not rare. They are potential danger for the environment as well as an unpleasant view.

1.1 Formulation of the task. Purpose of the research.

The purpose of the present report is to make a research of the fires occurred in containers before the commissioning of the plastic containers and after that. To ascertain the reasons for their formation from the point of view of pollution of the surrounding air space with harmful substances and the financial damages that were caused.

The task is to be created an organization for specialized collecting and transportation of the generated waste from service-stations, sewing factories, restaurants, food shops and preventing their self-ignition and the highly toxic pollution. To be given a proposal for replacement of the plastic containers with metal ones.

2. CONDITION OF THE PROBLEM

It was made a research about the condition of the containers for waste collecting on the territory of Blagoevgrad, located near to different objects – restaurants chains, building sites, sewing factories, service-stations, as well as the containers near to residential and public buildings and health centers.

Burnt metal containers and melted plastic ones can often be seen. And there some that are mechanically damaged: with a cracked corpus or a damaged or missing lid.

The research confirms that the main problem is the insufficient culture of the citizens about the use and preservation of the containers for waste.

Often the reason for the ignition is the throwing away of ash and cinder, unextinguished cigarettes, self-ignition of greasy threads

thrown away by the service-stations. There are cases of deliberate fire-raising.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Table1.[1]

№	*Materials*	*Products of burning and decay*
1	Wood and other cellulose materials	Carbon oxide, carbon dioxide, water, dehydrololysacchride, acrolein, aldehydes, high-molecular volatile substances, vinegar acid.
2	Wood planks	Carbon oxide, carbon dioxide, water, dehydrololysacchride, acrolein, ammonia, aldehydes, hydrogen cyanide, nitric oxides, chlorinated hydrocarbons.
3.	Cotton	Carbon oxide, carbon dioxide, water, methyl alcohol, acrolein, acetone, vinegar acid, formic acid
4.	Wool	Carbon oxide, carbon dioxide, ammonia, amines, nitrogen oxides, hydrogen cyanide, aldehydes, ketones and others
5.	Polyester , including threads	Carbon oxide, carbon dioxide, acrolein, aldehydes, ketones, hydrogen cyanide, styrene, nitric oxides
6.	Polyamide, including threads	Carbon oxide, carbon dioxide, ammonia, acetonitril, caprolactam, pyridine, pyrrolidine, methylperidin, diazomethane, benzonitril, nitric oxides, aldehydes, ketones
7.	Polypropylene	Carbon oxide, carbon dioxide, forlamdehyde, acetaldehyde, propylene
8.	Polyacrylic	Carbon oxide, carbon dioxide, acrylonitrile, ammonia, hydrogen cyanide, dicyanogen, divynil, nitric oxides
9.	Polyethylene	Carbon oxide, carbon dioxide, ethylene, methane, ethane, propane, propylene, butane, butane, paraffin, cycloaliphatic hydrocarbons, formaldehyde, acetaldehyde
10.	Polyurethane, including stiff and elastic penopolyurethane	Carbon oxide, carbon dioxide, hydrogen cyanide, nitric oxides, isocyanates (toluendiisicyanate, dimetilbenzilamin), acetonitril, pyriline, benzonitril, aniline, methane, ethane, acetaldehyde
11.	Polystyrene, including penopolystyrene	Carbon oxide, carbon dioxide, benzene, toluene, styrene, dimmers and trimmers of the styrene, ethylbenzene, acrylonitrile, hydrogen cyanide, nitric oxides
12.	Polymetrilmetacrilat	Carbon oxide, carbon dioxide, methylmethacrilat, saturated and non-saturated hydrocarbons
13.	Epoxide materials	Carbon oxide, carbon dioxide, epichlorhydrine, benzene, toluene, acetaldehyde, amines, nitric oxides
14.	Polyvinylchloride	Carbon oxide, carbon dioxide, methane, ethane, acetylene, propane, propylene, benzene, toluene, xylol, phosgene, hydrogen chloride, and other chlore-hydrogen combinations
15.	Amine-formaldehyde materials	Carbon oxide, carbon dioxide, ammonia, methylamine, phenol formaldehyde, hydrogen cyanide
16.	Phenols and phenol formaldehyde materials, including plastic foams.	Carbon oxide, carbon dioxide, hydrogen fluoride, hydrogen chloride, hydrogen cyanide, phenol, forlamdehyde, methyl alcohol, ammonia, formic acid

Figure 8.

Figure 9.

According to the official information for the incidents, issued by the Regional Directorate of Fire safety and Rescue – town of Blagoevgrad for the period from 01.01.2001 to 31.12.2010 were registered 78 cases of ignited containers. 73 of them are for the period 2007-2010 (Diagram 1). 16 of all the fires were registered in metal containers, and 60 in plastic ones. (Diagram 2)

Table 2. Total number of fires registered in containers for the period 2001-2010 [2]

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
January								1	1	4
February								3		2
March									1	1
April								1	1	1
May								1		
June										2
July								2	7	3
August								3	2	4
September			1					4	1	1
October							1	1	1	7
November		1			1			1		3
December							3		3	7

Table 3. Total number of destroyed containers for the period 2001-2010 [2]

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
January								1		4
February								3		
March										1
April										
May								1		
June										2
July								3	6	1
August								2	1	3
September								3	1	1
October										6
November										2
December							3		2	5

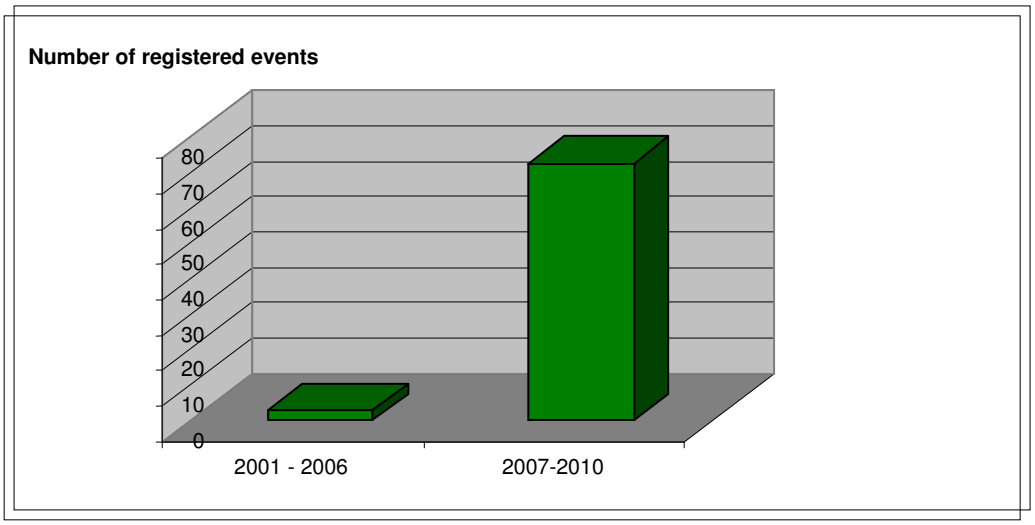

Diagram 1. [2]

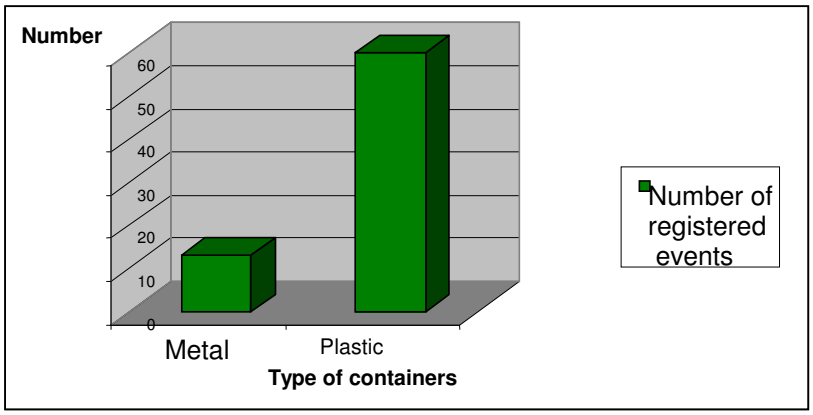

Diagram 2. [2]

Graphics 3, 4, 5 and 6 show the number of fires occurred in containers and their annual distribution according to seasons for the period 2007-2010.

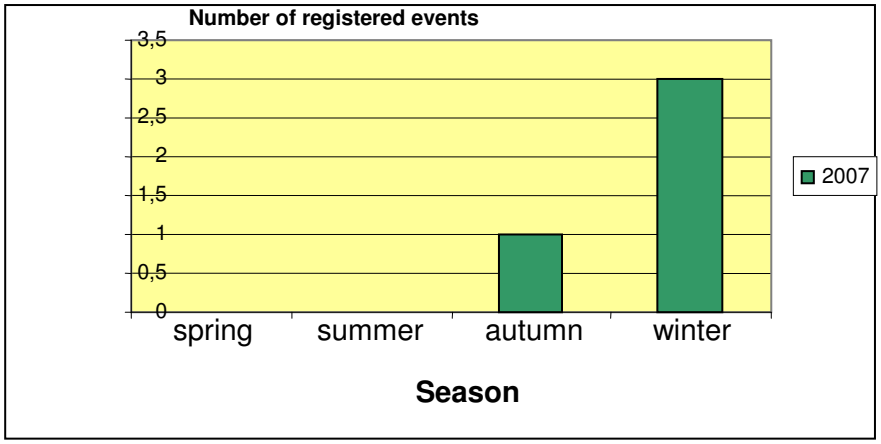

Diagram 3. [2]

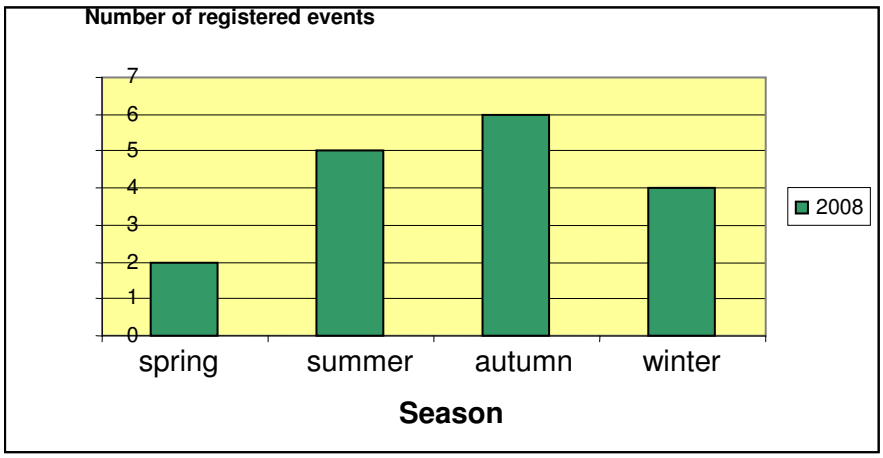

Diagram 4. [2]

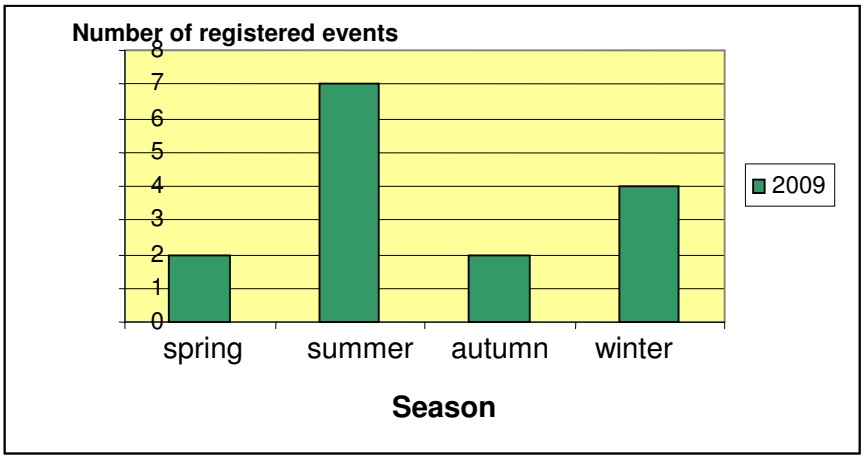

Diagram 5. [2]

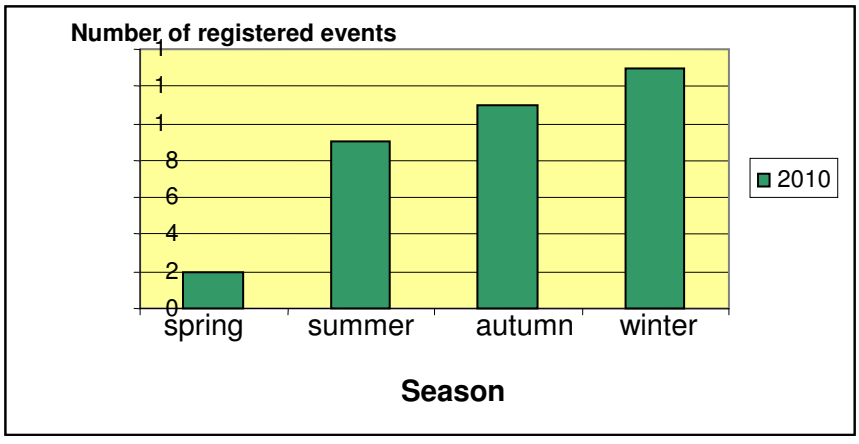

Diagram 6. [2]

Diagram 7 shows the distribution of the fires occurred in the spring-summer and autumn-winter period for 2007-2010. The number of the fires occurred in the autumn and winter is higher.

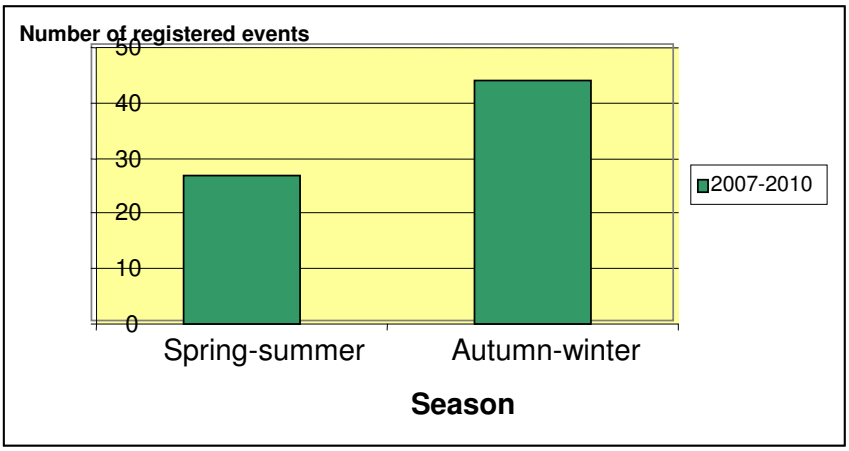

Diagram7. [2]

It became clear from the researches and on the basis of the required information for the fires occurred in containers for the period 2001-2010, received by the Regional Directorate of Fire Safety and Rescue- town of Blagoevgrad, that in the months September- February (autumn-winter period) the number of the registered fires is bigger compared to these registered in the months Match-August (spring-summer period).

The autumn-winter period is related to the use of heating. Moreover these are the months of the year which are described with the formation of stable temperature inversions. This means that in the ground air layer is formed a defence and the toxic gases cannot go higher in the air and that leads to pollution of the surrounding air environment.

The observation shows that these spot fires in the containers pollute the surrounding air environment for hours. If something like this happens near to health centers, kindergartens, homes for old people, buildings with a lot of people is possible to cause intoxication to the residents of these buildings even though it is temporary.

The long stay in the conditions of pollution has negative effect on asthmatics and especially on pregnant women and small children. [3]

Diagrams 8, 9, 10, 11 show the number of containers destroyed after fires occurred for the period 2007-2010, arranged by years.

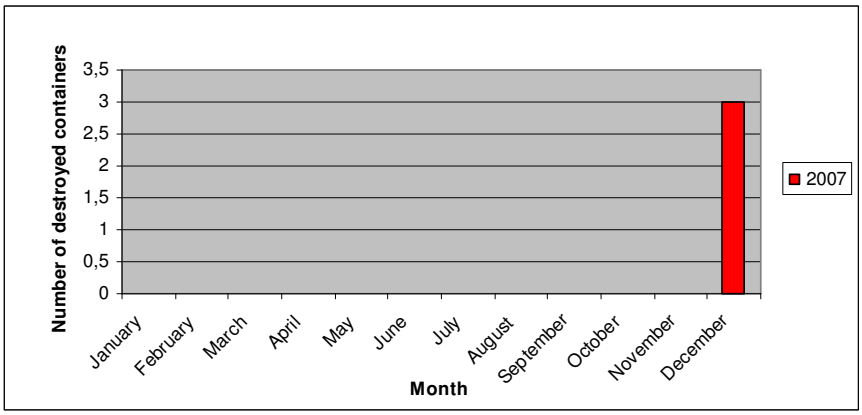

Diagram 8. [2]

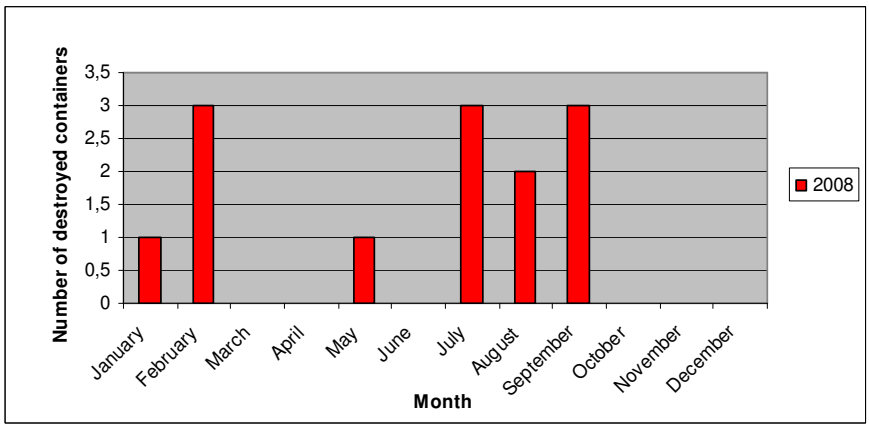

Diagram 9. [2]

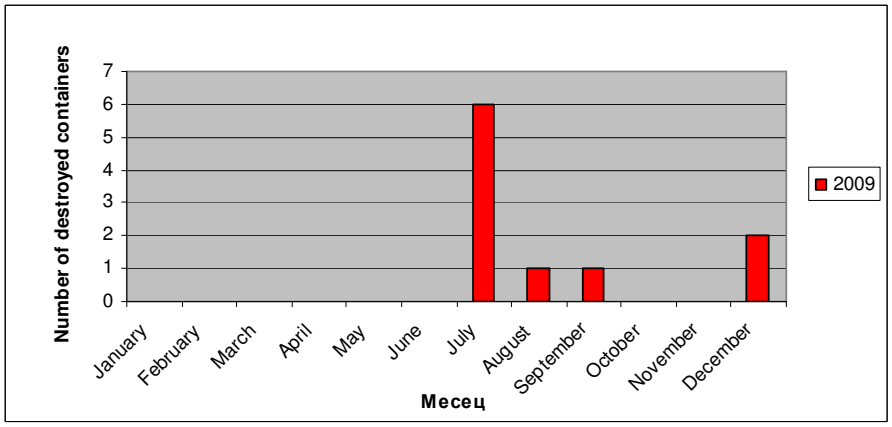

Diagram 10. [2]

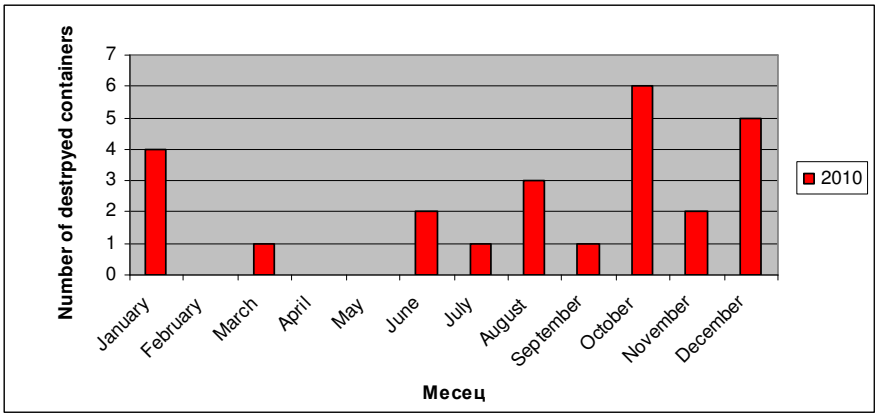

Diagram 11. [2]

As a result of the 60 fires occurred in plastic containers the number of the burned containers is 50.

This shows that in these areas metal containers should be used. It is also necessary to be created an organization for the collecting and transportation of the waste to the depots generated by the service-stations, sewing factories, restaurants and food shops for preventing the ignition and release of toxic substances.

The containers that are out of use are heaped in storages where they take a lot of place. It is necessary to be introduced a special programme for their recycle and this is connected with spending of additional funds. In addition the piles of containers are an unpleasant view.

CONCLUSIONS

- The plastic containers should be placed away from buildings with a lot of people such as kindergartens, schools, health centers, restaurants.

- From economic point of view the use of metal containers is cheaper.

- From a point of view of pollution of the environment with noxious substances the use of plastic containers should be stopped.

- It is necessary the problem with the condition of the containers to be put for consideration to the Municipal council of Blagoevgrad. The replacement of the plastic containers with metal ones will contribute for saving money to the municipality because even

though they are more expensive they can be used for longer period of time and are resistant to fire.

Figure 10.

3. LITERATURE

[1] T. Gradev, “Scientific and technical collection PO”, copy 3, from 1983 r.

[2]. Information for the incidents from 01.01.2001 to 31.12.2009 containing the word “container” required from the Regional Directorate of Fire Safety and Rescue.

The Free School Bus - Helping or Worsening the Problem of Village Depopulation? The Experience of Municipality of Blagoevgrad

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Abstract*: In 2008 a new social program started in Blagoevgrad municipality. Students from elementary schools located in the near villages begun to travel daily to the municipal center, due to closing their village elementary schools. This had double-sided effect on them and their families. From one side they started to receive high quality educational services without extra payment. Their transportation was also free of charge. On the other hand children had to travel different distances daily. The following survey investigated how this educational reform affected one of the most important and problematic processes in Bulgarian villages during the past decades – their depopulation.*

Keywords: *education, village depopulation, municipality of Blagoevgrad, Bulgaria*

1. INTRODUCTION

Present stages of life and urbanization in Bulgaria are an interesting object of investigation. During the past 25 years here were observed unique processes of population migration, distribution and depopulation. They originated from the shocking and general changes in Bulgarian political and socio-economic structure and everyday life, after changing the political and economic structure of the country. Most of these processes were barely expected and caused considerably deeper changes in people's lives than in other "older democracies" in Europe and the world. Demographic processes in Bulgaria after 1989 showed rapid changes in all the basic demographic indices. What elsewhere took decades, here needed only several years.

The demographic situation that emerged was among the worst possible. Sudden breakdown in the population number was observed, due to mass emigration. Birth rate levels reduced fast, followed by an increase of death rate and a negative population growth. Total population number melted down by 15%. In attempt to avoid approaching unemployment people undertook a mass internal migration from the villages and small towns to the big ones, especially the capital city. All these processes happened in a developed European country, not in a Third World one. The

difference came from the advanced educational and healthcare systems, and the good infrastructure as well. What followed, was a painful demographic situation, that combined negative features typical both for the advanced and the Third World countries. And this all happened very fast. For approximately one decade.

In order to provide a good educational service to the children of Blagoevgrad municipality and to save money on maintaining unprofitable schools, the municipal council decided to close some of them, and to ensure daily transport to the main city for the students. This research attempts to reveal whether this initiative helped solving or worsened the village depopulation problem in the municipality of Blagoevgrad.

2. METHODS OF RESEARCH

This research is based on the highly reliable statistical method. To achieve the best results, the most accurate sources of information are used. These are the data-bases of National Statistic Institute of Bulgaria and The General Direction Civil Registration and Administrative Services (GRAO). They provide annually updated tables of information, which are used for comparison of the researched demographic processes.

3. ESSENCE OF RESEARCH

In 2008 municipality of Blagoevgrad undertook a new social and educational program. Several unprofitable village elementary schools were closed. This was made due to financial optimization and improving the quality of the educational services for the population. As a result, the students from 11 villages began to travel daily to the municipal center. Their transportation was provided by the municipal council, and was free of charge. We named it “The Free School Bus”. There are 348 children who participate in the program. The students daily travelling is obtained by 8 school busses.

This program has double-sided effect on students and their families. From one side they started to receive high quality educational services without extra payment. Their transportation is also free of charge. On the other hand children have to travel different distances daily. The bus lines start about 6.00 am and finish at about 20.00 pm. depending on the school shifts and the different distances. This is hard and sometimes uncomfortable.

Blagoevgrad municipality possess relatively small area – appr. 628 km^2. It is situated in the south-western region of Bulgaria. The terrain is rugged, valley – mountainous. The area is densely populated, compared to the average levels of the country.Table 1 reveals the number of villages and their current population number for 2010 [1].

Tab. 1

Population number of Blagoevgrad villages for 2010, by contemporary and permanent address registration

Village	Contemporary address registration	Permanent address registration	Village	Contemporary address registration	Permanent address registration
Belo pole	3.830	679	Klisura	34	26
Bistritsa	47	73	Leshko	213	276
Buchino	77	67	Lisia	12	14
Bulgarchevo	254	345	Logodaj	593	309
Gabrovo	28	32	Marulevo	29	53
Gorno Harsovo	84	149	Moshtanets	32	59
Debochitsa	25	26	Obel	46	44
Delvino	33	56	Padesh	647	664
Drenkovo	90	62	Pokrovnik	1.669	882
Dubrava	74	86	Riltsi	1.431	800
Elenovo	172	165	Selishte	293	409
Zelendol	246	232	Tserovo	714	690
Izgrev	545	539	Total:	11.218	6.737

The daily travel directions and destinations, as well as the number of participants are shown on the figures below.

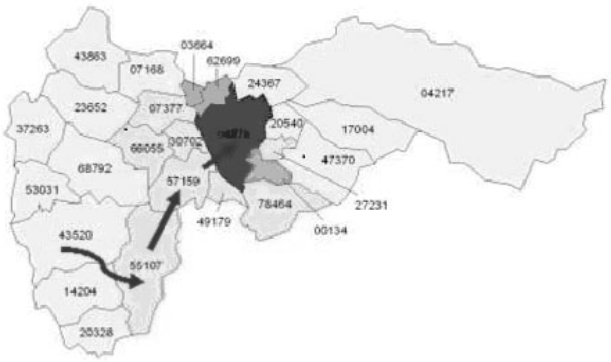

Fig. 1 School busses route on direction from the villages Pokrovnik(Code 43520), Padesh(Code 55107) and Leshko(Code 57159) to the town of Blagoevgrad.

On the direction Pokrovnik – Padesh – Leshko daily travel 79 students, including High school ones (Fig. 1)

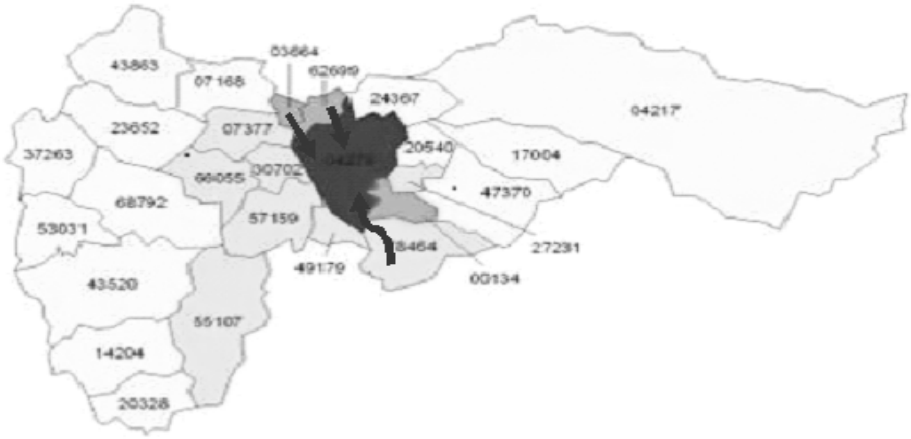

Fig. 2 School busses route on direction from the villages Tserovo(Code78464), Belo pole(Code 03664) and Riltsi(Code 62699) to the town of Blagoevgrad.

From the village of Tserovo daily travel 66 students with 2 busses. From the villages of Belo pole and Riltsi daily travel 73 students. (Fig 2.) From the villages of Balgarchevo, Zelendol, Selishte, Drenkovo and Logodazh daily travel 43 students (Fig. 3) And finally, from the “Staro Strumsko” quarter of Blagoevgrad to V^{-th} elementary school travel 23 students, from the Romany(gipsy) quarter 15 students travel free of charge to the II^{-d} elementary school, and other 37 – to IX^{-th} elementary school. The busses are also used by children from the Social house.

The essence of the problem comes from families attitude. There are two opposite positions. The first is that it is better for the family to move to town, because children have to travel every day to school. This is heavy and dangerous for them. The second position is that things got better in the new situation. The family can still live in a healthy environment, and close to its roots in the village. The children receive high-quality education in town without extra payment. The main question is: “Which opinion will prevail?”

To investigate how this situation will develop, I used the statistical method with official sources of information, such as the national population registers and the national address registration registers. In order to discover the rate of depopulation I researched statistical data about the population number variations in the villages involved for the

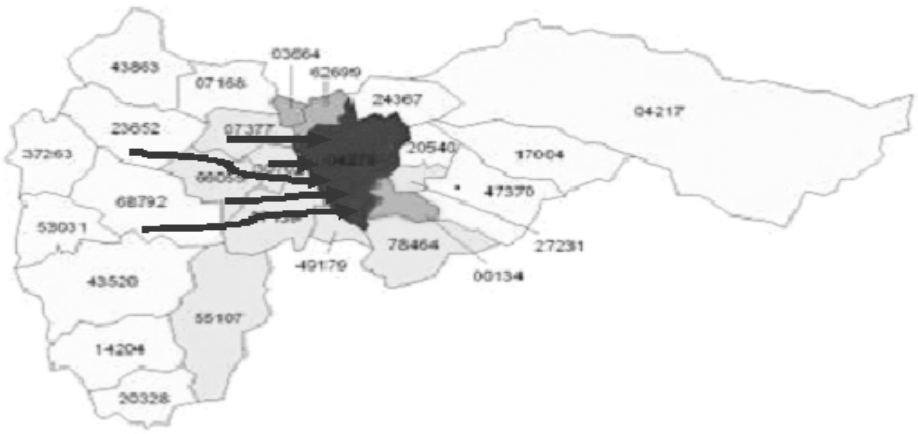

Fig. 3 School busses route on direction from the villages Balgarchevo(Code 07377), Zelendol(Code 23652), Selishte(Code 30702), Drenkovo(Code 66055) and Logodazh(Code 68792) to the town of Blagoevgrad.

period 2000-2007. I compared them with the population number data for the years 2008-2009-2010 expecting data for the year 2011.

Unexpected difficulties came from the significant number of Macedonian citizens, registered as Bulgarian ones with addresses in Blagoevgrad municipality. To avoid mistakes I used two kinds of information – permanent address registration and contemporary address registration from one side, and the total number of registered citizens from the other.

Macedonian citizens are registered at a permanent address, but don't really live in these villages, so their contemporary address isn't there. Tables, shown on Figures 4-6 reveal the dynamic changes in the population number for the last 3 years. This is the period passed by, since the new system started.

4. RESULTS AND CONCLUSIONS

Some very interesting conclusions were made during the research. One of them is, that administratively, the investigated villages **don't** suffer depopulation at all, but in the opposite – most of them are administratively growing. Such villages are Belo pole, Riltsi, Balgarchevo etc. (Ex.: **Riltsi** – **1 002** (2008) – **1 065** (2009) – **1 431** (2010)).

Some villages have an **impressive** number of people, only registered there, without being residents (mainly citizens from Macedonia).

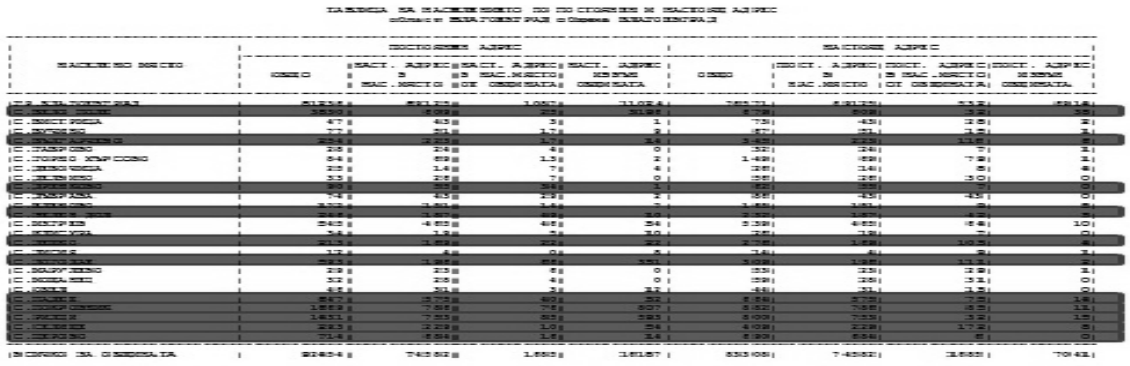

Fig. 4 Number of address registered citizens in Blagoevgrad municipality for 2010

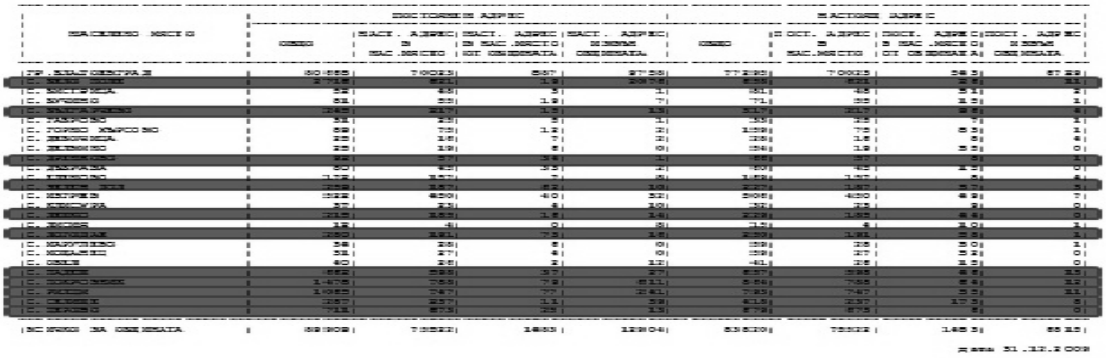

Fig. 5 Number of address registered citizens in Blagoevgrad municipality for 2009

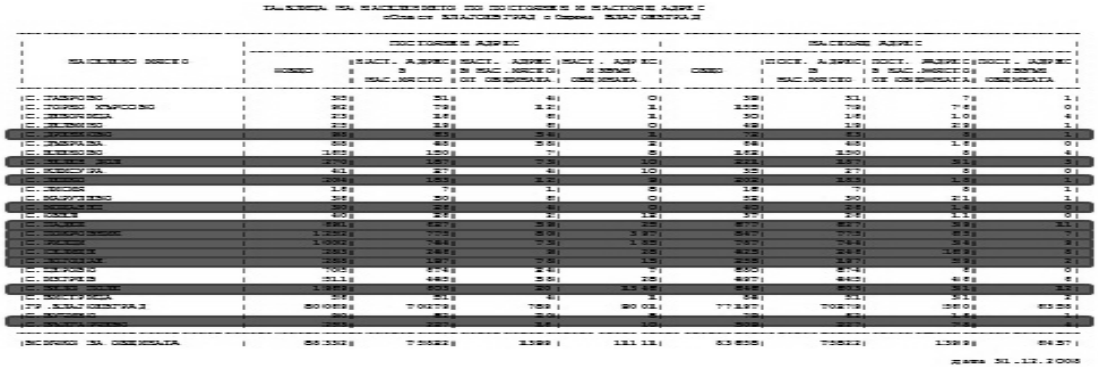

Fig. 6 Number of address registered citizens in Blagoevgrad municipality for 2008

This unusual process occurs mainly in the villages, nearest to the town of Blagoevgrad(Fig. 7).

Belo pole	Registered	Residents
2008	**1 969**	**603**
2009	**2 716**	**621**
2010	**3 830**	**609**

Fig. 7 Village of Belo pole – population number change

Drenkovo	Registered	Residents
2008	**98**	**63**
2009	**92**	**57**
2010	**90**	**55**

Fig. 8 Village of Drenkovo – population number change

Other villages show **typical processes of depopulation** (Fig 8)

After further analyses of population and address registers I came to the following conclusion:

At this stage "The Free School Bus" seems like a **good** and working **initiative**, which **don't worsen** the village depopulation problem in Blagoevgrad municipality. The situation, anyway, is influenced by other factors as well. The survey will continue in future with monitoring of statistical data.

The **period** of activity of this social initiative is still short for depicting tendencies with certainty. Conclusions are **preliminary**. The expected results may differ from the present ones.

5. REFERENCES

[1] http://www.grao.bg/tna/tadr-2010.txt

Tables of the population by permanent and contemporary address registration

[2] http://www.nsi.bg/nrnm/show2_1.php?sid=1007423&ezik=en&e=1002226&h=1

National Register of Populated places, National Statistic Institute, Sofia, Bulgaria

River order as a hydrological parameter: a case study in upper Tundja river catchment

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Abstract*: The paper focuses on river order and of its role as a criterion to estimate characteristics of rivers. As an example is used the upper part of Tindja river catchment – an area of mountainous and hollow topography, where river orders range from I to V. Analysis of data show clear dependencies between stream order and main hydrographical and hydrological characteristics within the catchment which can be used to estimate these river characteristics in other catchments with similar climate and topography.*
Keywords: *Drainage network, River order, length, catchment area.*

1. INTRODUCTION

Hydrography is the part of hydrology that deals with the spatial configuration of water bodies on Earth’s surface. The pattern of river network is everywhere unique because its generation and development reflects both the influence of topography and climate. In other words – all environmental factors are involved in its formation.

A temptation to use hydrographic characteristics for analysis of river behavior is derived from the fact that, despite the river regime, which involves large amounts of hydrological data (often in deficit and of doubtful quality), the spatial characteristics of river network can be easily obtained by a topography map and processed in full in a Geographical information system.

The scientific question here is to what extent the spatial configuration of drainage network at a particular place is usable to estimate hydrological characteristics of rivers and which characteristics in particular. At least partially, the present paper tries to give light on this problem.

2. RIVER ORDER

River order is a geometry based parameter of the river network, which reflects the rate of spatial development of the same. Basically, in hydrology two classifications of river order exist. In one of them order I rivers are those which end in the World ocean or in closed lakes. Order II rivers are all that

flow into the order I river, and so the order will increase from the mouth of the main river upwards. A drawback of this classification is that one order gathers rivers with quite a different magnitude – for example, river Danube that flows in the Black sea will be order I, and also the river Batova will be order I, although both rivers are hydrologically incomparable.

The present study keeps to the second classification which is postulated in the works of [1] and [2]. Here order I rivers are the river currents in their initial (highest) parts, where they usually start with a spring and in fact have no tributaries. An order II river forms where two order I rivers join, an order III river – where two order II rivers join an so on. Where a river of a lower order flows into a river of a higher order, the main river does not increase in order. Following this principle the order increases steadily from the river source towards river mouth in the sea, reaching a maximum value worldwide of XII at the Amazon river mouth in the Atlantic.

In the present work river orders are derived for the upper part of Tundja river catchment and an attempt is made to relate the observed pattern to both topographical and hydrological characteristics of the rivers in the area.

3. STUDY AREA

The basin of Tundja river occupies a large part of Central and Southeastern Bulgaria and takes 8884 km^2 of country's territory. The uppermost part of this basin that is in the focus of the present study includes the currents of the main river and its tributaries from the source down to Koprinka dam (figure 1.) with a total area of 867 km^2.

a. Environment

The area has a diverse, but well differentiated topography, which defines three natural zones within the catchment. The northern part is occupied by the southern slopes of Central Stara planina – to the west this is part of Kaloferska planina with the Triglav massif (highest point of all the area – Goliam Kademlia peak, 2276 m a. s. l.) built of granite, and to the east – Shipchenska planina (Ispolin prak, 1523 m a. s. l.) made of Triassic and Jurassic mainly carbonate rocks (limestone, dolomite). Here steep slopes and deep valley incision prevail. Valleys are often straight, determined by the spread of fault lines. In contrast the highest ridgetop parts, especially in granite, are often quite flat in result of weathering and denudation. The southern flank of the area is taken by the milder and gentler northern slopes of Sarnena Sredna gora (1236 m a. s. l.) made of Paleosoic granites and older metamorphic rocks (gneiss, amphybolites). Between the two mountains lies the flattened bottom of Kazanlak hollow (altitudes from 390 to 550 m a. s. l.). The bottom is flat, covered by young,

mostly alluvial deposits. Several granitic intra-hollow heights (50 – 150 m above the base level) spot the field mainly to the south. To the west the drainage divide follows the low ridge Strazhata.

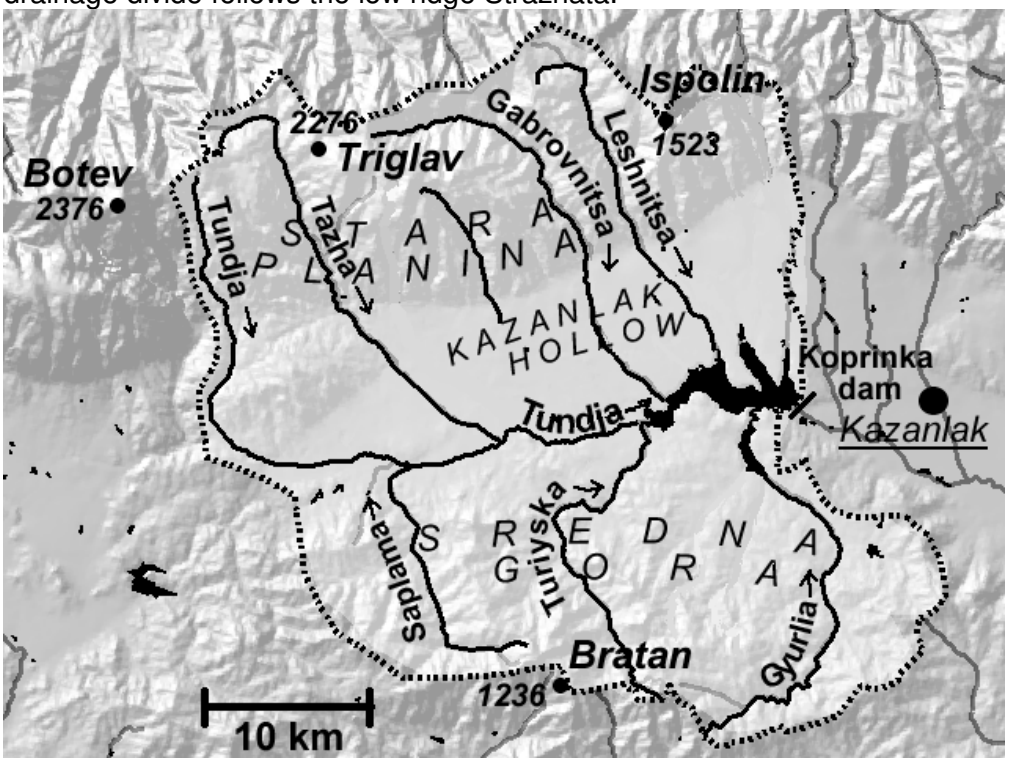

Fig. 1. The uppermost part of Tundja catchment.

The climate of the area shows a transition character between temperate-continental and transitional, according to the climatic regionalization of Bulgaria [3]. Annual temperature decreases in altitude by 0.53°C/100 m, ranging from 10.3°C to about 0°C. Precipitation amounts are greatest in Stara planina - above 1100 mm/y, while in Kazanlak field and in Sredna gora they are below 700 mm/y. Precipitation in spring-summer (Mar-Aug) accounts for 62–64% of the annual sum to the NW, to 55-56% to SE. The soil cover consists mainly of Cambisols (the mountain slopes), and Fluvisols (the hollow of Kazanlak). Vegetation in the mountains is presented by forest communities (oak, beech) and alpine grasses in the highest areas. Down in the field agricultural plants prevail.

The following aspects of human impact are most significant in the area: deforestation in the lowland, construction of irrigation channels, artificial water bodies – the main is Koprinka dam on Tundja river, built in 1954, that collects the water from all the rivers of the upper part of the catchment.

3. 2. River network

The river network (fig. 1) is presented by Tundja river and its tributaries. The main river starts in Kaloferska planina at 1940 m a. s. l. Initially it flows to the south, and then, coming out of the mountain after the town of Kalofer it turns to the east until it reaches Koprinka dam (389 m a. s. l.). The total river length till the dam is 46 km. The average gradient of the river in the mountain part is 85‰, within the hollow it drops to 10‰, and for the whole length of the river down to the dam it is about 42‰. The coefficient of river's curvature (Cc) is 1.78. Main tributaries are: Tazha, Gabrovnitsa, Leshnitsa (left), Saplama, Turiyska, Gyurlia (right). Area's diverse topography leads to a hydrographic asymmetry – the tributaries from Sredna gora are much more curvy (Cc's above 1.40) than those flowing from Stara planina (Cc's from 1.02 to 1.20). The ratio between the catchment areas of the left and right tributaries equals to 53:47.

4. RIVER ORDERS IN THE UPPER PART OF TUNDJA RIVER CATCHMENT

River orders as stated by [1] and [2] were outlined using ArcGIS9 software on the basis of georeferenced 1:50.000 scale topographic maps. Then calculations of river lengths and catchment areas were made. Finally, information about total lengths and average areas were derived after exporting the data from attribute tables to Microsoft Excel.

As shown in fig. 3, the highest order that appears within the area is V. The large rivers within the catchment belong to orders III (36 rivers), IV (9 rivers) and V (2 rivers). Fifth order rivers are only Saplama-Tundja and Gyurlia.

Analysis of the total length of river sections per order shows that the overall length decreases from order I to order V and this decrease has a well defined geometrical trend which can be expressed by an almost parabolic curve. The same is observed when comparing average catchment areas respectively for catchments of order III, IV and V.

Concerning river order a strong regional difference is observed within the area, splitting it almost into two halves. River orders in the southern part of the area, especially within the slopes of Sredna gora, rise much more quickly, i. e. on a much smaller distances than those to the N, and especially to the NE. A clear example of this is that at the spot where Saplama river flows from the right into Tundja river, Saplama has reached order V, while the main river is still at order IV.

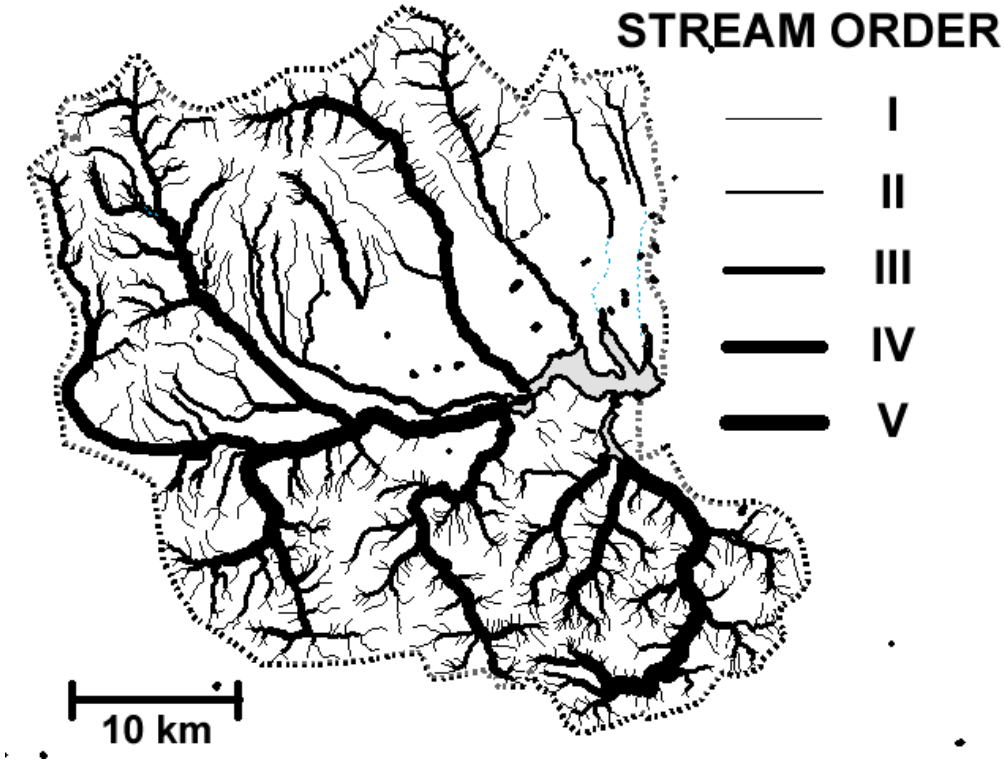

Figure 2. River orders in the researched area

This difference can be even more clearly seen when comparing catchment areas of the rivers of same order. Fig. 3 shows catchment areas for order III (a) and order IV (b). Areas to the north are 5 to 8 times larger than those to the south. In the northern half there is a slight difference between rivers in Kaloferska planina (to the NW) and those in Shipchenska planina (to the NE) as the first ones have smaller catchment areas.

These contrasts reflect the differences in drainage density, which are caused by the bedrock and the hypsometry expression of the surface. The relief in Sredna gora is older than that in Stara planina, rocks are crystalline, often tectonically reworked, highly weathered near the surface. As a result here the river network has the highest density. Relief in Stara planina is younger, with a high rate of neotectonic uplift. River valleys are often with unstabilised vertical profile with prevailance of vertical erosion. In most cases they are linear, straight for long sections, and follow fault lines of various magnitude. As a result here drainage density is smaller on a granite because of the strong physical weathering and smallest on limestone and dolomite, because of the very small susceptibility of these rocks to physical weathering.

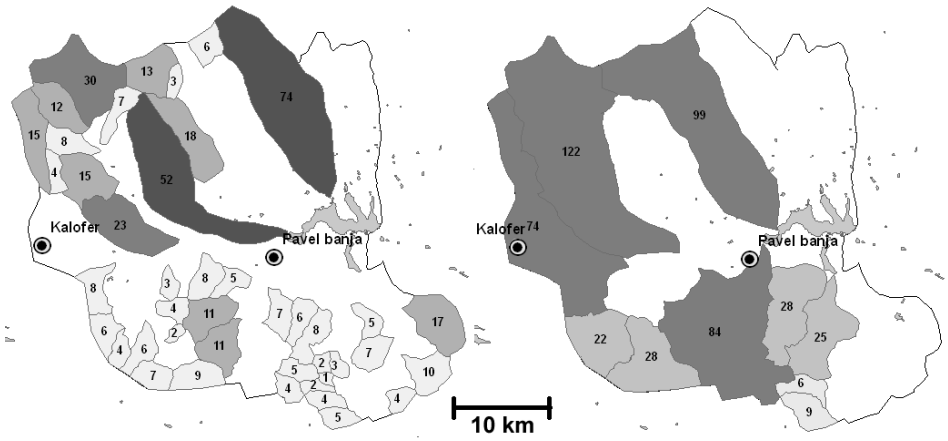

Fig. 3. Catchment areas of the rivers of orders III (a) and IV (b)

5. RIVER FLOW

Data about river flow is derived from 6 hydrometry stations within the area. Data analyzed for the hydrological years 1953/54-1982/83 (tab. 1) shows that the average annual discharge and the runoff module depend most of all on drainage basins' altitude and no relation to river orders is observed.

Tab. 1: Quantitative characteristics of river flow

Station	Catchment altitude, m a. s. l.	Average annual discharge, m^3/s	Discharge module, $l/s/km^2$	River order at the station
Tazha-VEC Tazha	1557	2.06	33.1	III
Tundja-Kalofer	1177	0.53	19.6	IV
Leshnitsa-Yasenovo	1168	0.95	20.3	IV
Tundja-Pavel banja	894	3.53	12.3	V
Turiyska-Turiya	749	0.41	7.4	IV
Gyurlja-Morozovo	700	0.59	8.0	V

The same can be seen also when looking at rivers' regime, expressed on fig. 5 by the average monthly discharde as a percentage of the total annual discharge. River regime is determined most of all by climate (temperature, precipitation, duration of snow cover). A transition in river regime is observed to occur from NW to SE. Stations on Tundja and Tazha rivers have clearly expressed flow maximum in Mai and generally a high phase from March to June. At Leshnitsa-Yasenovo the flow maximum shifts to April, at Turiiska-Turiia to March and at Gyurlja-Morozovo – even to February, and at the same time the high phase starts in winter, reaching 8 months (November-June) at Gyurlja-Morozovo.

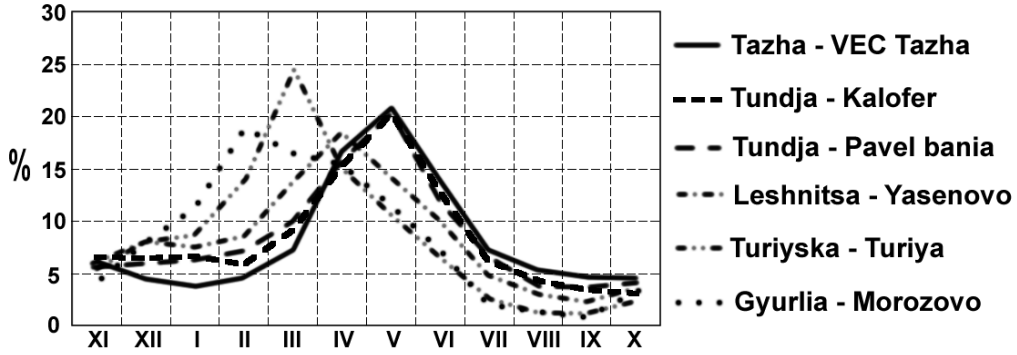

Fig. 4. Average monthly discharge (1953/54-1982/83) measured as a percentage of the total annual discharge

6. CONCLUSION

River order is a parameter, which is easily derivable from a topographic map. It reflects the unique topographic conditions at each particular location which are a result of the specific combination of hypsometry, geology and geomorphology. River order appears to be a good tool for evaluating geomorphological influences on river currents. In the area studied regional contrasts are observed in the pattern of river orders between the northern and the southern part of the catchment (the slopes of Stara planina and Sredna gora respectively). At the same time no relation is found between river order and characteristics of river flow, at least in general for the territory. Such dependencies can however be revealed at a regional scale within regions of similar topography, geology and geomorphology.

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PRINCIPAL TENDENCIES OF THE QUATERNARY MORPHOGENESIS IN THE EASTERN PART OF BALKAN PENINSULA

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Summary. The Quaternary Morphogenesis of the eastern part of the Balkan Peninsula is an effect from the Intracontinental collision between the Europa and Gondvana continental macroplates.

Kay words: morphogenese, intercontinental collision, microplates, positive and negative morphostructures.

The Quaternary Morphogenese in the eastern part of the Balkan Peninsula is realizing under the conditions of the active intra continental collision between the Europa Continental Macroplate and the sinked to the north Gondvana Continental Macroplate (Fig. 1). Its frontal parts are arriving down the mountain areas of Alps, Dinarides, Pind, Elenides and Rila-Rhodope Mountain Massif (Fig. 1). This process is provoking the very quickly and very intensive building of the heighten mountain massifs on the south west margin of the European continental macroplate. This type of the Quaternary morphogenese is affecting the south west part of the Bulgarian continental microplate (Fig. 2 and 3). The front of the Gondvana continental Macroplate is arriving on the Bulgarian territory till the area of the town of Plovdiv at one deep from around 200 km (Tzankov et all., 19). This process has given birth to the local collision between the north east end of the Bulgarian Continental Microplate and the south east margin of the Moesian Continental Microplate (Fig. 1, 2 and 3). The effect of those relationships is probably the building of the Stara Planina Mountain Change (Fig. 2 and 3).

The Quaternary Morphogenesis is the youngest part of the Late Oligocene-Neozoic morphotectonic evolution of the Bulgarian continental

microplate (Table 1). It long first Post Alpine period (Late Oligocene – Early Pleistocene) is connected with regional savanna similar paleogeographic setting. It was finished with the building of the Post Late Pleistocene orthoplain (Fig. 4). The last one is the starting point of the beguine before 990 000 years Quaternary Mountain Building. The mosaic mountain relief is composed by the older negative morphostructures (kettle morpostructures, morphostructural passages, morphostructural thresholds, rivervalley morphostructures) and younger positive morphostructures (concentric, dome-like or mountain morphostructures – Fig. 5). The relief building was realized in a march of the four regional morphostructural generations (Table 2).

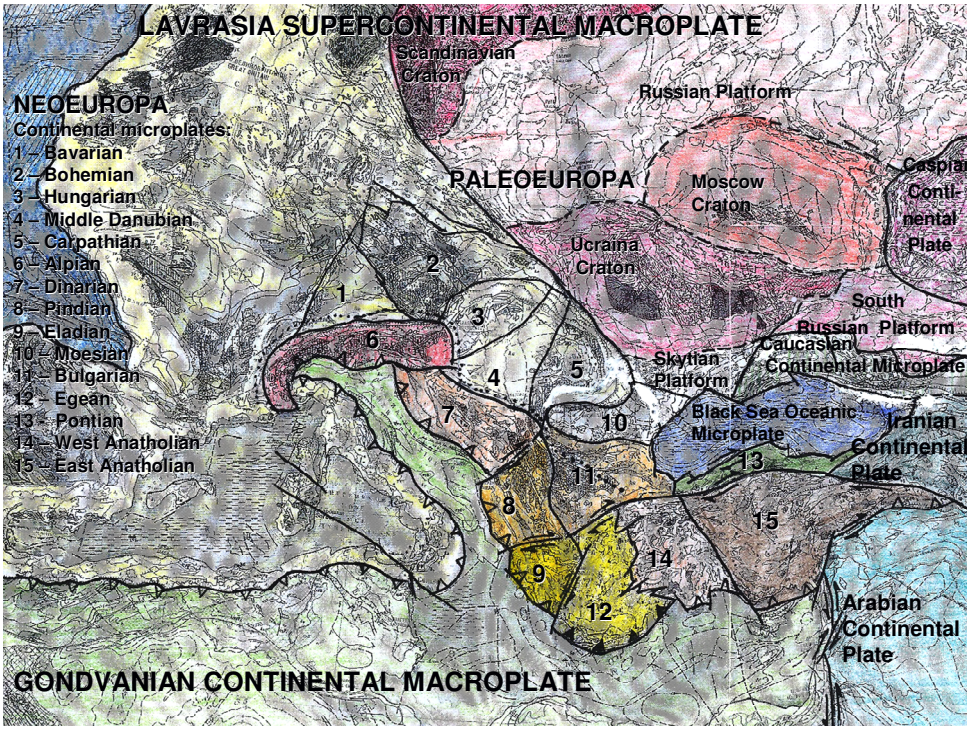

Fig. 1 Regional position of the Bulgarian continental microplate

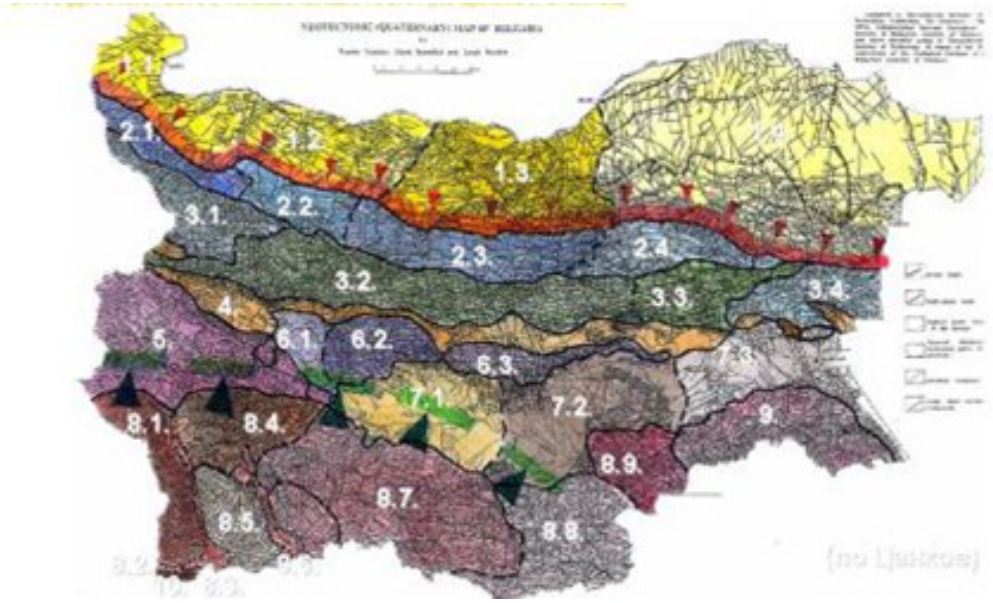

Fig. 2 Morphostructural map of Bulgaria (zones and areas): 1. South Moesian zone: 1.1. Vidin area, 1.2. Almus area, 1.3. Svishtov area, 1.4. Razgrad area; 2. Fore Balkan zone: 2.1. Belogradchik area, 2.2. Vratca area, 2.3. Turnovo area. 2.4. Veliki Preslav area; 3. Stara planina zone: 3.1. Midzhur area, 3.2. Mazalat area, 3.3. Udvoy-Mator area, 3.4. Maritime area; 4. Sub Balkan zone; 5. Vitosha zone; 6. Sredna gora zone: 6.1. Ihtiman area, 6.2. Panagyurishte area, 6.3. Surnena gora area; 7. Upper Thracian zone: 7.1. Plovdiv area, 7.2 Zagore area, 7.3. Burgas area; 8. Rila-Rhodopes zone: 8.1. Osogovo-Ograzhden area, 8.2. Strumeshnitca complex morphostructural passage, 8.3. Middle Struma complex morphostructural passage, 8.4. Rila area, 8.5. Pirin area, 8.6. Middle Mesta complex morphostructural passage, 8.7. West Rhodopes area, 8.8. East Rhodopes area, 8.9. Sakar area; 9. Strandzha zone; 10. Belasitca zone.

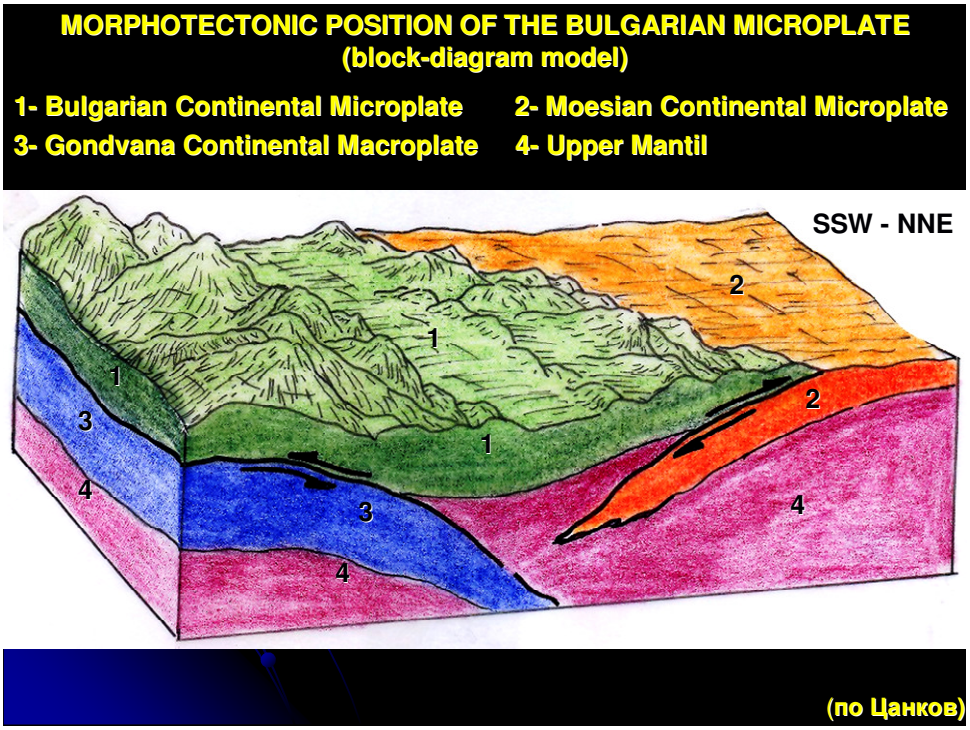

Fig. 3 Morphotectonic position of the Bulgarian Continental Mikroplate (principal block-diagram model): 1. Bulgarian Continental Microplate, 2. Moesian Continental Microplate, Gondvana Continental Macroplate, 4. Upper Mantil.

Table 1

NEOZOIC MORPHOTECTOGENESIS OF THE BULGARIAN CONTINENTAL MICROPLATE (*Tzankov, Stoyanov, Spassov*, 2004)

End of Early Oligocene – finish of Alpine Orogenesis
Late Oligocene- Middle Miocene – superficially tectonic “calm” and sicinematic deep crustal block destruction. Denudation of the Late Alpine Relief and orthoplan building.
Late Miocene – deposition of potent continental (alluvial and alluvial-proluvial) deposits of the braded rivers on the fragments of the older orthoplan superficias.
End of Late Miocene – origin of the post Late Miocene orthoplan
Pliocene- Early Pleistocene – manifestation of slight, local short-lived superficial crustal block movements.
End of Early Pleistocene – forming of the post Early Pleistocene orthoplan.
Before 990000 years – beginning of the intensive destruction and block denivelation of the post Early Pleistocene orthoplan under the influence of the

listric tectonics. The big orthoplan fragments were build the bottom of the kettle morphostructures and morphostructural passages. The other orthoplan fragments were marked the morphostructurell river valleys. Beginning of the dome-like morphostructure building.
Late Pleistocene-Early Holocene – forming and rapid denudation of the first generation of dome-like concentric morphostructures.
Late Holocene – forming of the second generation of dome-like and mountain morphostructures. Contemporary relief building.

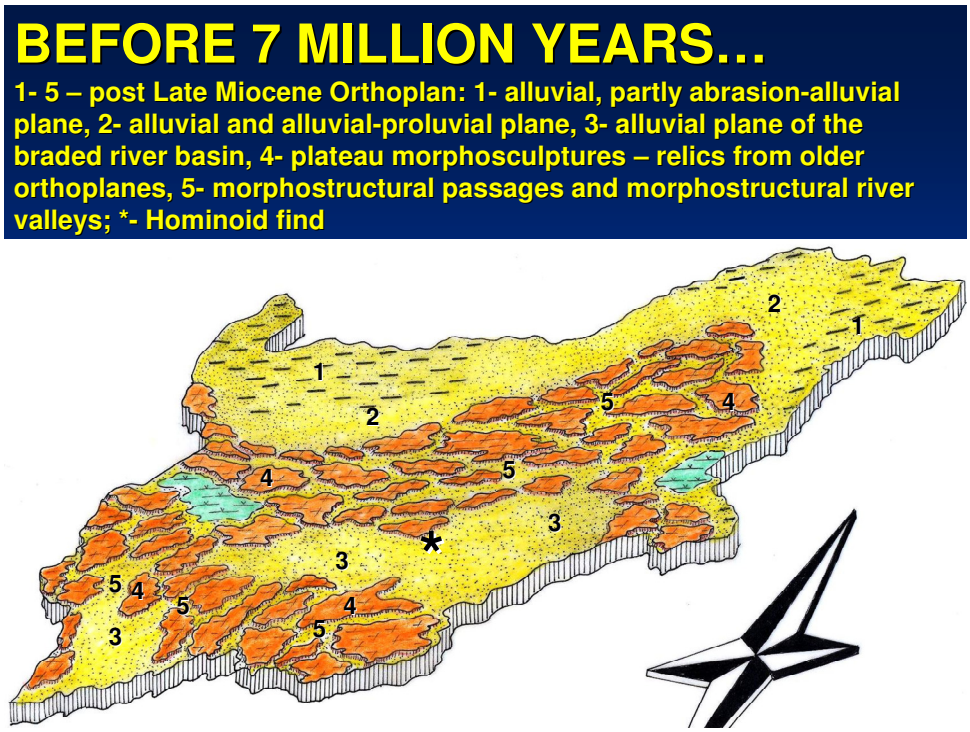

Fig. 4 Provisional paleogeographic model of Bulgarien for the time before 7 million years

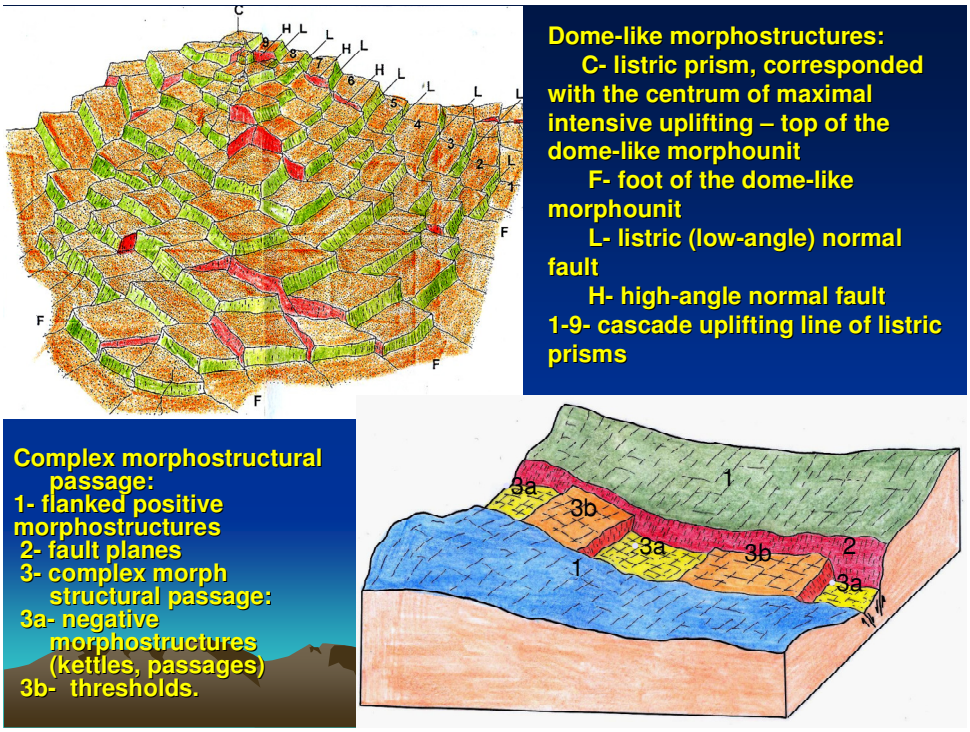

Fig. 5 Principal regional morphostructure types

Table 2

MORPHOGENERATIONS IN THE EASTERN PART OF THE BALKAN PENINSULA

POST EARLY PLEISTOCENE ORTHOPLAIN

Origin time – end of Early Pleistocene

Character – large alluvial savanna similar peneplain (orthoplain).

Beginning of destruction and denivelation – End of Early Pleistocene (in connection with the beginning of the Quaternary block-fault mountain building processes).

Contemporary relicts – block denivelated bottoms of the kettle morphostructures and morphostructural passages.

POST EARLY PLEISTOCENE CONCENTTRIC MORPHOSTRUCTURES

Origin time – Late Pleistocene and Early Holocene.

Character – relicts from earlier generation of Quaternary dome-like morphostructures (effects of the started Quaternary block-fault mountain building processes).

Beginning of destruction and denivelation – at the same time with the creasing beginning of the dome-like morphostructures over the orthoplain superficies

Contemporary relicts – concentric morphostructures in different good shape.

POST EARLY HOLOCENE DOME-LIKE AND MOUNTAIN MORPHOSTRUCTURES

Origin time – from Middle Holocene till now.

Character - mountain-hill and mountain relief.

Beginning of destruction and denivelation – none stop vertical and spatial increasing of the dome-like and mountain morphostructures. Those relatively quickly increasing processes are preventing the very active erosion.

Contemporary relicts – The mentioned dome-like and mountain morphostructures and the kettle bottoms are the principal morph elements of the contemporary regional relief.

HOLOCENE SYNMORPHOGENE UPLIFTINGS IN THE KETTLE BOTTOMS

Origin time –Holocene.

Character - synmorphogene upliftings in the kettle bottoms (nuclei of the future dome-like morphostructures) non stop realized vertical and spatial increasing of the synmorphogene upliftings.

Contemporary relicts – positive relief forms (hills. low mountain ridges) in the kettle bottoms.

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