"St. Kliment Ohridski" University - Bitola

HORIZONS

INTERNATIONAL SCIENTIFIC JOURNAL

SERIES B
Natural Sciences and Mathematics, Engineering and Technology, Biotechnology, Medicine and Health Sciences

Year X Volume 1 August 2014

For the publisher: Prof. Zlatko Zhoglev, PhD, Rector

Editor: Elena Kitanovska-Ristoska, MA

ISSN 1857- 8578
Print: AD Kiro Dandaro-Bitola, printing copies: 200

Dear readers,

The public has almost become a kind of used to the expectation that *Horizons* scientific journal with its every new edition, to trace a new pathway towards its further establishment on the international educational and scientific-research areas.

In its pronounced strive to achieve an increased level of quality, the *Horizons* that we know from before has been transformed and now it is coming out as two separate issues of the same brand name, but with an improved recognizability and an increased particularity in terms of the scientific-research contents it brings.

It is important to stress that, *Horizons* will, for the coming period, just as it did previously, continue respecting the principles of scientific impartiality and editorial justness, and will be committed to stimulating the young researchers in particular, to select *Horizons* as a place to publish the results of their contemporary scientific and research work. Also there is an emphasized need for those who, by means of publishing This is also in line with the need to provide place incorporated within the publishing activity for all those who through publishing their papers in international scientific journals, such as the two new series of our University *Horizons*, view their future career development in the realm of professorship and scientific research profession.

The internationalization of our *Horizons* journal is not to be taken as the further most accomplishment of our University publishing activity. Just as
the scientific thought does not approve of limitations or exhaustive achievements, so is every newly registered success of the *Horizons* editions going to give rise to new “appetites” for further objectives to reach.

Taken from the aspect of quality gradation, it is well justified if we announce the publishing of the international scientific journal *Horizons* with a significant quantifier – journal with impact factor. This initiative of “St. Kliment Ohridski” University – Bitola is given a

substantial place in the future undertakings outlined in the plan for increasing the overall quality of organization and functioning of the University.

Last, but not the least, as we have made public our future steps, we would
like to express our sincere appreciation for the active part you all took in the process of designing, creating, final shaping and publishing the scientific journal. Finally, it is with your support that *Horizons* is on its way to attain its deserved, recognizable place where creative, innovative and intellectually autonomous scientific reflections and potentials will be granted affirmation, as well as an opportunity for a successful establishment in the global area of knowledge and science.

Sincerely,
The editing board

CONTENT

621.643.43: 536.2

COMPARISON OF HEAT EXCHANGERS WITH EXTENDED SURFACE BY THE SHAPE OF THE RIBS[1]

Prof. Kire Popovski, PhD
Faculty of Technical Sciences, Bitola, Macedonija
kire.popovski@tfb.uklo.edu.mk

Abstract

With the comparison of extended surface heat exchangers, exactly by determining which one has a better heat transfer, methods for calculating the coefficient of convective heat transfer from the ribs on the environment α_r depending on the air velocity in the smallest flow section w_a and calculation of the heat transfer factor j_a depending on the Reynolds number, are used.

Extended surface heat exchangers are presented in this article. They are used for water and air as working medias, and can be differentiated by the shape of the ribs. The one has wave-like ribs, while the other has flat lamella ribs.

Better heat transfer can give the exchanger with higher values of coefficient α_r and factor j_a.
Key words: heat exchanger, heat transfer.

MATHEMATICAL MODEL

Temperature condition for the calculation of heat transfer through ribbed surface of tubes at lamella type heat exchangers, for working mediums water-air and where cooling of the air occurs is visible on Fig. 1. Here, we can see that heat from the fluid surrounding the pipe outside (air) is transferred on the fluid inside the pipe (water).

Heat transfer from the air onto the water is constant since there is neither heat source nor heat sink between both medias.

[1] original scientific paper

Total transferred heat is a sum of heat transferred through the outer surface of the pipe [without ribs] A_{cn}, and the heat transferred through ribs area, A_r.

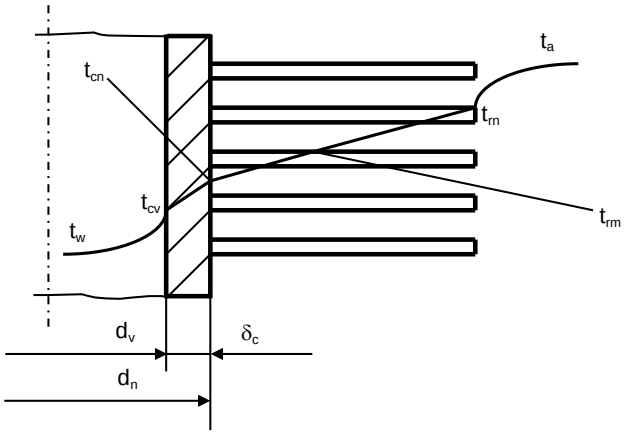


Fig. 1. Temperature variations on ribbed pipe

$$Q = \alpha_r \cdot A_r \cdot (t_a - t_{rm}) + \alpha_{cn} \cdot A_{cn} \cdot (t_a - t_{cn}) \quad \text{W}, \tag{1}$$

α_r and α_{cn} are almost equal,

$$Q = \alpha_r \cdot [A_r \cdot (t_a - t_{rm}) + A_{cn} \cdot (t_a - t_{cn})] \quad \text{W}, \tag{2}$$

Coefficient of convective heat transfer from the outer side is,

$$\alpha_{an} = \alpha_r \cdot \left(\frac{A_r}{A_n} \cdot \eta_r + \frac{A_{cn}}{A_n} \right) \tag{3}$$

Where,

$$\eta_r = \frac{t_a - t_{rm}}{t_a - t_{cn}} \tag{4}$$

The degree of usefulness is the ratio between heat transferring onto the ribs and heat that would be transferred on the ribs, when all of them would have temperature t_{cn}.

$$\eta_p = \frac{A_r}{A_n} \cdot \eta_r + \frac{A_{cn}}{A_n} \tag{5}$$

is heat exchanger's level of utility area,

$$\alpha_r = \frac{1}{L \cdot \eta_p \cdot \left(R - \frac{A_n}{A_v} \cdot \frac{1}{\alpha_v} - \frac{A_n}{A_v} \cdot \frac{\delta_c}{\lambda_c} \right)} \tag{6}$$

coefficient of convective heat transfer of ribs.

Expressions for η_p and α_r form system of two equations with two unknowns that is solved through iteration method. Approximately, for the first iteration η_p=0,8.

Air flows by the length of the rib and upright on the pipe. Cross-section of the fluid between ribs is changed through the current flow. Because of that and sinuous form of lamellas, local coordinates depend on the direction and value of speed.

Most of authors, [1] and [2], in their calculations, use maximum velocity of the air in the minimum cross-section,

$$w_{amax} = \frac{m_{sa}}{A_{min}} \tag{7}$$

Hydraulic diameter is taken as a characteristic value when Reynolds' number is calculated [1],

$$d_h = \frac{4 \cdot A_{min}}{A_{cn}} \tag{8}$$

where Reynolds' number,

$$Re_a = \frac{w_{amax} \cdot d_h}{\nu_a} \tag{9}$$

Heat transfer factor, j_a, is usually in non-dimensional form [3],

$$j_a = St \cdot Pr_a^n \tag{10}$$

Stanton's-number,

$$St = \frac{Nu}{Re_a \cdot Pr_a} \tag{11}$$

Solution of the previous two terms is,

$$j_a = \frac{\alpha_a \cdot A_{min}}{m_{sa} \cdot c_{pa}} \cdot Pr_a^n \tag{12}$$

A number of authors, in the calculation of convective heat transfer, take the value of exponent of Prantdl's number to be n =0,667. Kotke and Blenke examined the influence of flow on this exponent. They suggest the following function in the expression of convective heat transfer, [4],

$$Pr_a^n = f(\mathrm{Pr}_a) = 1{,}8 \cdot Pr_a^{0{,}3} - 0{,}8 \tag{13}$$

Now,

$$j_a = \frac{\alpha_r \cdot A_n}{m_{sa} \cdot c_{pa}} \cdot 1{,}8 \cdot Pr^{0{,}3} - 0{,}8 \tag{14}$$

Factor ja can be found as a function of Reynolds' number,

$$j_a = a \cdot Re_a^b \tag{15}$$

Constants a and b are coefficients of correlation of the values for j_a and Reynolds' number.

NUMERICAL EXAMPLE

Measurements are taken on two heat exchangers, and their dimensions are visible on Table 1. Heat exchanger number 1 has sinuous lamellas, while heat exchanger number 2 has flat lamellas, [5].

Table 1. Measured dimensions of heat exchangers

Dimensions	No. 1	No. 2
H_t [mm]	468	468
B_t [mm]	500	500
H_r [mm]	465	465
δ_r [mm]	0,15	0,15
B_r [mm]	172,8	172,8
R_r [mm]	2,6	2,6
n_r	192	192
C_h [mm]	33,3	33,3
C_b [mm]	28,8	28,8
d_v [mm]	11	11
d_n [mm]	12,3	12,3
n_{red}	6	6
n_{red1}	14	14
n_{pc}	16	16
n_c	84	84

Calculated surface areas of the heat exchangers are presented on Table 2. Calculations are made according to [6], while surface area is given in [2].

Table 2. Calculated dimensions of heat exchanger

Dimensions	No. 1	No. 2
Frontal surface area of heat exchanger: $A_f = H_t \cdot B_t$	0,234	0,234
Minimum flow cross-section: $A_{min} = (H_r - n_{cr} \cdot d_n) \cdot n_r \cdot R_r$	0,146	0,146
Ratio: $\sigma = \frac{A_{min}}{A_f}$	0,625	0,625
Surface area of non-ribbed pipes: $A_{cn} = d_n \cdot \pi \cdot n_r \cdot R_r \cdot n_c$	1,620	1,620
Surface area of ribs: $A_r = \frac{(d_r^2 - d_n^2) \cdot \pi}{2} \cdot n_r \cdot n_c$	29,812	27,102
Pipe surface area between ribs: $A_g = (R_r - \delta_r) \cdot d_n \cdot \pi \cdot n_r \cdot n_c$	1,527	1,527
Total area of heat transfer: $A_n = A_r + A_g$	31,339	28,629

Internal pipe area: $A_v = d_v \cdot \pi \cdot n_r \cdot n_c \cdot R_r$	1,449	1,449

Table 3. Measured and calculated values for heat exchanger number 1

m_{sa} kg/s	m_{sw} kg/s	t_{av} °C	t_{ai} °C	t_{wv} °C	t_{wi} °C	Q_a W	Q_w W	Q_s W	k W/m^{2}K	α_w W/m^{2}K	w_a m/s	α_r W/m^{2}K	Re_a	j_a	η_r	η_p
0,233	0,231	20,88	12,83	5,32	10,18	5029	4715	1965	17,20	513,19	1,309	27,86	2566	0,0143	0,89	0,88
0,315	0,231	19,90	13,40	5,32	10,27	5059	4802	2138	17,68	513,16	1,768	34,38	3473	0,0130	0,86	0,86
0,413	0,231	19,69	13,66	5,21	10,23	5126	4870	2586	17,81	512,80	2,318	43,97	4553	0,0127	0,83	0,83
0,491	0,231	19,94	13,86	5,22	10,31	5235	4938	3087	17,96	512,83	2,758	55,51	5407	0,0135	0,80	0,79
0,563	0,231	20,57	14,28	5,31	10,57	5341	5103	3652	17,65	513,12	3,168	61,04	6185	0,0129	0,79	0,78
0,665	0,231	18,77	13,42	5,49	10,12	4716	4492	3652	17,94	513,65	3,725	78,11	7349	0,0140	0,74	0,73
0,754	0,231	18,06	13,35	5,91	10,25	4335	4211	3638	17,88	514,95	4,218	84,45	8346	0,0134	0,73	0,72
0,833	0,231	19,66	14,46	5,82	10,78	5040	4812	4436	18,18	514,69	4,682	99,82	9167	0,0143	0,70	0,68
0,925	0,231	22,34	16,46	6,03	12,06	6100	5850	5568	18,61	515,39	5,241	121,37	10071	0,0156	0,66	0,64
1,009	0,231	22,77	17,13	6,04	12,40	6302	6170	5823	18,23	515,44	5,728	108,04	10958	0,0128	0,68	0,67
1,084	0,230	23,25	17,75	5,97	12,70	6395	6501	6097	18,64	514,11	6,165	133,03	11742	0,0146	0,64	0,62
1,138	0,231	25,81	19,16	5,28	13,42	8376	7897	7750	18,91	513,10	6,516	143,12	12214	0,0150	0,63	0,61

Table 4. Measured and calculated values for heat exchanger number 2

m_{sa} kg/s	m_{sw} kg/s	t_{av} °C	t_{ai} °C	t_{wv} °C	t_{wi} °C	Q_a W	Q_w W	Q_s W	k W/m^{2}K	α_w W/m^{2}K	w_a m/s	α_r W/m^{2}K	Re_a	j_a	η_r	η_p
0,235	0,225	24,45	15,42	6,16	12,64	6310	6124	2251	19,82	550,59	1,334	27,96	2552	0,0142	0,89	0,88
0,324	0,225	22,90	15,85	5,91	12,31	6142	6048	2408	19,77	549,71	1,836	30,98	3528	0,0114	0,88	0,87
0,415	0,225	22,25	15,97	5,95	12,11	5850	5821	2727	19,30	549,82	2,349	34,41	4525	0,0099	0,86	0,86
0,477	0,226	21,80	15,67	5,87	11,72	5593	5553	3041	18,87	550,75	2,697	37,77	5209	0,0094	0,85	0,85
0,542	0,226	21,54	15,45	5,74	11,41	5436	5382	3417	18,51	550,30	3,062	41,89	5926	0,0092	0,84	0,83
0,595	0,228	21,61	15,40	5,72	11,31	5359	5353	3812	18,16	552,65	3,361	45,00	6505	0,0090	0,83	0,82
0,717	0,217	20,67	14,88	5,59	11,04	5087	4967	4262	18,43	538,69	4,040	62,00	7865	0,0103	0,78	0,77
0,827	0,218	21,52	15,52	5,04	11,20	5624	5640	5087	18,42	538,13	4,672	68,59	9041	0,0099	0,77	0,75
0,923	0,219	22,83	16,28	3,84	11,07	6679	6650	6194	19,16	535,42	5,233	85,59	10042	0,0111	0,73	0,71
1,025	0,223	18,30	14,27	5,91	10,69	4578	4477	4219	19,45	547,11	5,746	84,78	11318	0,0099	0,73	0,71
1,104	0,226	18,39	14,51	5,84	10,74	4677	4651	4374	19,87	550,54	6,192	93,60	12182	0,0101	0,71	0,70
1,177	0,227	18,88	14,93	5,46	10,76	5071	5053	4747	20,04	550,49	6,612	98,11	12961	0,0099	0,70	0,69
1,200	0,227	20,80	16,37	5,57	11,63	5549	5778	5429	20,39	550,89	6,780	114,14	13115	0,0113	0,67	0,65

Measured values are taken according to [7].

CONCLUSIONS

Measured and calculated values for both heat exchangers are presented on Tables 3 and 4, respectively. Calculations are made for constant mass flow of water, with the aim of calculating heat transfer from the outer side of heat exchanger. Values for convective heat transfer of the ribs, αr, and heat transfer factor, ja, are also shown.

The dependence of both factors [α_r and j_a] relative to wa and Re is shown on Fig. 2, and Fig. 3., respectively, while analytical dependence is given with the following expressions,

- Heat exchanger number. 1,

$$\alpha_r = 22{,}104 \cdot w_a - 5{,}1119 \qquad j_a = 0{,}0086 \cdot \mathrm{Re}_a^{0{,}0531}$$

- Heat exchanger number 2,

$$\alpha_r = 15{,}476 \cdot w_a - 0{,}7355 \qquad j_a = 0{,}00233 \cdot \mathrm{Re}_a^{-0{,}0912}$$

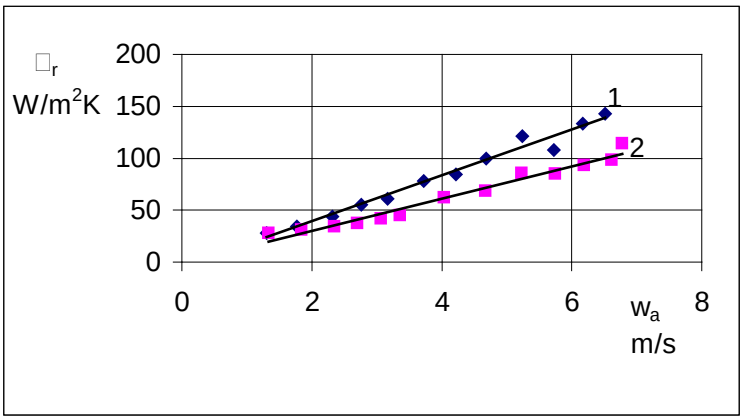


Fig. 2. Dependence of coefficient of convective heat transfer from the air onto pipe with ribs α_r, from air velocity in the minimum flow cross-section w_a

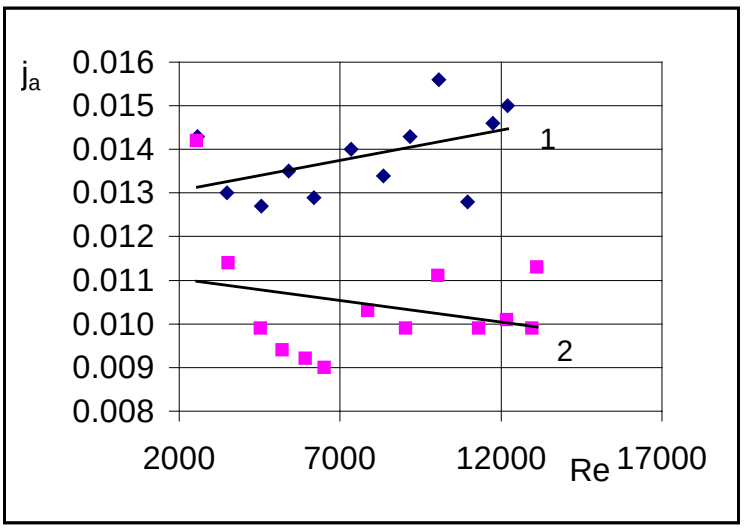


Fig. 3. Dependence of heat transfer coefficient, j_a, from Reynolds' number

Heat exchangers with higher values of coefficient α_r and factor j_a have better heat transfer. According to this, heat exchanger number 1, with

sinuous shaped lamellas has better heat transfer. This is expressed in larger values for w_a, or when $w_a > 4$ m/s and with greater Reynolds' number values, Re > 9000.

NOMENCLATURE

B_r - lamella's width [mm]
B_t - heat exchanger's width [mm]
C_b - distance between pipes onto heat exchangers' width [mm]
C_h - distance between pipes onto heat exchangers' height [mm]
d_n - external pipe diameter [mm]
d_v - internal pipe diameter [mm]
H_r - lamella's height [mm]
H_t - heat exchanger's height [mm]
j_a - heat transfer factor [dimensionless]
n_c - number of pipes [dimensionless]
n_r - number of lamellas [dimensionless]
R_r - spacing between lamellas [mm]
t_a - temperature of the air [°C]
t_{cn} - temperature on the pipe's external surface [°C]
t_{cv} - temperature on pipe's internal surface [°C]
t_m - mean temperature [°C]
t_{rm} - mean temperature on the rib [°C]
t_w - water temperature [°C]
α_{cn} - coefficient of convective heat transfer from the air onto pipe without ribs [W/m^{2}K]
α_r - coefficient of convective heat transfer from the air onto ribbed pipe [W/m^{2}K]
α_w - coefficient of convective heat transfer on the side of the water [W/m^{2}K]
δ_r - lamella's thickness [mm]

REFERENCES

[1] Kays W. M., London A. L., Compact Heat Exchangers, Mc Graw-Hill, New York, USA; 1984.
[2] Elmahdy A. H., A simple Model for Cooling and Dehumidifying Coils for Use in Calculating Energy Requirements for Buildings, ASHRAE Transactions, vol. 83, pp. 103-117, 1977.
[3] Rohsenow W. M., Hartnett J. P., Ganič E. N, Handbook of Heat Transfer Applications, McGraw-Hill Book Company, New York, USA, 1985.

[4] Kotke V., Blenke H., Mesmethoden konvektiever Stoffubertragung, Chemie – Ing. Tehnik, vol. 50, no. 2, pp. 81-90, 1978.
[5] Poredoš A., Allgemeines Modell zur Berechnung der Lamellen - warmeaustauscher, Fortschr.-Ber, VDI Reihe 19 Nr. 53. Dusseldorf: VDI - Verlag 1991, Dusseldorf, Germany, 1991.
[6] Slipčević B., Heat exchangers, SMEITS, Beograd, Serbia, 1987.
[7] Poredoš A., Calculations and measurements of lamella type air coolers, Univerza v Ljubljani, Fakulteta za strojništvo, Slovenia, 1979.
[8] Mojsovski A., Prenos na toplina, Univerzitet "Sv. Kiril i Metodij" - Skopje, Makedonija, 1992.

621.87.065:531.3

METHODOLOGY FOR DETERMINING OF THE TENSILE FORCE WITHIN THE STEEL ROPE OF CONVEYOR[2]

Prof. Dr. Sc. Elizabeta HRISTOVSKA
St. Ivo Lola Ribar b.b. Bitola, Faculty of Technical Sciences-Bitola,
elizabeta.hristovska@uklo.edu.mk

Abstract

This paper presents a methodology for determining of the tensile force within the steel rope of conveyor, specifically ropeway-chairlift with fixed-grip. This methodology defines a model for tensile force calculation within the steel rope under all exploitation conditions, and based on this it defines a competent case for analyzing of the forces and intensity of stresses. This objective is significant due to the fact that the tensile force represents a factor needed for determining the size of driving mechanisms applied at the conveyors comprising a pulling element (rope). This model has been applied to calculate the above parameters on a specific ropeway-chairlift with buckets for two persons, located on "Begova-Kopanki" ski-lane on the mountain Baba, near Bitola, R. Macedonia. This paper relates the final results of this calculation.

Keywords: conveyor with rope, ropeway-chairlift, steel rope, tensile force.

INTRODUCTION

To define the model for mathematical calculation of the tensile force within the steel rope of a conveyor (in this case, a ropeway-chairlift), it is necessary to determine some input data for this calculation, and these are the following:

Z_q - component of the force originating from the own weight of the steel rope,

q_j - weight of the steel rope per meter length,

g - gravity acceleration,

h - vertical difference between uppermost and nethermost level of the ropeway,

[2] review scientific paper

W_q - component of the force originating from the own weight of the buckets and from the useful load,
W - own weight of the ropeway,
Q_t - useful load (load of passengers),
w - distance between two chairs,
R_v - friction resistance force which is created between the steel rope and the pulleys along which it moves,
L - length of lane "Begova-Kopanki",
μ_{tr} - coefficient of friction between the rope and the pulleys,
h_{tr} - vertical difference of friction,
G_m - force of tension on the rope stemming from the balance weight, in kg,
G - force of balance weight itself,
T_v - tensile force within the steel rope at the entry to the driving pulley,
T_v' - tensile force within the steel rope at the exit from the driving pulley,
Q_q - required tensile force within the steel rope,
μ - coefficient of friction between the rubber layer and the steel rope,
Θ - angle of contact on the steel rope and the driving pulley,
Q_u - force of inertia,
L_H - horizontal length of ski-lane "Begova-Kopanki",
a - acceleration of the steel rope,
$Q_{vk,v}$ - required overall tensile force within the steel rope.

METHODOLOGY FOR TENSILE FORCE DETERMINING

For determining the tensile force within the steel rope, it is necessary to calculate previously the following magnitudes:

1) The component of the force originating from the own weight of the steel rope, "Z_q"

$$Z_q = \sum_0^L q_j \cdot g \cdot (dL) \cdot \sin\alpha = q_j \cdot g \cdot h \ \text{[N]}$$

2) The component of the force originating from the own weight of the buckets and from the useful load, "W_q"

$$W_q = \sum_0^L \frac{W + Q_t}{w} \cdot g \cdot (dL) \cdot \sin\alpha = \frac{W + Q_t}{w} \cdot q \cdot h \ \text{[N]}$$

3) The friction resistance force which appears between the steel rope and the pulleys along which it moves, "R_v"

$$R_v = (q_j + \frac{W + Q_t}{w}) \cdot L \cdot \mu_{tr} \cdot g \ \text{[N]}$$

$$h_{tr} = L \cdot \mu_{tr}$$

$$R_v = (q_j + \frac{W + Q_t}{w}) \cdot h_{tr} \cdot g \ \text{[N]}$$

4) The force of tension on the rope stemming from the balance weight, "G_m"

$\frac{G_m}{2}$ [kg] - force of tension from the balance weight, per side of the ropeway

CHARACTERISTIC CASES
I - CASE, FULL CHAIRS GOING UPHILL, EMPTY CHAIRS GOING DOWNHILL

- Tensile force within the steel rope at the entry to the driving pulley:

$$T_{vI} = \left[\frac{G_m}{2} + \frac{Q_t}{w} \cdot h + (2q_j + \frac{2W}{w} + \frac{Q_t}{w}) \cdot h_{tr} \right] \cdot g \ \text{[N]}$$

- Tensile force within the steel rope at the exit from the driving pulley:

$$T_{vI}' = \frac{G}{2} \ [N]$$

- Required tensile force within the steel rope:

$$Q_{qI} = T_{vI} - T_{vII}' = \underbrace{\frac{Q_t}{w} \cdot h \cdot g}_{\text{load}} + \underbrace{h_{tr} \cdot g \cdot (\frac{Q_t}{w} + 2q_j + \frac{2W}{w})}_{\text{resistance}} \ [N]$$

In this case for the uphill movement of the load, the required tensile force within the rope is "Q_{ql}".

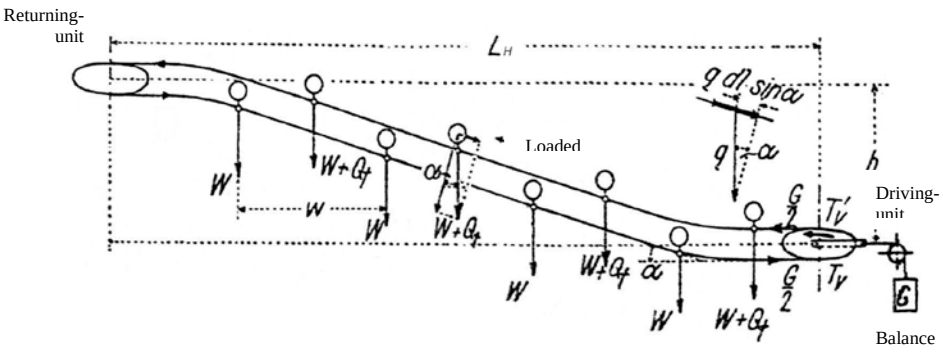


Figure 1 Simple scheme of ropeway-chairlift with the forces which react on the rope

II - CASE, EMPTY CHAIRS GOING UPHILL, FULL CHAIRS GOING DOWNHILL

- Tensile force within the steel rope at the entry to the driving pulley:

$$T_{vII} = \left[\frac{G_m}{2} - \frac{Q_t}{w} \cdot h + (2q_j + \frac{2W}{w} + \frac{Q_t}{w}) \cdot h_{tr} \right] \cdot g \ \text{[N]}$$

- Tensile force within the steel rope at the exit from the driving pulley:

$$T_{vII}' = \frac{G}{2} \ \text{[N]}$$

- Required tensile force within the steel rope:

$$Q_{qII} = T_{vII} - T_{vII}' = \underbrace{h_{tr} \cdot g \cdot (\frac{Q_t}{w} + 2q_j + \frac{2W}{w})}_{\text{resistance}} - \underbrace{\frac{Q_t}{w} \cdot h \cdot g}_{\text{load}} \ [N]$$

In this case the load is bigger than resistance, and for that reason the required tensile force within the rope is "Q_{qII}" , and it is with minus character.

III - CASE, FULL CHAIRS GOING UPHILL, FULL CHAIRS GOING DOWNHILL

- Tensile force within the steel rope at the entry to the driving pulley:

$$T_{vIII} = \left[\frac{G_m}{2} + (2q_j + \frac{2W}{w} + \frac{2Q_t}{w}) \cdot h_{tr} \right] \cdot g \ \text{[N]}$$

- Tensile force within the steel rope at the exit from the driving pulley:

$$T_{vIII}' = \frac{G}{2} \ \text{[N]}$$

- Required tensile force within the steel rope:

$$Q_{qIII} = T_{vIII} - T_{vIII}' = \underbrace{2h_{tr} \cdot g \cdot (\frac{Q_t}{w} + q_j + \frac{W}{w})}_{\text{resistance}} \ \text{[N]}$$

In this case the required tensile force within the rope is used merely for overcoming of the friction resistances between the steel rope and the pulley, the required tensile force within the rope is "Q_{qIII}", and it is at its lowest.

From all of these three quoted cases, it may be concluded that the required tensile force is biggest in I-case, and accordingly this case is the most proper for further calculation. It is particularly important in this case to check out the slipping between the steel rope and the rubber layer on driving pulley. That can be realized with the following equation:

$T_{vI} \le T_{vI}' \cdot e^{\mu \cdot \Theta}$, if this condition is met, there is no slipping of the rope, and in that case the calculation of the required overall tensile force within the rope can be carried on with.

To obtain the required overall tensile force it is necessary to calculate the forces of inertia which emerge when the ropeway is put into work, and these forces of inertia can be calculated with the equation:

$$Q_u = (\frac{Q_t}{w} + 2q + \frac{2W}{w}) \cdot \frac{L_H}{\cos\alpha} \cdot a \ \text{[N]}$$

The sum of the required tensile force and the forces of inertia is equivalent to the required overall tensile force within the rope, i.e. it is determined with the equation:

$$Q_{vk,v} = Q_{qI} + Q_u$$

APPLICATION OF THE MODEL

The presented methodology defines a model for determining of the tensile force within the steel rope of ropeway-chairlift when the driving-unit is at the lowest point (at the nethermost level of the ropeway).

The model is applied for calculation on specific ropeway, located on “Begova-Kopanki" ski-lane on mountain Baba, near Bitola.

The results of the calculations are displayed on the charts-1.

CONCLUSION

The model for calculation of tensile force within the steel rope of ropeway-chairlift is a model which offers a simplified calculation, but with reliable results.

The accuracy of the model has been verified on a specific object, whereby the calculated magnitudes are confirmed by the experimental measurements.

The cited methodology can be used for determining of these parameters with other ropeways of this type as well.

Charts-1 Results of the calculations

q_j [kg/m]	2,34
g [m/s^2]	9,81
h [m]	208,48
W [kg]	76
Q_t [kg]	160
w [m]	20
L [m]	685,33
μ_{tr}	0,02
h_{tr} [m]	13,06
G_m [kg]	12436,3

G [N]	122000
μ	0,16
Θ [°]	180
L_H [m]	652,85
a [m/s^2]	0,2

T_{vI} [N]	79959,81
T_{vI}' [N]	61000
Q_{qI} [N]	18959,75
T_{vII} [N]	47236,8
T_{vII}' [N]	61000
Q_{qII} [N]	-13763,26
T_{vIII} [N]	64623,24
T_{vIII}' [N]	61000
Q_{qIII} [N]	3623,2

$e^{\mu \cdot \Theta}$	1,65
T_{vI} / T_{vI}'	1,31
Q_u [N]	2771,5
$Q_{vk,\,v}$ [N]	21731,25

REFERENCES

[1] Hristovska E., Defining calculation methodology for load forces and cable deformations between the support towers of cableway-chairlift, Proceeding, Faculty of technical sciences-Bitola, Bitola, 2012.

[2] Hristovska E., Calculation methodology for the load on the support towers of cableway-chairlift, Proceeding, Faculty of technical sciences-Bitola, Bitola, 2013.
[3] POMAGALSKI S.A., ski-lane Begova-Kopanki, Grenoble France, 1976, set up in Macedonia
[4] LEITNER S.P.A., ski-lane Tresca, Bolzano, 1982, set up in Italy
[5] www.doppelmayr.com

539.234

LOW VACUUM EVAPORATED CUPROUS OXIDE THIN FILM FOR SOLAR CELL APPLICATION[3]

Ratka Neshkovska[1], Mimoza Ristova[2], Julijana Velevska[2]

[1]Faculty of Technical Sciences, University "St. Climent Ohridski", Bitola, Macedonia

[2]Faculty of Natural Sciences and Mathematics, Institute of Physics, P. O. Box 162, Skopje, Macedonia

e-mail: ratka_neskovska@yahoo.com

Abstract

Low vacuum evaporation method was used to prepare thin cuprous oxide, Cu_2O, films. Solid copper was used as a starting material. The films were deposited on a fluorine doped tin oxide pre-coated glass substrates, prepared by spraying pyrolysis technique. The films were characterised by X-ray diffraction and spectrophotometry. The XRD study showed that films are of Cu_2O phase when prepared at pressure of $0.67\,Pa$. Optical transmittance spectrum in the prepared films was measured in the $330-850\,nm$ wavelength range. The data were used to calculate absorption coefficient spectrum and the optical band gap. Determined value $2.97\,eV$, was found to be higher than the reported values.

Key words: cuprous oxide, thin films, low vacuum evaporation, band gap

INTRODUCTION

A major motivator for solar cell research and development is a reduction in cost of the finished module. Presently about half the cost of a finished module is due to the material itself [1]. Cuprous oxide, which is a promising semiconductor material for fabrication of photovoltaic devices like solar cell, has advantages of material abundance, low-cost, non-toxicity and manufacturability. The potential for cost reduction when using materials

[3] original scientific paper

which do not require dicing is therefore substantial. That is why cuprous oxide cells are a promising candidate and are suitable for photovoltaic, photoelectrochemical, photothermal and gas sensor application. Recently, it was found that cuprous oxide thin films exhibit electrochromic properties [2-7], coloring at negative potentials when are incorporated in electrochromic devices.

Even though Cu_2O is not a very attractive photovoltaic material owing to its not so narrow band gap, it is stable and abundant and there are inexpensive device fabrication techniques for it.

Cu_2O is generally prepared by high temperature oxidation of Cu [8], low temperature oxidation [9], electrochemical deposition [10], chemical deposition [11], sputtering [12], sol-gel-like dip techniques [13], anodic oxidation [14, 15], laser ablation [16], etc.

Method of low vacuum evaporation of cuprous oxide thin films on conductive and transparent substrates is reported below, XRD analyses of deposited films and some of their optical properties.

EXPERIMENTAL

Microscopic glasses ($25 \times 75 \times 1 mm$) were used as substrates in this experiment. Prior to every deposition, the substrates were immersed in a mixture of chromic and sulphuric acid for 24 h. After that the glass substrates were rinsed with distilled water and wiped off. A conductive and transparent fluorine doped tin oxide electrode (FTO) was obtained onto the substrates, using the spray pyrolysis method. Spraying was performed with BOSH Type 0603 260 403 sprayer, spraying $300 ml$ $0.05 M$ of aqueous solution of $SnCl_2 \cdot 2H_2O$. The fluorine doping was done by adding NH_4F crystals, until neutrality was achieved. The spraying lasted about $1 s$, with pauses $5 - 6 s$ between. The temperature of the glass substrates during deposition was maintained at $400^0 C$. Such FTO films were about $2 \mu m$ thick, with a resistance of $18 - 38 \Omega/cm^2$ and 80 % transparency for visible light.

Cuprous oxide film was deposited onto such prepared substrates employing low vacuum evaporation method. The melting temperatures of Cu, CuO and Cu_2O are $1083^0 C$, $1326^0 C$ and $1235^0 C$ respectively. The temperature difference between elemental and oxides melting points makes

the evaporation technique attractive for depositing of copper oxide thin films. Stable copper oxides can be deposited over a source temperature region of $1090-1350^0\,\mathrm{C}$. In general, the oxidation rate and the evaporation rate of the source material define the deposition rate of the product grown on the substrate surface. Copper oxide thin films were deposited on glass substrates pre coated with FTO by the low vacuum evaporation technique, using granulated ($0.3\,\mathrm{mm}$) copper with 99.8 % purity as a starting material. Deposition was performed in a Balzers Automatic BA 510 apparatus. The distance between the source (copper) and the substrates was about $50\,\mathrm{cm}$. The evaporation pressure was $0.67\,\mathrm{Pa}$. During evaporation the transparency of the substrates changed by 50 %. The deposition lasted several minutes, until all of the starting material from the tungsten boat was evaporated. If the vacuum in the chamber is very high, pure copper will be deposited on the glass substrates. In our case the vacuum was not so high, so evaporated copper reacted with the gasses in the chamber. As a result of that reaction cuprous oxide thin films were obtained on the substrates. Some films were deposited onto conducting glasses and some were deposited onto glasses without conductive oxide film onto them.

The deposited films were yellowish in appearance. The film thickness, measured by weight different method was about $130\,\mathrm{nm}$.

The films deposited onto glass without a transparent conducting layer were characterized by Siemens D-500 X-ray diffractometer, with $V = 40\,\mathrm{kV}$, $I = 30\,\mathrm{mA}$, using Cu K_α radiation with a wavelength of $0.154\,\mathrm{nm}$, with a graphite monohromator and scintillation counter. The Bragg angle was varied in the interval from 20^0 to 40^0.

The films composition was also studied with scanning electron microscope JEOL JSM 35 CF.

The visible transmission spectrum was recorded for deposited films, using Varian CARY 50 Scan UV-Visible spectrophotometer in the wavelength range from 330 to $850\,\mathrm{nm}$. Prior to the recording of the spectrum, transmission spectrum for glass/FTO substrate (blank probe) was recorded and it was normalized to 100 % transmission.

RESULTS AND DISCUSSION

The X-ray diffraction analyses of the films confirm that they are cuprous oxide (Cu_2O), without traces of CuO.

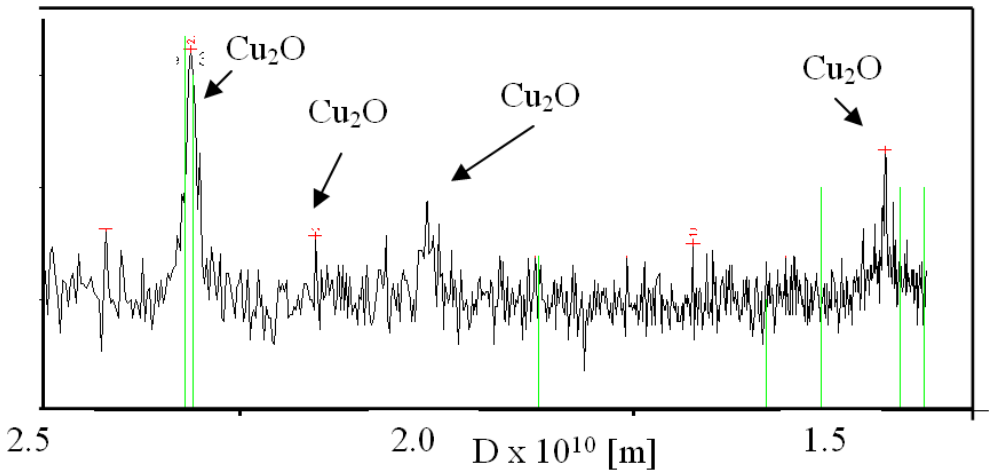


Fig.1. X-ray diffraction pattern for low vacuum evaporated Cu_2O films.

Peaks (JCPDS, 35-1091)	$D \cdot 10^{10}$ **(m)**	2Θ **(°)**
1.	2.218	40.62
2.	2.121	42.57
3.	2.020	44.81
4.	1.455	63.90

Table 1. Cu_2O peaks identification and conversion from D spacing to 2Θ.

The four detected XRD peaks at $2.218 \cdot 10^{-10}$ m, $2.121 \cdot 10^{-10}$ m, $2.020 \cdot 10^{-10}$ m and $1.455 \cdot 10^{-10}$ m correspond to the crystalline Cu_2O [Fig. 1]. Table 1 gives Cu_2O peak identification and D values to 2Θ values conversion [17].

The transmission spectrum of films in as prepared state is given in Fig. 2. Minimal and maximal values of transmittance is given in Table 2.

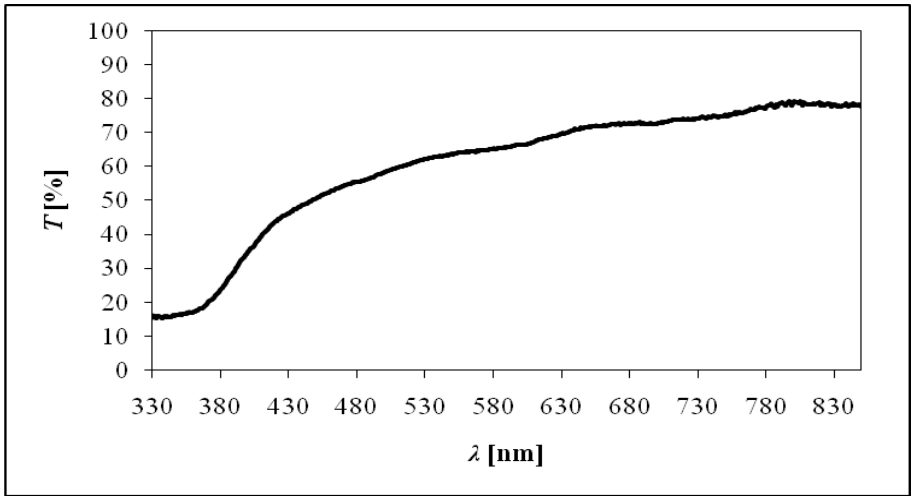


Fig. 2. Optical transmittance spectrum for a low vacuum evaporated Cu_2O thin film.

State of film	T_{min} [%]	T_{max} [%]
As prepared	16	79

Table 2. Minimal and maximal values of transmittance for a Cu_2O film in visible rang of spectrum.

Incident, $I_0(h\nu)$ and transmitted, $I(h\nu)$ intensity of radiation through the film with thickness *d* are related with equation:

$$I(h\nu) = I_0(h\nu)e^{-\alpha(h\nu)d}\,, \tag{1}$$

where $\alpha(h\nu)$ is the absorption coefficient for a given film with thickness *d*. The coefficient $\alpha(h\nu)$ is related with the photon's energy $h\nu$ and the optical band gap E_g [18]:

$$(\alpha h\nu)^{2/n} = A(h\nu - E_g)\,, \tag{2}$$

where A is a constant, and n is a number which depends on the type of transition. The absorption coefficient was evaluated from:

$$\alpha = \frac{1}{d} \ln \frac{100}{T(\%)}, \quad (3)$$

T are transmittance data values. Calculated values of coefficient α versus wavelength of incident radiation are presented on Figure 3.

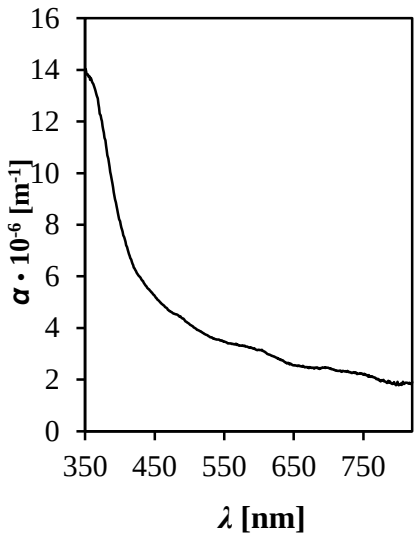


Figure 3.

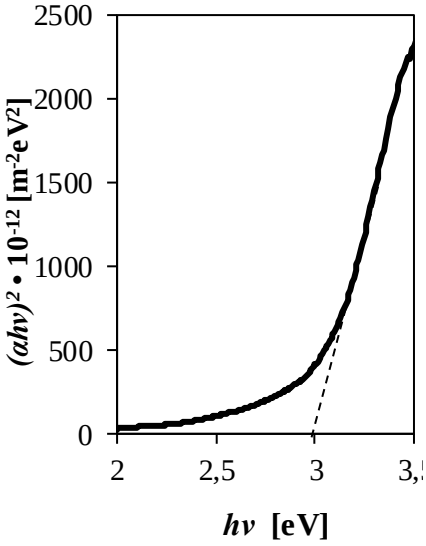


Figure 4.

Fig. 3. Absorption coefficient versus the wavelength of incident radiation for a $130\,\text{nm}$ thick Cu_2O film.

Fig. 4. $(\alpha h\nu)^2$ versus photon energy.The interception of the strait dashed line with the $h\nu$ - axsis coresponds to the direct energy band gap.

The value of number n and the type of transition was estimated from the graphical presentation of $(\alpha h\nu)^{2/n}$ versus photon energy [Figure 4]. Linear dependence of $(\alpha h\nu)^{2/n}$ versus $h\nu$ is obtained for $n = 1$, which corresponds to direct band to band electron transition mechanism. The band gap energy was evaluated from the graph in Fig. 4, as interception of the linear part with the photon energy axis. The evaluated value for the prepared film by method of low vacuum evaporation was $2.97\,\text{eV}$. The obtained

values are higher than reported values for films obtained with other methods of preparation [19, 20].

CONCLUSION

Cuprous oxide, Cu_2O is a semiconductor which shows a varying optical behaviour because of stoichiometric deviations arising from its preparation methods and parameters. Pure Cu_2O films with higher energy band gap than reported in literature are obtained with the proposed preparation method of low vacuum evaporation.

Although that, cuprous oxide is attractive alternative for silicon and other semiconductors for application in solar cells devices.

REFERENCES

[1] M. J. McCann, K. R. Catchpole, K. J. Weber, A. W. Blakres, Solar Energy Materials & Solar Cells 68 (2001) 135-171.
[2] H. Demiryont, US Patent 4, 830,471.
[3] F. I. Brown, S. C. Schulz, US Patent 5, 585, 959.
[4] N. Özer, F. Tepeha, Solar Energy Materials & Solar Cells 30 (1993) 13-26.
[5] T. J. Richardson, J. L. Slack and M. R. Rubin, Electrochimica Acta 46 (2001) 2281-2284.
[6] R. Neškovska, M. Ristova, J. Velevska, M. Ristov, Thin Solid Films 515 (2007) 4717-4721.
[7] M. Ristova, R. Neškovska, V. Mirčeski, Solar Energy Materials & Solar Cells 92 (2007) 1361-1365.
[8] A. E. Rakhshani, Solid State Electronic Vol. 29, No. 1 pp. 7-17, 1986.
[9] A. Ross, T. Chibue, B. Karlsson, Solar Energy Materials 7 (1983) 453-465.
[10] V. Georgieva, M. Ristov, Solar Energy Materials & Solar Cells 73 (2002) 67-73.
[11] M. Ristov, Gj. Sinadinovski, I. Grozdanov, Thin Solid Films 123 (1985) 63 – 67.
[12] A. A. Ogwu, E. Bouquerel, O. Ademosu, S. Moh, E. Crossan, F. Placido, Journal of Physics D: Applied Physics 38 (2005) 266-271.
[13] N. S. C. Ray, Solar Energy Materials & Solar Cells 68 (2001) 307-312.
[14] E. Fortin, D. Masson, Solid State Electronic Vol. 25, No. 4, pp. 281-283, 1982.
[15] H. S. Potdar, N. Pavaskar, A. Mitra, A. P. B. Sihna, Solar Energy Materials 4 (1981) 291-299.

[16] S. B. Ogale, P. G. Bilurkar, S. Joshi, G. Marest, Phys. Rew. B 50, 9743-9751 (1994).
[17] JCPDS – International Centre for Diffraction Data 35-1091.
[18] X. Mathew, N. R. Mathews, P. J. Sebastian, Solar Energy Materials & Solar Cells 70 (2001) 277-286.
[19] Y. Chang, J. J. Teo, H. C. Zeng, *Langmuir* 21/3 (2005) 1074-1079.
[20] Lj. Aljinović, V. Gotovac, M. Smith, *Fizika*, Vol. 21, Supplemet 1 (1989) 109-112.

515.126

DIFFERENT NOTIONS FOR CONTINUITY[4]

Marzanna Seweryn-Kuzmanovska, PhD
Faculty of Education, Bitola
marzanna.kuzmanovska@yahoo.com
Sonja Chalamani, M.Sci.
Technical Faculty, Bitola
scalamani@yahoo.com

ABSTRACT

In this paper we defined some different notions for continuous function of topological spaces and we examined the connections about them.

Keywords: cliquish map, quasi-continuity, semi-continuity, simple continuity, pseudo-continuity and almost continuity.

1. INTRODUCTION

The notion of continuity played a very important role in the development of mathematics, not only in mathematical analysis, but also outside of it. You can say that this notion became an inspiration for creating the topology.

In the XX^{th} century, it had many attempts for generalization of this notion. One of these attempts is the attempt of Polish mathematician Stefan Kempisty in 20^{th} years of XX^{th} century, who introduced the notion of quasi-continuity. Then other mathematicians as A. Neubrunnova, W.W. Bledsoe, S. Marcus, N. Levine, H.P. Thielman, N. Biswas, T. Husain introduced the notions of cliquish function, semi-continuity, simple continuity, pseudo-continuity, almost continuity, etc. These notions are characterized by not giving any continuity defined by using some topology if they share many properties with topological continuity.

The purpose of this paper is to review some of these continuity that have been studied in the works of A.. Neubrunnova ([9],[10],[11]).

In this paper the notion of function, we understand as mapping between topological spaces.

[4] review scientific paper

2. SEMI-CONTINUITY AND QUASI-CONTINUITY

The notion of quasi-continuity function was introduced by S. Kempisty in [5]. Equivalent definition was given by W.W. Bledsoe in [2], where quasi-continuity functions are called functions with neighborhoods. This equivalence was proved by S. Marcus in [8]. One of these definitions is the following:

Definition 2.1. Let X and Y be topological spaces. Function $f : X \to Y$ is called *quasi-continuity* in point $x \in X$ if for any open neighborhood V of the point x and for any open neighborhood G of the point $f(x)$ there is nonempty open set $U \subset V$ such that $f(U) \subset G$.

We will show that the notion of quasi-continuity function is equivalent to the notion of semi-continuity function defined by N. Levine in [7] by using the concept of semi-open set.

Definition 2.2. The set $A \subset X$ is called *semi-open* if there is an open set O such that $O \subset A \subset \overline{O}$.

Definition 2.3. Function is called *semi-continuity* if for any open set $G \subset Y$, the set $f^{-1}(G)$ is semi-open.

Theorem 2.1. Let $f : X \to Y$. The function f is semi-continuity if and only if f is quasi-continuity (i.e. quasi-continuity at any point $x \in X$).

Proof. Let the function f be semi-continuity. Let $x_0 \in X$ and let the open set G be such that $f(x_0) \in G$. Let V be an open set which contains x_0. From the assumption follows that $f^{-1}(G)$ is a semi-open set. Then $\overline{Intf^{-1}(G)} \supset f^{-1}(G)$. Let $U = V \cap Intf^{-1}(G)$. Since $x_0 \in f^{-1}(G) \subset \overline{Intf^{-1}(G)}$, then there is point in V that belongs to $Intf^{-1}(G)$. Accordingly, U is open set. Hence $U \subset V$ and

$$f(U) = f\left(V \cap Intf^{-1}(G)\right) \subset f\left(f^{-1}(G)\right) \subset G.$$

It follows that f is quasi-continuity at the point x_0. Because x_0 is arbitrarily chosen, it follows that the function f is quasi-continuity of X.

Conversely, let f be quasi-continuity of *X*. Let *G* be a nonempty open set. Let $x_0 \in f^{-1}(G)$ and let *V* be an open set containing the point x_0. Quasi-continuity of *f* at x_0 implies that there is an open set $U \neq \varnothing$, $U \subset V$ such that $f(U) \subset G$ i.e. $U \subset f^{-1}(G)$. It follows that $U \subset Intf^{-1}(G)$. Accordingly,

$$\varnothing \neq U = V \cap U \subset V \cap Intf^{-1}(G).$$

Hence, it follows that for the open set *V*, which contains x_0 we have $V \cap Intf^{-1}(G) \neq \varnothing$. Accordingly, $x_0 \in \overline{Intf^{-1}(G)}$. Because the point x_0 is arbitrarily chosen, it follows that $f^{-1}(G)$ is semi-open. ♦

The notion of semi-continuity can be defined for a point.

Definition 2.4. Function $f : X \to Y$ is called *semi-continuity at a point* $x \in X$ if for arbitrary open set $G \subset Y$ for which $f(x) \in G$ there is a semi-open set U such that $x \in U$ and $f(U) \subset G$.

The question is raised, whether semi-continuity at point is equivalent to the quasi-continuity of the function at that point.

That semi-continuity at a point x entails quasi-continuity at a point x, we can show in the same way as in the first part of Theorem 2.1. The second part of Theorem 2.1 uses the quasi-continuity at each point $x \in X$. It follows that the proof in this side must be modified.

Theorem 2.2. Function $f : X \to Y$ is quasi-continuity at a point $x_0 \in X$, if and only if f is semi-continuity in x_0.

Proof. From that, we showed above. It is sufficient to show that the quasi-continuity in x_0 entails semi-continuity in x_0.

Let G be an open set such that $f(x_0) \in G$. Let *V* be an open set that contains the point x_0. There is an open set $U \subset V$ such that $U \neq \varnothing$ and $f(U) \subset G$. Union by all such sets U, for all open sets *V* containing x_0, is the open set W. Let $S = W \cup \{x_0\}$. The set S is semi-open. Accordingly, $f(S) \subset G$. ♦

Theorem 2.3. Function $f : X \to Y$ is semi-continuity of X if and

only if f is semi-continuity at each point $x \in X$.

Proof. Let f be semi-continuity of X. By Theorem 2.1 the function f is quasi-continuity of X, i.e. quasi-continuity at each point $x \in X$. Thus, f is semi-continuity at each point $x \in X$ (by Theorem 2.2).

Conversely, let f be semi-continuity at each point $x \in X$, then f is quasi-continuity at each point $x \in X$ (by Theorem 2.2), i.e. quasi-continuity of X. Therefore, f is semi-continuity of X (by Theorem 2.1). ♦

Next we will show that in the case of real functions the notion of semi-continuity is different from the notion of semi-continuity from below and above.

Definition 2.5. Real function $f : X \to R$ is called *semi-continuity from above* (*from below*) at the point x_0 if for arbitrary $a \langle f(x_0)$ ($a \rangle f(x_0)$) there is an open set U such that $x_0 \in U$, and for each $x \in U$, $f(x) \rangle a$ ($f(x) \langle a$).

Example 2.1. Let $X = Y = [0,1]$. Defined $f : X \to Y$ as follows:

$$f(x) = \begin{cases} 0 & \text{if } x \in \left[0, \frac{1}{2}\right) \cup \left(\frac{1}{2}, 1\right] \\ 1 & \text{if } x = \frac{1}{2} \end{cases}.$$

f is not semi-continuity at the point $\frac{1}{2}$, but it is semi-continuity above at arbitrary point $x \in [0,1]$.

Example 2.2. Let $X = [0,1]$, $Y = (-\infty, \infty)$. We will consider the following sequence of intervals:

$$I_1 = \left[\frac{1}{2}, 1\right],\ I_2 = \left(\frac{1}{3}, \frac{1}{2}\right),\ I_3 = \left[\frac{1}{4}, \frac{1}{3}\right],\ I_4 = \left(\frac{1}{5}, \frac{1}{4}\right),\ I_5 = \left[\frac{1}{6}, \frac{1}{5}\right], \ldots$$

Accordingly, $\bigcup_{i=1}^{\infty} I_n = (0,1]$. We define function f on $[0,1]$ as follows:

$$f(x)=\begin{cases}-1 & if \quad x\in I_{3n-1}\\ \dfrac{1}{2} & if \quad x\in I_{3n}\cup\{0\}\\ 1 & if \quad x\in I_{3n-2}\end{cases}.$$

The function *f* is not semi-continuity nor below nor above at the point 0. But it is obviously quasi-continuity, and thus semi-continuity at each point $x\in\left[0,\frac{1}{2}\right]$.

3. SIMPLE CONTINUITY AND CLIQUISH CONTINUITY

The notion of cliquish function was introduced by W.W. Bledsoe in [2] as a notion of function with neighborhoods for real variable with values in metric spaces. It is a generalized notion of H.P. Thielman in [12] for a function defined on a topological space with values in a metric space.

Definition 3.1. Function $f:X\to Y$, where X is a topological space and Y is a metric space with metric ρ is called *cliquish* at a point $x\in X$ if for any $\varepsilon\rangle 0$ and any neighborhood U of x there is nonempty open set $G\subset U$ such that for any $x_1,x_2\in G$, $\rho[f(x_1),f(x_2)]\langle\varepsilon$.

Obviously, this notion is much more general than continuity or quasi-continuity of a function. Simple examples show that cliquish functions cannot be quasi-continuity.

Example 3.1. Let $X=[-1,1]$, $Y=(-\infty,\infty)$ be a metric space with ordinary metric. We defined $f:X\to Y$ as follows:

$$f(x)=\begin{cases}-\dfrac{1}{2} & if \quad x\in[-1,0)\cup(0,1]\\ \dfrac{1}{2} & if \quad x=0\end{cases}.$$

The function f is cliquish at the point 0, but it is not quasi-continuity at that point.

The notion of a simple continuity function in terms of a simple open sets was introduced N. Biswas in [1].

Definition 3.2. The set A is called *simple open* if $A = O \cup N$ where O is an open set and N is a nowhere dense set.

Definition 3.3. Function $f : X \to Y$ where X, Y are topological spaces is called *simply continuity* if for any simple open set $G \subset Y$, the set $f^{-1}(G)$ is simply open.

Because each semi-open set is simply open, hence it follows that each semi-continuity function is simply continuity. The opposite statement is not true.

Example 3.2. Let $X = Y = R$. We defined $f : X \to Y$ as follows:

$$f(x) = \begin{cases} 0 & if \quad x \neq 0 \\ 1 & if \quad x = 0 \end{cases}.$$

The function *f* is simply continuity, but is not semi-continuity.

Theorem 3.1. Let X be a topological space of second category at each point and let Y be a metric space. Then each function $f : X \to Y$ which is simply continuity is also cliquish.

Proof. Let $\varepsilon \rangle 0$, $x_0 \in X$ and let V be open set which contains the point x_0. Let $\{y_n\}$ be a countable dense set in Y. By $K\left(y_n, \frac{\varepsilon}{2}\right)$ we denote the open ball with center y_n and radius $\frac{\varepsilon}{2}$. Since $\bigcup_{n=1}^{\infty} K\left(y_n, \frac{\varepsilon}{2}\right) = Y$ then $\left[\bigcup_{n=1}^{\infty} f^{-1}\left(K\left(y_n, \frac{\varepsilon}{2}\right)\right)\right] \cap V = V$. From the above assumptions $f^{-1}\left[K\left(y_n, \frac{\varepsilon}{2}\right)\right] = G_n \cup Z_n$, where G_n is open set and Z_n is nowhere dense in X. Then

$$\left[\bigcup_{n=1}^{\infty} G_n \cap V\right] \cup \left[\bigcup_{n=1}^{\infty} Z_n \cap V\right] = V.$$

Since $\bigcup_{n=1}^{\infty} Z_n \cap V$ is of first category in V and V is a second category, then

$\bigcup_{n=1}^{\infty} G_n \cap V \neq \varnothing$. Taking $U = G_{n_0} \cap V$ we get open set $U \subset V$ such that for any $x_1, x_2 \in U$, $f(x_1), f(x_2) \in K\left(y_{n_0}, \frac{\varepsilon}{2}\right)$, i.e. $\rho[f(x_1), f(x_2)] \langle \varepsilon$. Thus, f is cliquish at the point x_0.♦

The opposite statement does not necessarily apply.

Example 3.3. Let $X = Y = [0,1]$. Let f be a Riemann function

$$f(x) = \begin{cases} \frac{1}{q} & if \quad x = \frac{p}{q} \in [0,1], NZD(p,q) = 1, q \rangle 0 \\ 1 & if \quad x \in [0,1], x \in I \end{cases},$$

where I is a set of irrational numbers. Then f is cliquish, but is not simply continuity because if $G = (0,1]$ and then $f^{-1}(G)$ is set of rational numbers which is not simple-open.

The proof of Theorem 3.1 uses the fact that X is of second category in each of its points. It is interesting to show that this assumption is not necessary at least in the case when Y is a metric space.

Theorem 3.2. Let X be a metric space and let Y be a completely bounded metric space. Then each function $f: X \to Y$ which is simply continuity on X is cliquish on X.

Proof. Let $\varepsilon \rangle 0$, $x \in X$ and let V be open neighborhood at a point x. Since Y is completely bounded, it follows that there is a finite number of open sets $G_1, G_2, ..., G_n$ such that their diameters are smaller than ε and $Y = \bigcup_{i=1}^{n} G_i$. We have $f^{-1}(G_i) = U_i \cup Z_i$, where U_i is open and Z_i is nowhere dense in *X*. It is enough to show that there is i_0 such that $U_{i_0} \cap U \neq \varnothing$. This is true because

$$U = X \cap U = f^{-1}(Y) \cap U = \left[\bigcup_{i=1}^{n} f^{-1}(G_i)\right] \cap U = \left[\bigcup_{i=1}^{n} (U_i \cup Z_i)\right] \cap U =$$

$$= \left[\bigcup_{i=1}^{n} U_i \cap U\right] \cup \left[\bigcup_{i=1}^{n} Z_i \cap U\right].$$

The set $\bigcup_{i=1}^{n} Z_i \cap U$ is nowhere dense in U. Then $\bigcup_{i=1}^{n} U_i \cap U \neq \varnothing$. Accordingly, $U_{i_0} \cap U \neq \varnothing$ for some i_0.♦

4. PSEUDO-CONTINUITY AND OTHER TYPES OF CONTINUITY

The notion of a simple continuity function can be generalized to the notion of pseudo-continuity function by pseudo-open sets.

Definition 4.1. The set A in a topological space *X* is called *pseudo-open* if $A = O \cup N$ where O is open set and N is of the first category.

Definition 4.2. Function $f : X \to Y$ where X, Y are topological spaces is called *pseudo-continuity* of X if for any open set $G \subset Y$, the set $f^{-1}(G)$ is pseudo-open.

Since simply open sets are pseudo-open, then it follows that each simply continuity function is pseudo-continuity. The opposite statement is not true. As an example it is sufficient to consider the function of Riemann.

The following theorem is generalization of Theorem 3.1 and can be proved as that theorem.

Theorem 4.1. Let X be a topological space of the second category at each of its points and let Y be a metric space . Let $f : X \to Y$ be pseudo-continuity. Then f is cliquish.

The opposite theorem of the above can be proved in a general form.

Theorem 4.2. Let X be a topological space and let Y be a metric space. Let $f : X \to Y$ be cliquish. Then f is pseudo-continuity.

Proof. It suffices to show that if f is cliquish then the set of points of noncontinuous is of first category in *X*.

Let $C(f)$ be a set of points of continuity of function *f*. Then $C(f) = \bigcap_{n=1}^{\infty} G_n$, where G_n are open $(n = 1,2,...)$ (by theorem: The set of

points of continuity of a function $f : X \to Y$ is of type G_δ). Thus, the set of points of a noncontinuous has the form

$$D(f) = X \setminus C(f) = X \setminus \bigcap_{n=1}^{\infty} G_n = \bigcup_{n=1}^{\infty} (X \setminus G_n) = \bigcup_{n=1}^{\infty} F_n .$$

If $D(f)$ is of the second category then at least one of the sets, for example F_{n_0}, is of the second category, and this implies that the $IntF_{n_0} \neq \varnothing$. Let $x \in IntF_{n_0}$. Since f is cliquish at the point x, it follows that there is an open set $U \neq \varnothing,\ U \subset IntF_{n_0}$ such that the diameter $d(f(U)) \leq \frac{1}{2n_0}$. By the definition of the set F_{n_0} it follows that if $x \in U$ then there is a point $x' \in U$ such that $\rho[f(x), f(x')] \geq \frac{1}{2n_0}$. This contradicts to the assumption that f is cliquish function, i.e. the set $D(f)$ must be of the first category. Thus, f is a pseudo-continuity.♦

Theorem 4.3. Let X be a topological space of second category at each of its points and let Y be a metric space. Function $f : X \to Y$ is pseudo-continuity if and only if f is cliquish.

Proof. This is a consequence of theorems 4.1. and 4.2.♦

The notion of almost continuity was introduced by T. Husain in [3] and [4].

Definition 4.3. Function $f : X \to Y$ where X, Y are topological spaces is called *almost continuity* at a point $x \in X$ if for any open set $G \subset Y$ such that $f(x) \in G$, $x \in Int\overline{f^{-1}(G)}$.

Almost continuity functions need not to be pseudo-continuity.

Example 4.1. Let $X = Y = [0,1]$. Let

$$f(x) = \begin{cases} 0 & if \quad x \in Q \\ 1 & if \quad x \in I \end{cases},$$

where Q is a set of rational number, and I is a set of irrational number. Function f is a almost continuity, but it is not pseudo-continuity because if

$G = \left[0, \frac{1}{2}\right)$ then $f^{-1}(G)$ is a set of irrational number in $[0,1]$ which is not pseudo-open.

To show that the other previously mentioned notions of continuity withdraw almost continuity, it is sufficient to show that the quasi-continuity does not entail almost continuity.

Example 4.2. Let $X = Y = [0,1]$. Let

$$f(x) = \begin{cases} 0 & if \quad x \in \left[0, \frac{1}{2}\right] \\ 1 & if \quad x \in \left(\frac{1}{2}, 1\right] \end{cases}.$$

Function f is quasi-continuity at any point $x \in [0,1]$, but it is not almost continuity at the point $x = \frac{1}{2}$.

LITERATURE

[1] Biswas, N. (1970). *On some mappinge in topological space*, Thesis submitted to the University of Calcutta for the D. Phil. Arts Degrec.

[2] Bledsoe, W. W. (1952). *Neighbourly functions*, Proceedings of American Mathematical Society 3, 114-115.

[3] Husain, T. (1966). *Almost continuous mappings*, Ann. Soc. Math. Polonaise, Serie 1, Prace Matematyczne 10, 1-7.

[4] Husain, T. (1967). *Some remarks about real almost continuous functions*, Math. Mag. 40, 250-254.

[5] Kempisty, S. (1932). *Sur les functions quasicontinues*, Fundamenta Mathematicae 19, 184-197.

[6] Kotlicka, E., & Maliszevski, A., (2002). *On quasi-continuity and cliquishness of sections of functions of two variables*, Tatra Mt. Math. Publ. 19, 105-108.

[7] Levine, N. (1963). *Semi-open sets and semi-continuity in topological spaces*, American Mathematical Monthly 70, 36-43.

[8] Marcus, S. (1971). *Sur les functions quasicontinues an sens de S. Kempisty*, Collog. Math., 47-53.

[9] Neubrunnová, A. (1973). *On certain generalizations of the notion of continuity*, Matematický časopis 23, 374-380.

[10] Neubrunnová, A. (1974). *On quasi-continuous and cliquish functions*, Casopis Pest. Math. 99, 109-114.

[11] Neubrunnová, A. (1975). *On transfinite sequences of certain types of functions*, Acta Fac. Rer. Natur. Univ. Comenianae Math. 30, 121-126.

[12] Thielman, H.P. (1953). *Types of functions*, American Mathematical Monthly 60, 156-161.

551.506(497.172)

MONTHLY VALUES OF METEOROLOGICAL PARAMETERS FROM PUBLIC SOURCES AVAILABLE ON LOCATION SKOPJE - PETROVEC[5]

Professor Gjorgji Trombev*,
Associate professor Vladimir Mijakovski*

** University "St. Kliment Ohridski" - Bitola, Faculty of Technical Sciences - Bitola,* str. Ivo Lola Ribar nn, Bitola, Republic of Macedonia,
gtrombev@gmail.com; vladimir.mijakovski@tfb.uklo.edu.mk

ABSTRACT

For a variety of HVAC calculations, data for monthly values of individual meteorological parameters are required.

Given that for the locations in the Republic of Macedonia, there are no official publicly available data on meteorological parameters, in numerous cases, it is complicated to perform certain HVAC calculations.

The paper is an attempt, on the basis of publicly available sources, to indicate monthly values for individual meteorological parameters for the location Skopje-Petrovec, with emphasis on the parameters of the solar radiation. Data for the so-called "solar geometry" are also considered, that are, in turn, closely related to the parameters characteristic for solar radiation. Given the above mentioned, for the location of Skopje, the paper examines the sunrise and sunset times, length of day and night, path of the sun during the day and other parameters in the area of so-called "solar geometry".

Location Skopje-Petrovec is taken into consideration because there are more publicly available sources of meteorological data, and it can be used for making comparisons and evaluation of data from different sources.

Keywords: meteorological parameters, monthly values, publicaly available sources/data.

[5] original scientific paper

INTRODUCTION

Nowadays, the topic of buildings energy efficiency is very attractive. This topic is closely related to monthly values of certain meteorological parameters, typical for the location of the object.

Utilisation of renewable energy sources (in the context of above mentioned, and of solar energy) is also closely related to monthly values of certain meteorological parameters, typical for the location of the object.

At the same time, also for many other HVAC calculations (heating, ventilation, air conditioning, drying, etc.) meteorological data are used as primary input data as bases for individual locations. For certain calculations and defining of certain indicators, individual monthly values of meteorological parameters specific to the location where the facility is located is of high importance.

In this papre, for the location of Skopje – Petrovec, on the bases of publicly available sources, monthly values of certain meteorological parameters are considered.

As a source of data, publicly available sources, i.e. internet websites, are used.

MONTHLY METEOROLOGICAL DATA

For the preparation of the article, the following data are used:

- NASA's website **https://eosweb.larc.nasa.gov/sse/** ,
- Website **http://www.gaisma.com/en/location/skopje.html.**

Website **https://eosweb.larc.nasa.gov/sse/** contains data on a number of grounds (according to **NASA Surface meteorology and Solar Energy**).

The choice of locations is in terms of longitude and latitude, and an additional parameter is altitude. In addition, the reported data are for the period of observation from 1983 to 2005.

Furthermore, the methodology used is listed in L.3, which occurs as a side material for the structure of data from specified website.

From many features that are available on the website, the paper uses data for average monthly values of meteorological parameters for the individual location of Skopje - Petrovec. The data presented below, are systematized by groups such as:

- Temperatures,

- Other (relative humidity, precipitation, etc.),
- Wind,
- Data for the so-called “solar geometry”,
- Parameters for solar radiation,
- Parameters for sizing and pointing of solar thermal panels,
- Parameters for tilted solar panels,
- Parameters for sizing battery or other energy - storage systems,
- Parameters for sizing surplus-product energy systems.

From the website **http://www.gaisma.com/en/location/skopje.html**, the diagrams presented in the article are taken over, which complete the picture for “solar geometry” typical for the location.

The structure on diagrams presented in the article, is explained by Labels with the description of numbers in each figure.

On diagram (Fig. 1), for the location of Skopje, for the entire year, a visual representation of the sunrise, sunset, beginning of dawn and end of dusk, dawn and twilight and the duration of day/night is given.

On diagram (Fig. 2), for the location of Skopje, daily path of the sun is visually presented, by which a daily path of the sun, for any day in the year, can be drawn.

Due to limited space, some data given on the websites are omitted (data for clouds, part of the data in the field of "solar geometry", etc.).

In order to avoid burdening of the article, the reviewed data for location of Skopje – Petrovec, arranged in tables, are given in Annex

It must be noted that some of the data presented, specifically data on meteorology (temperature and other) do not coincide completely with the data from other publicly available sources.

The differences in values and the reasons for these differences can be on several grounds (different periods of observation, different way of measuring - measurements in meteorological stations, satellite measurements, hybrid data base models, etc.). Furthermore, the identified differences and the reasons for them can be clarified with a deeper analysis of various data from different sources, which can be of interest for further work in this area.

CONCLUSION

In the paper, reviewed monthly average values for individual meteorological parameters taken from public data sources (internet sites) are used. This exceeds, sometimes existing problem on the availability of meteorological data for individual locations in the Republic of Macedonia.

Considered data is for the period 1983 – 2005, systematized in groups.

In websites used, which is followed in the paper, emphasis is placed on data parameters from solar radiation. However, despite these data parameters from solar radiation, cited data refer to other meteorological parameters.

Also, for the location considered (Skopje - Petrovec), data from the area of so-called "solar geometry" are also reviewed. Time of sunrise and sunset, appearance of dawn and dusk, duration of day and night, path of the sun during the day and other data are also considered.

Monthly values of individual meteorological variables, data about the location of Skopje – Petrovec, are of interest to define the input for a number of HVAC calculations, especially when lack of access to publicly available official data exists.

With these data we get a global picture of climate conditions and features of the location during the entire year.

LITERATURE AND LINKS

1. **https://eosweb.larc.nasa.gov/sse/**
2. **http://www.gaisma.com/en/location/bitola.html**
3. Surface meteorology and Solar Energy (SSE) Release 6.0 Methodology, Version 3.1.1 January 10, 2013
4. Трombев Ѓ., Маркоски А., Климатски податоци за локации во Р. Македонија од јавно достапни извори, Зборник ТФБ 2011, Битола, 2011
5. Трombев Ѓ., Маркоски А., Трombева-Гаврилоска А., Годишен од на дневни вредности на метеоролошки параметри на база на јавно достапни податоци за локација Скопје_Петровец (аеродром "Александар Македонски"), ЗЕМАК 2012, Охрид, 2012
6. Трombев Ѓ., Мијаковски В., Месечни вредности на поодделни метеоролошки параметри од јавно достапни податоци за локација Битола, Зборник ТФБ 2013, Битола, 2013
7. Трombев Ѓ., Мијаковски В., Параметри од "сончева геометрија" за локација на Битола, Зборник ТФБ 2013, Битола, 2013

APPENDIX

NASA Surface meteorology and Solar Energy - Available Tables

Location — Skopje-Petrovec

Latitude, °	41,96
Longitude, °	21,65
Altitude, m	238

Geometry Information

Elevation: **741** meters taken from the NASA GEOS-4 model elevation

Northern boundary	42	Western boundary	21
Southern boundary	41	Eastern boundary	22

Center Latitude, ° 41,5 Longitude, ° 21,5

Parameters / Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Meteorology (Temperature):													
Monthly Averaged Air Temperature At 10 m Above The Surface Of The Earth (°C)													
22-year Average	-1,48	0,08	4,19	9,4	15,1	19,4	22,1	22	17,2	11,2	4,72	-0,46	10,3
Minimum	-4,73	-3,49	0,28	4,4	9,3	13	15,9	16,4	12,2	7,04	1,32	-3,82	5,71
Maximum	1,27	3,47	8,34	14,4	20,6	25	27,6	27,3	22,5	15,9	8,03	2,25	14,8
Air Temperature At 10 m Above The Surface That Has Been Adjusted For A Site Elevation Of 238 m (°C)													
22-year Average	0,85	2,41	6,52	11,7	17,4	21,7	24,4	24,3	19,6	13,6	7,05	1,87	12,7
Minimum	-2,47	-1,23	2,53	6,65	11,5	15,3	18,1	18,6	14,5	9,29	3,57	-1,56	7,97
Maximum	3,39	5,59	10,4	16,5	22,7	27,1	29,7	29,4	24,6	18	10,1	4,37	16,9
Average Daily Temperature Range (°C)							* Warmest month						
22-year Average	6	6,95	8,05	10	11,3	11,9	11,7 *	10,9	10,2	8,92	6,72	6,07	
Monthly Averaged Cooling Degree Days Above 18 °C													
22-year Average	0	0	0	0	7	52	119	123	28	2	0	0	331
Monthly Averaged Heating Degree Days Below 18 °C													
22-year Average	611	508	423	257	101	20	3	3	46	203	399	581	3155
Monthly Averaged Arctic Heating Degree Days Below 10 °C													
22-year Average	363	282	181	50	2	0	0	0	0	35	167	333	1413
Monthly Averaged Arctic Heating Degree Days Below 0 °C													
22-year Average	88	50	11	0	0	0	0	0	0	0	12	73	234
Monthly Averaged Earth Skin Temperature (°C)													
22-year Average	-1,11	0,67	5,36	10,8	17	22	24,9	24,6	19,4	12,5	5,19	-0,16	11,8
Average Minimum, Maximum and Amplitude Of The Daily Mean Earth Temperature (°C)													
Minimum	-5,01	-3,95	-0,41	3,35	8,22	12	14,8	15,4	11,5	6,58	1	-4,07	
Maximum	3,93	6,68	13	19,7	27,1	32,8	36,2	36	30	21	10,7	4,59	
Amplitude	4,47	5,31	6,75	8,19	9,45	10,3	10,6	10,3	9,28	7,23	4,89	4,33	20,6
Monthly Averaged Frost Days (days)													
22-year Average	25	22	14	3	0	0	0	0	0	2	12	23	101
Dew/Frost Point Temperature At 10 m (°C)													
Daily Average	-3,91	-3,6	-1,45	1,55	5,01	7,36	8,23	8,44	6,43	4,42	1,35	-2,81	
Meteorology (Other):													
Monthly Averaged Relative Humidity (%)													
22-year Average	84,3	78,1	69,9	62	55,4	50	45,2	45,6	52,5	66	80,3	84,9	64,4
Monthly Averaged Humidity Ratio At 10 m Above The Surface Of The Earth (%)													
22-year Average	0,003	0,004	0,004	0,005	0,006	0,007	0,008	0,008	0,007	0,006	0,005	0,004	
Monthly Averaged Atmospheric Pressure (kPa)													
22-year Average	93,3	93,1	93	92,8	93	93	93	93,1	93,2	93,4	93,3	93,3	93,1
Atmospheric Pressure That Has Been Adjusted For A Site Elevation Of 238 m (kPa)													
22-year Average	99,3	99,1	98,9	98,5	98,6	98,6	98,5	98,5	98,8	99,1	99,1	99,2	98,9
Monthly Averaged Total Column Precipitable Water (cm)													
22-year Average	0,84	0,8	0,92	1,14	1,55	1,85	1,99	2	1,73	1,5	1,19	0,95	1,37
Monthly Averaged Precipitation (mm/day)													
22-year Average	2,02	2,17	1,81	2,18	1,91	1,65	1,37	1,18	1,72	1,97	2,85	2,57	1,94

Parameters / Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year

Meteorology (Wind):

Monthly Averaged Wind Speed At 50 m Above The Surface Of The Earth (m/s)													
10-year Average	4	4,16	3,92	3,68	3,28	3,19	3,36	3,41	3,36	3,69	3,92	4,17	3,67
Minimum And Maximum Difference From Monthly Averaged Wind Speed At 50 m (%)													
Minimum	-10	-9	-11	-8	-18	-12	-11	-10	-8	-8	-14	-11	-11
Maximum	13	10	12	7	14	13	11	16	6	13	8	12	11

It is recommended that users of these wind data review the SSE Methodology,
The user may wish to correct for biases as well as local effects within the selected grid region,
All height measurements are from the soil, water, or ice/snow surface instead
of "effective" surface, which is usually taken to be near the tops of vegetated canopies,

Monthly Averaged Percent Of Time The Wind Speed At 50 m Above The Surface Of The Earth Is Within The Indicated Range (%)													
0 - 2 m/s	20	17	20	25	32	33	32	33	34	25	22	19	26
3 - 6 m/s	74	76	76	74	67	67	67	67	66	74	74	72	71
7 - 10 m/s	6	7	4	1	1	0	1	1	0	1	5	8	3
11 - 14 m/s	0	0	0	0	0	0	0	0	0	0	0	0	0
15 - 18 m/s	0	0	0	0	0	0	0	0	0	0	0	0	0
19 - 25 m/s	0	0	0	0	0	0	0	0	0	0	0	0	0
Monthly Averaged Wind Speed At 50 m Above The Surface Of The Earth For Indicated GMT Times (m/s)													
Average@0130	4,58	4,71	4,46	4,32	4,04	4,08	4,57	4,53	4,36	4,5	4,53	4,83	4,45
Average@0430	4,5	4,57	4,22	3,84	3,36	3,15	3,53	4,04	4,19	4,34	4,36	4,74	4,06
Average@0730	3,71	3,33	2,54	2,06	1,81	1,68	1,74	1,8	1,72	2,43	3,28	3,96	2,5
Average@1030	2,7	3,23	3,38	3,24	2,74	2,62	2,37	2,45	2,38	2,64	2,66	2,58	2,74
Average@1330	3,27	3,64	3,61	3,5	3,02	2,97	2,61	2,57	2,54	3,02	3,24	3,26	3,1
Average@1630	3,91	4,12	3,85	3,61	3,16	3,14	3,16	3,1	3,11	3,57	3,9	4,13	3,56
Average@1930	4,63	4,79	4,61	4,37	3,91	3,82	4,28	4,24	4,19	4,48	4,67	4,9	4,4
Average@2230	4,68	4,84	4,66	4,51	4,18	4,09	4,63	4,53	4,4	4,58	4,7	4,93	4,56
Monthly Averaged Wind Direction At 50 m Above The Surface Of The Earth (degrees)													
10-year Average	263	281	30	250	248	250	257	268	268	273	277	280	
Monthly Averaged Wind Direction At 50 m Above The Surface Of The Earth For Indicated GMT Times (degrees)													
Average@0130	268	52	73	218	240	252	41	57	41	84	118	23	
Average@0430	267	37	40	231	251	253	43	65	47	71	119	291	
Average@0730	261	38	79	216	271	247	67	95	62	67	148	288	
Average@1030	249	219	156	223	232	278	350	89	226	169	168	293	
Average@1330	261	257	170	230	248	285	328	325	285	218	207	290	
Average@1630	271	46	98	245	280	306	345	346	316	288	120	25	
Average@1930	286	68	85	236	303	330	12	22	90	78	116	32	
Average@2230	272	70	99	235	316	339	32	45	29	89	128	29	
Monthly Averaged Wind Speed At 10 m Above The Surface Of The Earth For Terrain Similar To Airports (m/s)													
10-year Average	3,16	3,29	3,1	2,91	2,59	2,52	2,65	2,69	2,65	2,92	3,1	3,29	2,9

It is recommended that users of these wind data review the SSE Methodology,
The user may wish to correct for biases as well as local effects within the selected grid region,
All height measurements are from the soil, water, or ice/snow surface instead
of "effective" surface, which is usually taken to be near the tops of vegetated canopies,

Difference Between The Average Wind Speed At 10 m Above The Surface Of The Earth And The Average Wind speed At 50 m Above The Surface Of The Earth (%)													
Vegetation type **"Airport": flat rough grass**													
10-year Average	-20	-20	-21	-20	-21	-20	-21	-21	-21	-20	-21	-20	-21
Monthly Averaged Wind Speed Adjusted For Height And Vegetation Type (m/s)													
Height **100 meters** Vegetation type **"Airport": flat rough grass**													
10-year Average	4,43	4,61	4,34	4,08	3,63	3,53	3,72	3,78	3,72	4,09	4,34	4,62	4,07

Parameters / Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Monthly Averaged Wind Speed At 50, 100, 150 and 300 m Above The Surface Of The Earth (m/s)													
Vegetation type **"Airport": flat rough grass**													
50m	4	4,16	3,92	3,68	3,28	3,19	3,36	3,41	3,36	3,69	3,92	4,17	3,67
100m	4,43	4,61	4,34	4,08	3,63	3,53	3,72	3,78	3,72	4,09	4,34	4,62	4,07
150m	4,71	4,9	4,62	4,33	3,86	3,76	3,96	4,02	3,96	4,35	4,62	4,91	4,33
300m	5,23	5,44	5,12	4,81	4,29	4,17	4,39	4,46	4,39	4,82	5,12	5,45	4,8
Monthly Averaged Wind Speed For Several Vegetation And Surface Types (m/s)													
Height **100 meters**													
35-m broadleaf-everg	5,54	5,76	5,42	5,09	4,54	4,41	4,65	4,72	4,65	5,11	5,42	5,77	5,09
20-m broadleaf-decid	5,06	5,3	5,03	4,75	4,29	4,26	4,55	4,56	4,4	4,76	5,03	5,31	4,77
20-m broadleaf and n	5,69	5,76	5,28	4,88	4,29	4,15	4,37	4,53	4,52	5,07	5,46	5,89	4,99
17-m needleleaf-ever	5,38	5,45	5,03	4,65	4,18	4,09	4,34	4,4	4,34	4,8	5,13	5,54	4,77
14-m needleleaf-deci	5,31	5,45	5,06	4,69	4,18	4,03	4,25	4,43	4,49	5	5,31	5,61	4,81
Savanna:18-m broadl	5,31	5,52	5,2	4,88	4,35	4,23	4,46	4,53	4,46	4,9	5,2	5,54	4,88
0,6-m perennial grour	4,82	5,01	4,72	4,43	3,95	3,84	4,05	4,11	4,05	4,44	4,72	5,02	4,43
0,5-m broadleaf shrut	4,82	5,01	4,72	4,43	3,95	3,84	4,05	4,11	4,05	4,44	4,72	5,02	4,43
0,5-m broadleaf shrut	4,82	5,01	4,72	4,43	3,95	3,84	4,05	4,11	4,05	4,44	4,72	5,02	4,43
Tundra: 0,6-m trees/s	4,82	5,01	4,72	4,43	3,95	3,84	4,05	4,11	4,05	4,44	4,72	5,02	4,43
Rough bare soil	4,65	4,84	4,56	4,28	3,82	3,71	3,91	3,97	3,91	4,29	4,56	4,85	4,28
Crop: 20-m broadleaf	4,85	5,12	4,59	4,69	4,18	4,06	4,28	4,34	4,28	4,63	4,85	5,09	4,58
Rough glacial snow/ic	5,09	5,22	4,82	4,46	3,98	3,87	4,07	4,14	4,13	4,63	4,96	5,31	4,55
Smooth sea ice	4,53	4,61	4,26	3,91	3,49	3,39	3,57	3,7	3,72	4,2	4,47	4,75	4,05
Open water	4,28	4,45	4,2	3,94	3,51	3,41	3,6	3,65	3,6	3,95	4,2	4,46	3,93
"Airport": flat rough gr	4,43	4,61	4,34	4,08	3,63	3,53	3,72	3,78	3,72	4,09	4,34	4,62	4,07

Parameters / Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year

Solar Geometry:

Monthly Averaged Solar Noon (GMT time)												
Average	1044	1048	1043	1034	1030	1033	1040	1038	1029	1020	1018	1027
Monthly Averaged Daylight Hours (hours)												
Average	9,5	10,6	11,9	13,3	14,5	15,1	14,9	13,8	12,5	11,1	9,86	9,18
Monthly Averaged Daylight Average Of Hourly Cosine Solar Zenith Angles (dimensionless)												
Average	0,3	0,35	0,45	0,5	0,58	0,58	0,56	0,54	0,5	0,4	0,31	0,27
Monthly Averaged Cosine Solar Zenith Angle At Mid-Time Between Sunrise And Solar Noon (dimensionless)												
Average	0,32	0,41	0,5	0,58	0,62	0,63	0,63	0,6	0,54	0,45	0,35	0,3
Monthly Averaged Declination (degrees)												
Average	-21	-12	-1,8	9,71	18,8	23	21,2	13,7	3,08	-8,5	-18	-23
Monthly Averaged Sunset Hour Angle (degrees)												
Average	70	78,6	88,3	98,8	107	112	110	102	92,7	82,3	72,8	67,6
Monthly Averaged Maximum Solar Angle Relative To The Horizon (degrees)												

Table 1. *Sunrise/sunset, duration of day/night for the location of Skopje – Petrovec (for the day 24.10.2013.)*

Date	Sunrise	Sunset	Length	Change	Dawn	Dusk	Length	Change
24.10.2013	*06:57*	*17:39*	10:42		*06:28*	*18:07*	11:39	
+1 day	*06:58*	*17:38*	10:40	00:02 shorter	*06:30*	*18:06*	11:36	00:03 shorter
+1 week	06:05	16:29	10:24	00:18 shorter	05:37	16:58	11:21	00:18 shorter
+2 weeks	06:14	16:21	10:07	00:35 shorter	05:45	16:50	11:05	00:34 shorter
+1 month	06:34	16:07	09:33	01:09 shorter	06:03	16:38	10:35	01:04 shorter
+2 months	07:00	16:07	09:07	01:35 shorter	06:28	16:39	10:11	01:28 shorter
+3 months	06:56	16:36	09:40	01:02 shorter	06:25	17:06	10:41	00:58 shorter
+6 months	*05:40*	*19:25*	13:45	03:03 longer	*05:11*	*19:55*	14:44	03:05 longer

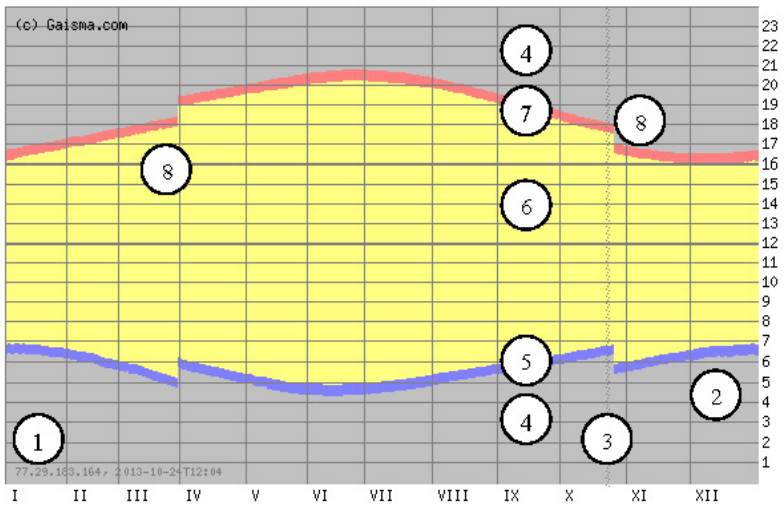


Figure 1. *Sunrise/sunset, duration of day/night for the location of Skopje-Petrovec*

Labels: 1. Month, 2. Hour, 3. Current day considered, 4. Night, 5. Dawn, 6. Day, 7. Dusk, 8. Possible beginning/ending of daylight saving time

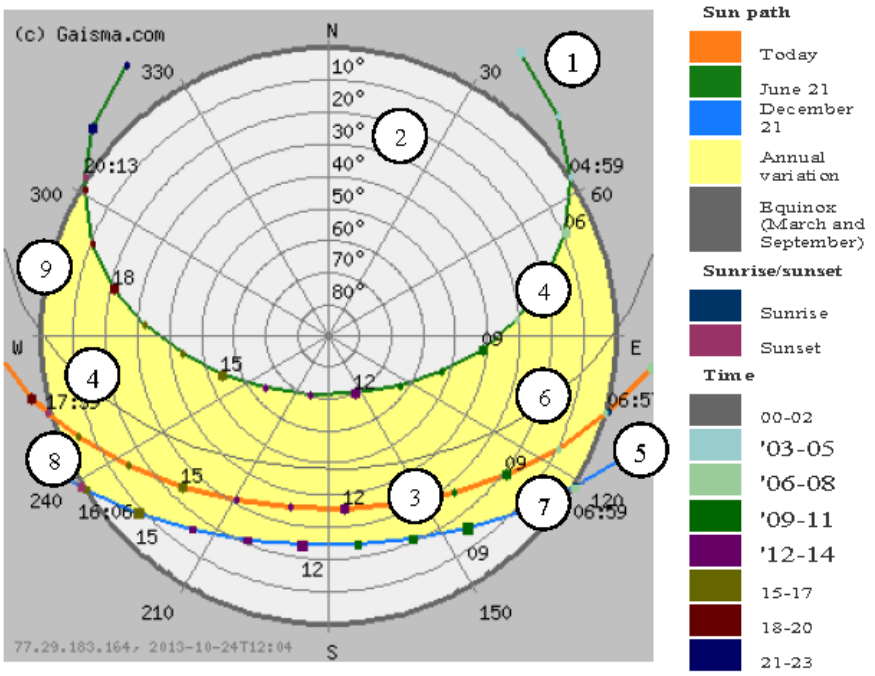


Figure 2. *Path of the sun for location Skopje - Petrovec*

Labels : 1. Angle of azimuth, 2. Elevation angle, 3. Considered path of the sun (to date), 4. Path of the Sun on June 21, 5. Path of the Sun on December 21, 6. Path of the sun during equinox, 7. Sunrise, 8. Sunset, 9. Horizon

Parameters / Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year

Parameters for Sizing Battery or other Energy-storage Systems:

Minimum Available Insolation Over A Consecutive-day Period (%)													
Min/1 day	13,6	8,98	16,3	18,2	13,1	13,3	13,3	11,5	13,9	4,13	4,39	4,86	
Min/3 day	30,9	25,3	30,4	36,5	40,4	34,3	29,2	37,3	33,7	24,3	12,6	24,5	
Min/7 day	48,9	44,6	48,9	55	55	49,4	50,1	57,1	44,2	32,3	23	39,5	
Min/14 day	58,1	56,6	51,1	67	69,6	68,5	75,8	66,9	58,7	48,5	49	48,3	
Min/21 day	62,9	64,8	58,2	69,2	76,4	72,7	82,1	72,4	70,2	64,5	58	57,9	
Min/Month	71	81,2	72	72,9	80	82,5	90,3	84	74,5	80	70,8	66,6	
Solar Radiation Deficits Below Expected Values Incident On A Horizontal Surface Over A Consecutive-day Period (kWh/m^2)													
1 day	1,58	2,33	2,96	3,45	4,49	5,47	5,57	4,98	3,69	2,78	1,74	1,37	
3 day	3,79	5,73	7,39	8,03	9,24	12,4	13,6	10,5	8,52	6,58	4,76	3,26	
7 day	6,54	9,92	12,6	13,2	16,2	22,3	22,4	16,8	16,7	13,7	9,8	6,09	
14 day	10,7	15,5	24,2	19,4	21,9	27,7	21,7	26	24,8	20,9	12,9	10,4	
21 day	14,2	18,8	31	27,2	25,5	36	24,1	32,5	26,7	21,6	16	12,7	
Month	16,4	13,4	30,6	34,2	31,9	33	19,2	27,8	32,7	17,9	15,9	14,8	
Equivalent Number Of NO-SUN Or BLACK Days (days)													
1 day	0,86	0,91	0,83	0,81	0,86	0,86	0,86	0,88	0,86	0,95	0,95	0,95	
3 day	2,07	2,23	2,08	1,9	1,78	1,96	2,12	1,88	1,98	2,26	2,62	2,26	
7 day	3,57	3,87	3,57	3,14	3,14	3,53	3,48	2,99	3,9	4,73	5,38	4,22	
14 day	5,85	6,06	6,83	4,6	4,25	4,39	3,38	4,62	5,78	7,2	7,13	7,23	
21 day	7,78	7,37	8,75	6,44	4,93	5,71	3,75	5,78	6,24	7,45	8,8	8,84	
Month	8,97	5,25	8,66	8,1	6,17	5,22	2,98	4,95	7,62	6,2	8,73	10,3	

Parameters for Sizing Surplus-product Storage Systems:

Available Surplus Insolation Over A Consecutive-day Period (%)													
Max/1 day	188	188	183	186	167	147	137	146	158	181	207	192	
Max/3 day	173	185	170	171	162	140	135	135	151	179	201	178	
Max/7 day	162	165	157	153	144	131	128	130	140	164	188	165	
Max/14 day	147	140	143	129	139	126	120	123	132	149	157	143	
Max/21 day	141	126	139	118	130	121	117	117	126	143	135	135	
Max/Month	125	117	127	112	116	111	115	111	120	127	121	125	

Supporting Information:

Monthly Averaged Top-of-atmosphere Insolation (kWh/m^2/day)													
22-year Average	4,01	5,52	7,58	9,59	11	11,6	11,2	10	8,24	6,16	4,4	3,58	7,76
Monthly Averaged Surface Albedo (0 to 1,0)													
22-year Average	0,3	0,28	0,21	0,16	0,18	0,2	0,19	0,17	0,15	0,15	0,17	0,26	0,2

004.4:339.13(497.7)

ANALYSIS OF THE SOFTWARE MARKET IN THE REPUBLIC OF MACEDONIA[6]

Associate professor Dr. Dejan Zdraveski
" Gorce Petrov " Street bb , Faculty of Economics - Prilep
e-mail: dejan_zdrave@yahoo.co.uk

Msc. Marija Midovska
" Gorce Petrov " Street bb, Faculty of Economics - Prilep
e-mail: marija_midovska@yahoo.com

Abstract

Software markets are the fastest growing markets globally. There are not relevant data concerning the situation of the Macedonian software market.

In this research will be surveyed the largest software companies in the R. Macedonia, applying on-line questionnaire in order to obtain initial information about the characteristics of Macedonian software market. The software market in our country is still a relatively small market, but with the increasing globalization of world markets, there are great conditions for intense growth and development of the software market in the R. Macedonia.

This research will give detailed answers about the trends in the Macedonian market for software , what is the size of that market , which are the participantes in that market, how much the world famous software manufacturers are present at the Macedonian market etc.

Key words: software market, software solution, IT services.

INTRODUCTION

The subject of the research in this paper presents software market in Macedonia and actual movements in this market . The purpose of this study is to provide relevant information of the situation in the Macedonian software market. According the World Bank , IT spending per capita in Macedonia is $ 70 , which is the fourth highest consumption in the Balkans , although the differences are obvious. Slovenia leads with an average of 430 dollars, Croatia has 235 dollars to spend on IT and Serbian citizen 95 dollars.

[6] original scientific paper

Macedonia 's 70 $ are just 8.1 % of the average consumption per capita in the European Union.[7]

The methodology of this research is determined by the nature of the research. a structured questionnaire was applied in this research. Also, the on-line questionnaire on zoomerang.com was used. This website offers some simple analysis of the answers.

In this research will be implemented quantitative and qualitative analysis. Qualitative analysis enters into the heart of the subject, and because it explores the software market, such analysis will examine a number of factors that effects on that market. Studies of this type are performed by number of respondents that have features that are important for the purpose of research, because they are an important part of the basic set. In the qualitative analysis will be used inductive method or analysis will be developed on individual facts and data collected and analyzed in order to perform some general conclusions. It will be an analysis of certain issues at the end of all this analysis to separate some general conclusions.

The results will be analyzed by different statistical methods, correlation and regression analysis, various statistical tests, the test for independence (chi square), ANOVA, etc. Processing the results will be done using modern software solutions, as well as in Microsoft Excel.

First in order to perform a proper survey is necessary to formulate an appropriate sample. By default are taken 50 most successful companies in the software area in the R. Macedonia. The sample is determined by the Decision analyst STATS which defined 21 companies with max error level of 6 % , the level of risk of 5 % , a level of reliability of 95 % , and the desired confidence level of 90 %.

Companies covered in this sample are: Estek BSc, IT labs, Re - Active, Sigma WB, Neon Systems, Gord systems, BMG universe, Edusoft, bar ecem, Planet Interactive, Digit Computer Engineering, Pelings, Asseko, Integra Solution, Seavus, Anhoch, Point Plus, Entire logic, Facility X, SDC software, Inovation Academy .

RESULTS OF THE RESEARCH FOR THE SOFTWARE MARKET IN MACEDONIA

In this paper will be covered only those questions that are extremely important for this research, due to limitations on the size of the paper.

[7] www.worldbank.org

1. *Do you develop software by your own or you only sale it?*

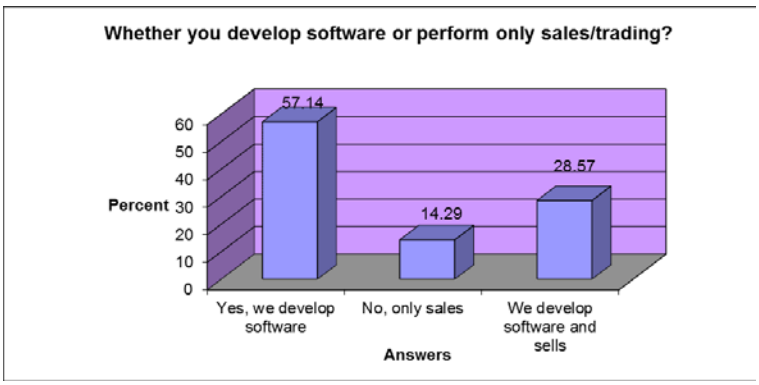


Chart 1.

From the results can be seen that most of the companies (57.14 %) are developing software solutions alone. That is very positive trend in the Macedonian software market. This is the reason why most of the Macedonian software companies become competitive in the global software market with their innovative solutions . This is also confirmed by research of IDC according to which already 4-5 Macedonian software companies are listed on the world software market with their innovative software solutions . On the other hand it is a small number of companies that perform only selling / trading software, which sell mostly is related to the Microsoft products.

2. *What software tools are offered by the companies?:*

Company	Software tools
Sigma SB	MS SQL analytics, MS Dynamics, NAV Business Analytics
Gord systems	IBM/SPSS Predictive Analytics:PASW Statistics (SPSS Base), PASW Modeler Pro (Clementine), Jasper report
Object X	oXEnteprise Solution, Business Process modeler
Digit computer engineering	ERP software
Acceco	Microsoft, IBM, Oracle
Seavus	Most of the Microsoft products and open source solutions
Entire logic	MOSS, MS SQL, MS SQL AS
Re-activ	Microsoft products
Neon systems	POS software (their own solutions)

Pint plus	ERP software, software for finance and sell (their own solutions)
Edusoft	Different software solutions by customer order
BMG universum	Different software solutions by customer order

Table 1.

From the Table 1 it can be noticed that most of the software tools that are offered on the Macedonian market are products of Microsoft. Also , most of the Macedonian software companies develop their own solutions that are adjusted to the needs of the Macedonian companies. Besides the innovative software solutions that Macedonian companies produce, they often complementary their offer with Microsoft products mostly as world's most widespread software in the Macedonian market. Quite characteristic is that the most of the software solutions developed by Macedonian software are developed by direct orders from the customers.

3. *Do you have partnership with some of the world's software developers?*

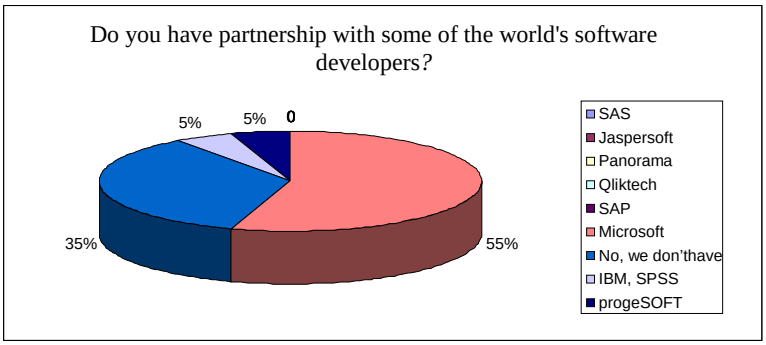


Chart 2.

From the results can be noted that most of the Macedonian companies have not established any partnership with any of the world's software companies, while most of them who had some kind of partnership, they have with Microsoft. Even 55% of companies have a partnership with Microsoft and if we added those 35% who do not have a partnership with any of the world's software, then only 10 % of Macedonian software companies have partnership with the other producers of software. It would mean that from all world producers of software, Microsoft have monopoly on the Macedonian market.

4. *What is the price of software that you have to offer?*

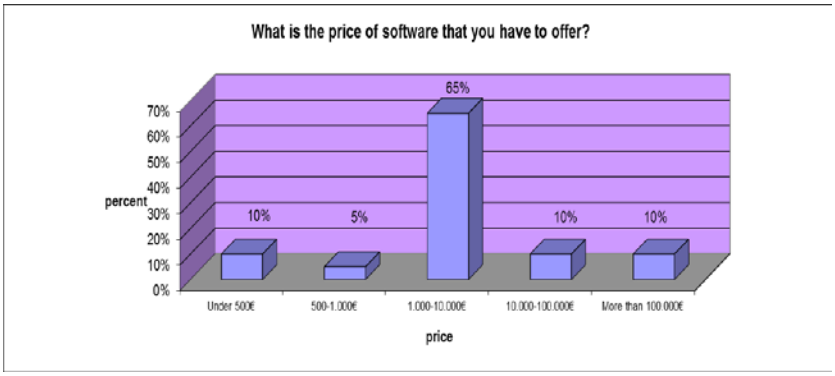


Chart 3.

When we analyze the price of the software tools that are offered on the Macedonian market, it usually varies in the range of 1.000-10.000 €, although there are companies that offer software over 100.000 €. In the past only the large companies can afford the software tools because of the high price of the software, but today more and more software companies are working on developing software tools with an affordable price for small and medium-sized companies. That acceptable price ranges from 1.000-10.000 € even for small and medium-sized companies.

HYPOTHESES TESTS AND REGRESSION MODEL

In this paper will be tested several hypotheses that are of exceptional importance for research .

Hypothesis 1

Test the zero hypothesis that the number of software tools sold in one year does not depend of the price of tools .

Below are the results obtained from hypothesis tests:

Number of Columns	Number of Rows	Alpha Error	Degrees of Freedom	Critical chi-square	Computed chi-square	p value
5	5	0.05	16	26.2962	6.7347	0.9780
Conclusion: Do not Reject Hypothesis						

Table 2.

From the results can be seen that the set zero hypothesis is accepted. It means that the number of software tools sold in one year does not depend of the price of tools. In this case, it doesn't mean that the lower price of the tools will increase the number of tools sold, but sales of software for business intelligence depends of a number of other factors that would be the subject of a separate study. To determine which other factors could affect the sales tools will be set multiple regression model in which one as dependent variable is the number of software tools sold in one year. To determine what other factors could affect the sales tools will be placed in multiple regression model which as dependent variable defines the number of software tools sold throughout the year. As independent variables are defined way of sales (X1), the type of software sell by the companies (X2), partner relationships established with a worldwide manufacturer (X3) and how much are companies informed about the software offer (X4). By applying correlation analysis, which was performed in Microsoft Excel determined that the independent variables are mutually independent, we can be seen from the value of the correlation coefficients are given in the following table:

Correlation matrix (correl, r)				
	X1	**X2**	**X3**	**X4**
X1	1	0,41	0,05	0,17
X2	0,41	1	-0,36	0,42
X3	0,05	-0,36	1	-0,48
X4	0,17	0,42	-0,48	1

Table 2.

The equation of regression model is :

$$Y = B0 + B1 * X1 + B2 * X2 + B3 * X3 + B4 * X4 + e_{ij}$$

where :
X1- a way of sale
X2- type of software sell by the companies
X3- partner relationships established with a worldwide manufacturer
X4- how much are companies informed about the software offer

e_{ij}-total error

The correlation coefficient, based on the established model is approximately 0.7, which already shows some correlation. Coefficient B0 shows how much is the expected or theoretical value of the line of

regression coefficients if other variables show how much the independent variable will change if any of the dependent variables change. Also, this regression model allows to perform certain predictions about future trends in the sales tools based on the obtained results.

Hypothesis 2

Analysis of variance was used to test zero hypothesis that there are no statistically significant differences in information of the companies for the offer in the Macedonian software market .

The results are given in the following table :

Source of variance	Sum of squares	Degrees of freedom	Mean squared
Columns	*77.400*	*4*	*19.350*
Error	*3.500*	*5*	*0.700*
Totals	*80.900*	*9*	
Computed F-Value: 27.643			
Critical F (Col): 5.19			
Reject Null Hypothesis			

Table 3.

We used ANOVA test and we can conclude that this hypothesis is rejected which means that there are statistically significant differences in awareness of companies for the Macedonian software market. In other words Macedonian companies that operating in business sector have different information about what is offered as software tools by Macedonian software companies.

CONCLUSION

The results obtained of the survey suggest that most of the software that is offered on the Macedonian market is developed by software companies that sell it. On the other hand, very few number of the most prevalent worldwide producers of software are present in the Macedonian software market. This possibly brings that the sell of the software for business intelligence to does not depend on the price of the software. The movement of prices of software up and down does not affect on the number of software tools sold by companies. There are several other factors that are involved in the research , which affect the sales of software . Also, impact on the software sell has the small information that companies have about the software market in Republic of Macedonia. This will be a recommendation to the Macedonian software companies to better promote and advertise their products.

However, despite this, there are positive trends in the Macedonian market for business intelligence software. They are related to the companies that aim to develop their own software solutions. They are companies that can cope with modern global trends and can compete on the global software market. This can be seen of the type of software that companies sell, the number of software tools that are sold and their price.

References:

1. Коста Сотироски, Статистика, Универзитет "Св. Климент Охридски", Економски факултет, Прилеп, стр. 301-313, 2004
2. Mirta Bensic, Nenad Suvak, Primijenjena statistika, Sveuciliste J.J Strossmayera u Osijeku, str. 109-119, 2013
3. Nikola Koceic Bilan, Primijenjena statistika, Prirodoslovno-matematicki fakultet u Splitu, str. 74-83, 2011

INTERNET SOURCES:

1. www.idc.com
2. www.worldbank.com
3. www.gartner.com
4. www.zk.com.mk
5. www.stat.gov.mk
6. www.mio.gov.mk

339.1:004.783.5

NETWORK THREATS THAT CAN AFFECT ELECTRONIC BUSINESS[8]

MSc Viktorija Stojkovski
"Partizanska" - nn,
Faculty of Administration and Management of Information Systems,
Bitola
stojkovskiviktorija@gmail.com
MSc Blagoj Nenovski
Faculty of Technical Sciences - Bitola
cyberbaze@gmail.com

ABSTRACT

The development of the information and communication technology especially the internet has brought to the growth to businesses with the electronic commerce. Electronic commerce is taking a pitch when it comes to communication of the stake holders, although some still mistrust it. When it comes to electronic commerce, we are witnessing the wider usage of the internet as a paying medium. This means that there are users that need to be more familiar with the possibilities but also the risks and the threats. The subject of this paper is to look at the threats that may occur while the electronic transactions are made. With this paper the costumers and the businesses can get deeper knowledge about the threats that can jeopardize their working or their identity. This brings to more information that benefits the costumers and the businesses in the transformation of the traditional to the more contemporary methods of buying and selling.

Keywords: electronic commerce, internet, threats, network

[8] original scientific paper

INTRODUCTION

The growth of the World Wide Web allows an easier remote connection to other computers. The simplicity of using the internet helped to expand the commercial aspect such as the electronic commerce. E-commerce means using the information and communication technology (ICT) to run a business on the internet which includes not just selling and buying goods but also services and collaboration with other business partners (Manivannan,S;2009). The methods of electronic commerce help the companies to connect their inner and outer systems for data processing in a more efficient and flexible way, to work with their suppliers and partners and to satisfy the needs and expectations of their clients.

But the rapid development of new software and communication systems often results with users that are not familiar enough with the software and the architecture of the system. This makes those users unaware about the flaws that may lead to serious security risks. Electronic commerce is surrounded by different threats that can slow down or even stop function. Also electronic commerce is becoming a field for computer criminal with the different thefts that occur around electronic transactions.

THREATS TO THE NETWORK

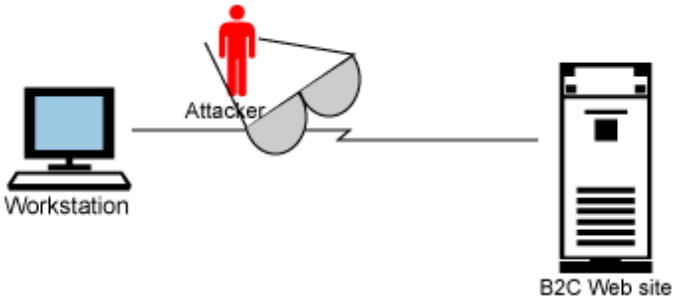
In the group of threats to the network we find the sniffing software that has the ability to listen and intercept the data that travels though the network. (Laudon, K.Laudon, J;2001).

The sniffer applications are software that **monitors the data flowing** over the computer network. The sniffer application is able to listen and copy the computer conversations. After all, this conversations are in binary form, so the network sniffers are known as “protocol analysis” which enables “decoding” of the computer traffic. Because of the fact that many networks use common mediums, the sniffer applications have the advantage compared to telephone bugging.

The sniffer applications can be categorized in two forms. The legal or commercial sniffer packets are used to help maintain the computer

networks. This sniffer packets are commercial devices which are used to manage the networks and maintain the network security. They are also used as a diagnostics tool to back up the network systems and to examine a networking system that has impaired security. On the other site there are the illegal sniffer packets which are used by the hackers in order to gain unauthorized access to sensitive information and network data. The illegal sniffer packets are installed without the knowledge of the IT administrator and can be positioned in different areas of the network with the purpose of spying or stealing the information that flows though the network.

Image 1. Attacker positioned between the client and the server



Typical usage of this programs include:

- Automatic obtaining of clear text usernames and passwords from the network which are used by hackers/crackers to break into systems;
- Converting the data in a form that is human readable, so people can read from the traffic;
- Fake analysis to discover the network problems, such as why a certain computer can not talk to another one;
- Analysis of the performance, to discover network difficulties;
- Imposing network detection to find out hackers/crackers;
- Logging the network traffic, to create profiles that the hackers can not crack.

There are three types of sniffing packets:
- **ARP sniffing**: ARP sniffing include information packets that are sent to the administrator via the ARP cache on the two computers. In this case the data instead of the two hosts in the network are sent directly to the administrator.
- **IP sniffing**: IP sniffing works through the network card which is used to monitor all the information packets that respond to the set up filter on the IP address. This enables monitoring all the data for analysis and testing.
- **MAC sniffing** : MAC sniffing like the IP sniffing works through the network card which enables the device to monitor all the information packets that match the filter, this time the MAC address.
Sniffer components:
- **Hardware -** most products work on the standard network adapters, although some require special hardware. The special hardware can be used to analyze hardware errors such as the CRC errors, voltage problems, cable problems, dribbles, oscillation and else.
- **Recording driver** – this is the most important part, whose purpose is to record the network traffic over the wire, to filter the data that needs to be recorded and save the data in a temporary memory.
- **Temporary memory** – after the data is recorded from the network, it is saved to a temporary memory. The frames that are captured from the network are stored in a tampon. There are a few ways of recording: recording until there is free memory or storing the new data means moving the old ones.
- **Decoding** – the task of the decoding is to show the network data in a human readable form which helps to understand what is going on the network.
- **Editing/transmission** – some products include features that enable them to edit the network packets and to send them over the network.

REASONS THAT HOLD BACK THE INTERNET TRANSACTIONS

The most common reason why the internet transactions are held back is the **credit card fraud**. Buyers are afraid of being tricked and

their credit card information stolen. But stealing the information from transactions is far less likely then system hacking and stealing corporative servers where the information related to the credit cards is stored.

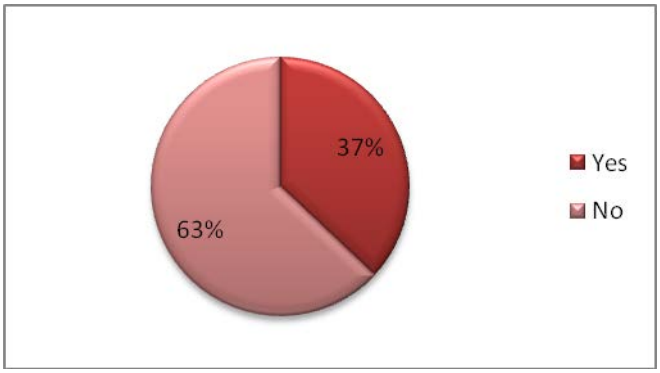
The problem with the security of the credit card date occurs on the sellers side when he accepts to save the data. Most of the data that is stolen is in a group of thousands of entries saved on the sellers records.

This means that the right problem with the systems that include credit card transactions is not to create a security channel that lets the buyer and the seller communicate but the inability to identify the parties in those transactions, together with the security of the data that is stored on the sellers servers. The seller can not validate the identity of the person who enters the credit card data and whether that person is the owner of the credit card. This problem becomes much worse when there is an international order, because once it is made and then canceled, that order can not be proved together with the identity of the credit card owner. That is why the identity of the clients is the key importance for the businesses in order to reduce their potential losses.

SURVEY IN THE REPUBLIC OF MACEDONIA

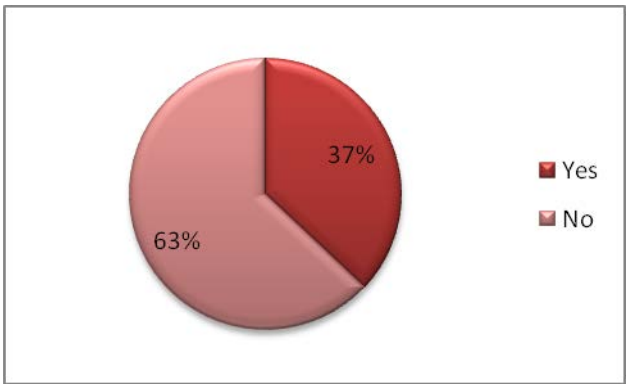
A pilot survey in the Republic of Macedonia was implemented in 2012 using the method of examination and survey questionnaire as an instrument to commit the pilot study. The survey questionnaire contained mostly closed questions, which were previously structured. The answers gained from all the 31 subjects were individually processed in Microsoft Excel which resulted in a graphical representation.

From the pilot survey conducted in Macedonia, 14 companies or 45% answered that offer their products online, while 17 or 55% of the companies do not offer their products and stick to the traditional way of selling their goods.



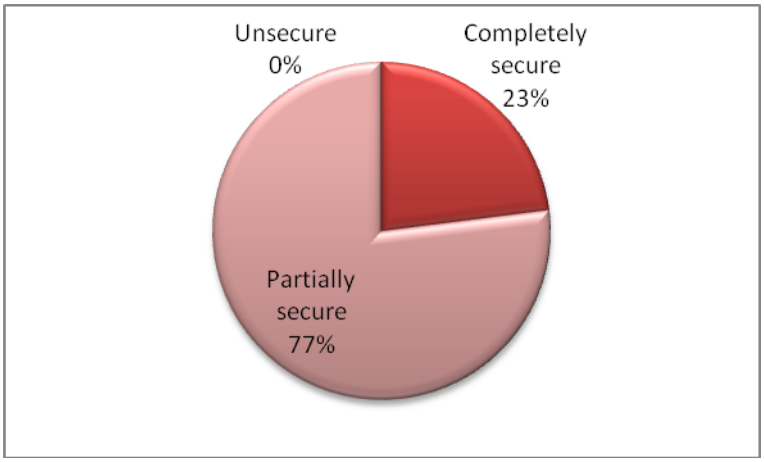
Graphic 1. How much the companies offer their products on Internet

Some of the companies offer their products only for marceting purposes but not for sale. The data from this survay shows that 12 or 37% of those companies had their security breached and the other 20 or 63% had been secured.



Graphic 2. Threat to the security of computer systems companies

An individual analysis of the answers showed that the security breach had ocured at the big and medium companies. Although the percentige of the companies that havent their security breched is larger then the secured ones, 24 of all the companies or 77% think that the electronic commerce and the electornic transactions are partaly save and the other 7 or 23% think that the electronic commerce and electronic trasnactions are completely save.



Graphic 3. Security of electronic commerce and electronic payment

Encouraging is the face that none of the business entities considers e-commerce unsecure which helps the e-commerce to expand.

CONCLUSION

The continuous growth of the information and communication technology results in an overall increased usage and use cases of the internet. One of them is the electronic commerce which is proving to be more contemporary, simple and efficient. But this technology is prone hacking attempts which can result with inefficient store for the businesses or stolen identity for the costumers. One of the most common attacks on the network are done with sniffers that can monitor, intercept or even edit the data that travels through the network and resend it to other computers. This type of attack can happen on three levels: ARP, IP or MAC. The reasons that hold back the internet transactions mainly consist of credit card frauds. When a survey was done in the Republic of Macedonia, with the main focus to discover how many of the businesses offer their goods or services online we found out that 45% do offer them online. Out of 31 companies 37% have had their security breached and the other 63% have not. None of the companies believes that electronic transactions are unsecure, 77% that are partially secure and 23% that the electronic transactions are completely secure. Having non of the companies answer that they think the electronic commerce and transactions are unsecure is a good pointer that allows e-commerce growth.

REFERENCE LIST

1. Kenet K. Laudon, Djejn P.Laudon, *Menadzment na informaciski sistemi: Upravuvanje so digitalna kompanija*, Skopje, 2010, p.302
2. Kenet K. Laudon, Karol G.Traver, *Elektronska trgovija: biznis, tehnologija, opshtestvo, Skopje*, 2010, p.281
3. Manivannan S.Velmurugan, *Security and trust in e-business: problems and prospects*, International Journal of Electronic Business Management, Malaysia, 2009
4. Colin Combe, *Introduction to e-business management and strategy*, Butterworth-Heinemann, 2006
5. Diter Golman, Kompjuterska sigurnost, AD Verbum Skopje, 2010
6. Efraim Turban, R.Kelly Rainer, Richard E.Potter, *Introduction to information technology*, second edition, Wiley 2003
7. Gojko Grubor, Milan Milosavljevic, *Osnove zastite informacija: Metodolosko-tehnoloske osnove*, Univerzitet Singidunum, Beograd 2010
8. Karen Scarfone, Paul Hoffman, *Computer Security*, National Institute of Standards and Technology, September 2009
9. http://www.windowsecurity.com/whitepapers/Sniffing_network_wiretap_sniffer_FAQ_.html
10. http://www.ibm.com/developerworks/websphere/library/techarticles/0504_mckegney/0504_mckegney.html

004.738.5:378.091.214.18

ADJUSTING THE MASSIVELY OPEN ONLINE COURSES IN CLOUD COMPUTING ENVIRONMENT[9]

Aleksandar Karadimce, MSc
University of information science and technology "St. Paul the Apostle"
Ohrid, Macedonia
aleksandar.karadimce@uist.edu.mk, akaradimce@ieee.org

Abstract

Massively Open Online Courses (MOOC) is new trending model for delivering learning content online to any person with no limit on attendance for everyone that wishes to attend to a course. Following the MOOC trend there is an expectation that till 2015 there will be more than 6 million unique students worldwide. In order to provide appropriate quality learning user experience for the students we propose how to optimize the cloud computing resources, such as Virtual Machine (VM) distribution per contents to support the MOOC. For this purpose we have used a simulation tool, called CloudAnalyst, which supports visual modelling and simulation of large-scale applications that are deployed on cloud infrastructures. The results will provide information for the geographic distribution of traffic and location of data centres and number of resources for each data centre.

Key words: Massively Open Online Courses, Coursera, Cloud Computing, CloudAnalyst.

INTRODUCTION

University study provides students with the opportunity to learn by working in groups during class time, presenting their work in class, and even collaborating together on a project, which as we all know is happening in real-time. Recently, there is a need to shift from a monolithic *learning environment* in which everything must be controlled and predictable to a more pluralistic *learning ecology* in which both prescriptive and emergent IT application domains and models of learning have their place [1]. Another research, had asked participants in *online learning environment* to describe their learning experience in the context of multiple communities and found that there's an apparent importance of expressing new perspectives across

[9] original scientific paper

multiple communities that spring from online courses [2]. Using this approach, students are expanding the ability for creating, sharing and collaborating through emerging technologies such as blogs, wikis, podcasts, and social networks. In the same time professors and teaching assistants will spent less time on lecturing the students, and they can be more effective in scaffolding and tutoring the students to improve their skills.

Recent research has proposed cloud computing (CC) to be used as approach for online user-assessment and classification of learning materials, in order to provide personalized resource recommendation [3]. The last two years there is a trend called massively open online course (MOOC), which have generated wide attention due to initiatives made by high-profile institutions such as Stanford and MIT, which have formed start-ups such as Coursera, Udacity, and edX [4]. Distance learning and the MOOC have a great potential for informal and lifelong learning. The MOOC presents important challenge related to student engagement and evaluation, in order to ensure an exceptional student experience and to avoid high dropout rates researchers are using pedagogic approach by experiential learning and collaborative learning theories [4]. The MOOC allows hosting university to open its curriculum to a wider audience. In order to be able to support simultaneously large number of users from all around the world there needs to be optimal distribution of CC resources. Considering that nowadays the trend of MOOC reputation is to be able to deliver real-time uninterrupted delivery of multimedia contents promptly to all students [5]. The main contribution in this paper is to provide appropriate optimal configuration of CC environment for the providers of MOOC to deliver high-quality learning material. To be able to provide finest configuration of CC environment we have used simulation tool, called CloudAnalyst, to plan the resources needed for MOOC to be accessible and reliable worldwide.

This paper is organized as follows: Firstly we present the concept of the cloud-based massively open online courses. Next it is described the simulation of MOOC use case and comparison of two simulations with CloudAnalyst. At the end is provided discussion for the results and conclusion of the paper.

CLOUD-BASED MASSIVELY OPEN ONLINE COURSES

The MOOC networks can be used for creating, sharing, and refining the knowledge between the participants. Learners are encouraged to represent their knowledge or questions through diversity of platforms and to connect to each other around issues and topics of shared interest. That way,

MOOC builds a model of collaborative networks of unprecedented rapidly expanding educational resources. The MOOC environment is a self-guided course that could have thousands of participants. It requires that a participant is willing to engage, and has some confidence and comfort with the discourses of an autodidact and a self-starter [5]. MOOC offers opportunities for interaction of student with the material as well as student with their peers. The open online course can be used by potentially large number of students from all over the world. The real potential of MOOC is that CC based support for the emergence of learning networks among participants in a many-to-many relationship, rather than the traditional one-to-many model of interactions between a teacher and his or her students [6].

Common for all MOOC providers is that all of them have been established during 2012 by leading world universities and they all have large number of participants. Another common feature for MOOCs is that they are cloud-based learning platforms. The Google Engine platform is the base for Udacity and Khan Academy, whereas, the Amazon Web Service Infrastructure is support for Coursera, Instructure, LoudCloud Systems and Lore [7]. Considering the significant large number of students enrolled in Coursera we have decided to conduct further and deeper research for this MOOC. The popularity of Coursera in world scale, broken down by country [8], is given in Figure 1 (left). Another research made by Outsell [9] have estimated that by the end of 2012, about 3.17 million unique students worldwide were enrolled in courses from the major MOOC providers, see Figure 1 (right). Following the MOOC trend and popularity they are expecting that till 2015 there will be more than 3 million unique students only from North and South America, and the rest of 3 million unique students will be from other worldwide continents [9].

MOOCs allow learning to happen across space and time due to its mainly asynchronous and online architecture. The MOOC is a gathering of people with generally good internet connection, it has a unique social advantage that relates to a more open and connected way of thinking. Considering that nowadays the trend of MOOC reputation the providers should be able to deliver real-time uninterrupted delivery of multimedia contents promptly to all students. In order to provide appropriate and optimal configuration of CC environment for the MOOC providers we will use the CloudAnalyst simulator.

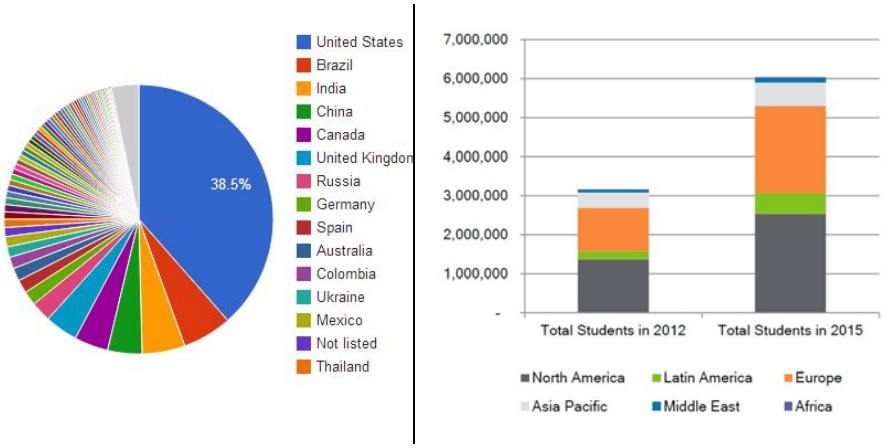


Figure 1. Country distribution [8] (left), Global MOOC audience [9] (right)

In this research we have used CloudAnalyst [10] to model a simulated environment to study the behavior of a MOOC platform in CC environment. It provides graphical output in the form of tables and charts is highly desirable to summarize the potentially large amount of statistics that is collected during the simulation. The simulator is developed on Java platform, using Java SE 1.6, and the GUI component is built using Swing components [10]. CloudAnalyst, built on top of CloudSim, allows description of application workloads, including information of geographic location of users generating traffic and location of data centers, number of users and data centers, and number of resources in each data center [10]. A User Base models a group of users that is considered as a single unit in the simulation and its main responsibility is to generate traffic for the simulation. We have used Throttled Load Balancer [10] that ensures only a pre-defined number of Internet Cloudlets are allocated to a single VM at any given time. With this balancer if more request groups are present than the number of available VM's at a data center, some of the requests will have to be queued until the next VM becomes available. Modeling bandwidth for a complex network like the MOOC is an extremely difficult task. In the current version of CloudAnalyst it is used a hypothetical parameter, available bandwidth, which is assumed to be the quota of Internet bandwidth available for the application being simulated, ignoring other external factors [10]. For that purpose we model the behavior of MOOC platform for the use case Coursera and using CloudAnalyst we will evaluate time response of data centers and performances related to use of CC to host MOOCs courses worldwide.

A CASE STUDY: SIMULATION OF A MOOC IN CLOUDANALYST

Streaming video requires reasonable quality of bandwidth, and a reasonably new computer with good quality video/graphics card. Most of the MOOC participants from North America in rural and remote communities may face bandwidth challenges similar to their African peers, but even when they do not, challenges still arise with respect to such things as the possession and use of microphones, web cams, and headsets [5]. Also, time zones can also be concerns in MOOCs, especially if regular live sessions are planned. Therefore, the use of synchronous tools should be carefully planned in a MOOC, in order to overcome the issue with different time zones [6]. The CloudAnalyst allows clear overview of analysis for different time zone intervals in different regions of the World. The massive size of the participating group maximizes the possibility for participants to find peers who share complementary interests and skills, and with whom they can collaborate to achieve mutually defined goals. The CloudAnalyst simulator environment, identified by CloudAnalyst Region IDs, is divided into 6 'Regions' that correspond with the 6 main continents in the World. Considering the Coursera students distribution by country, given in Figure 1, we have created the approximate percentage distribution of the Coursera user base across the world is given in Table 1. We have defined 6 user bases representing the above 6 regions corresponding to the CloudAnalyst Region IDs with the following parameters are also given in Table 1.

TABLE I. PERCENTAGE DISTRIBUTION AND USER BASES

User base	Region ID and continent	Users in %	Peak Hours (GMT)	Simultaneous Online Users During Peak Hrs	Simultaneous Online Users During Off-peak Hrs
UB1	0- North America	43,8	02:00-09:00	430,000	43,000
UB2	1- South America	8,9	06:00-13:00	89,000	8,900
UB3	2- Europe	32,9	10:00-17:00	329,000	32,900
UB4	3- Asia	11,9	15:00-22:00	119,000	11,900
UB5	4- Africa	0,9	11:00-18:00	9,000	900
UB6	5- Australia & Oceania	1,6	20:00-03:00	16,000	1,600

For the sake of simplicity in the simulation configuration each user base is contained within a single time zone and it is assumed that most users use the MOOC platform for about 7 hours, per day. Also, it is also assumed that only (1/10) one tenth of that number of users is on line during the off-

peak hours. The cost for hosting Coursera platform in a Cloud is closely following this pricing plan: Cost per VM per hour $0.10; Cost per 1GB of data transfer (from/to Internet): $0.10 [17]. Size of virtual machines (VM) in data centers used to host Coursera in the experiment is 10,000MB. The virtual machines have 1GB of RAM memory and have 1000MB of available bandwidth. Simulated hosts have x86 architecture, virtual machine monitor Xen and Linux operating system. Data center nodes have six core L5640 CPU processors 24GB of RAM and 60x600GB Dual channel SAS disks of storage. Each machine has 2 CPUs, and each CPU has a capacity power of 37006 MIPS. A time-shared policy is used to schedule resources to VMs. Users are grouped by a factor of 1000, and requests are grouped by a factor of 100. Each user request requires 4096 instructions to be executed.

a) Scenario 1 – Coursera hosted on a single data center

Considering the centralized approach for Coursera we assume initially the platform is deployed in a single location, in Region 0 (North America). The simulated data center hosts 50 virtual machines dedicated to Coursera, each one with 1024MB of memory in each VM running on physical processors capable of speeds of 37006 MIPS. After running the simulation in CloudAnalyst for the first scenario with single data center we have received the following simulation output, see Table 2. The response times experienced by each user base for the first scenario are shown graphically in Figure 2.

TABLE II. SCENARIO 1: OVERALL RESPONSE AND PROCESSING TIME

	Avg (ms)	**Min (ms)**	**Max (ms)**
Overall response time:	1021	91	3018
Data center processing time:	74	0.15	522

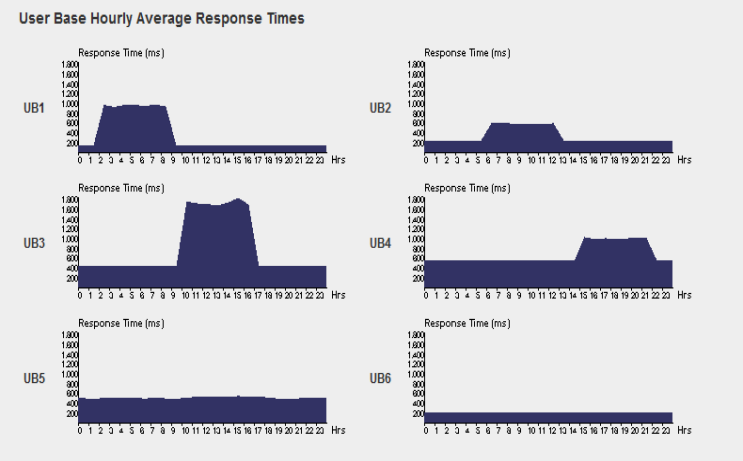


Figure 2. Scenario 1: Response time across regions with the single data center

The spikes in response times can be seen clearly during the seven hour peak period, and it can be observed how the peak loads of one user base could affect other user bases as well. The UB1 has the peak between 02:00-09:00 GMT, similar UB3 has significantly increased peak time between 10:00-17:00 GMT and all other user bases have small spikes during this same period. Overall, during the 1 day simulation we can see different distribution depending of the user base region and different peak hours per regions. During the high load of the UB1 peak from Region 0 (North America) the time for processing has been highest compared to the processing times of the other regions.

b) Scenario 2 – Coursera hosted on a two data centers

When Coursera grow in popularity on the Internet the most common approach to improve service quality is to deploy the application in several locations around the globe. Consequently for the second scenario in CloudAnalyst, we kept the user bases the same and we add one more data center, in region 2 (Europe). In order to preserve the cost the same 50 virtual machines are spitted on half for each data center. After running the simulation from second scenario with two data centers we have received the following response time and request processing time, see Table 3.

TABLE III. SCENARIO 2: OVERALL RESPONSE AND PROCESSING TIME

	Avg (ms)	Min (ms)	Max (ms)
Overall response time:	825	75	2535
Data center processing time:	414	0.19	1618

Overall, response time in second scenario is significantly lower than the corresponding response time in first scenario with single data center. Contrary, we have increased data center processing time in the second scenario with two data centers, this is because we are using half of the number of VMs in each data center compared to the first scenario. Substantial improvement in the second scenario is evident for the response time by region where the average response time has balanced distribution, see the second column Avg (ms) from Table 4.

TABLE IV. SCENARIO 2: RESPONSE TIME BY REGION

User Base	Avg (ms)	Min (ms)	Max (ms)
UB1	994,941	92,687	2.535,985
UB2	545,046	189,154	1.738,521
UB3	719,439	75,094	1.817,187
UB4	749,981	280,650	1.335,600
UB5	346,825	259,448	876,667
UB6	208,679	166,418	370,501

Significant difference is noticeable in the data center processing times and response times shown in Figure 3. The average processing time of both data centers is increased because of the decreased number of VMs. In the same time we can notice decreased loading traffic for the first data center (DC1), now the peak is 6M requests per hour. Reducing the number of virtual machines by half during each of these peak loads effectively lengthens the time taken to process by about two times in each data center.

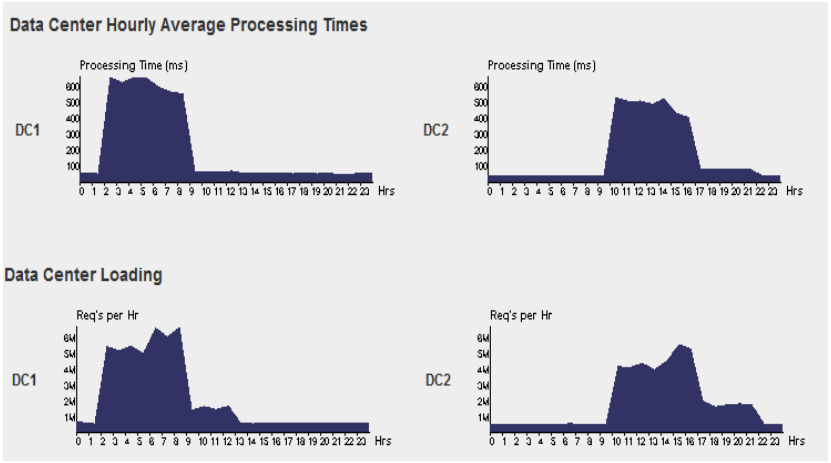


Figure 3. Scenario 2: Data center processing and loading times

Considering the MOOC trend there is an expectation that till 2015 there will be more than 6 million unique students worldwide. In this research we were able to conduct excellent analysis using the simulator CloudAnalyst and we received substantial improvement for the response time in the 6 regions and lowered loading traffic for the first data center (DC1).

CONCLUSION

We have researched the massive online teaching infrastructures on a worldwide scale because it offers remarkable collaborative and conversational opportunities for students to gather and discuss the course content. We demonstrated how CloudAnalyst can be used to model and evaluate a real world MOOC through a case study of a Coursera deployed on the cloud. We have illustrated how the simulator can be used to effectively identify overall usage patterns and how such usage patterns affect data centers hosting the application. This paper provides appropriate configuration for distribution of the resources by geographic location depending on the workload of CC environment for the providers of MOOC to deliver high-quality learning material. We have proposed to use environment with two data centers, one in North America and the other in Europe, in order to bringing the service closer to the users. This improves the response time in the 6 regions and has shown how to improve the Coursera load balancing at the application level across data centers.

REFERENCES

1. R. Williams, R. Karousou, and J. Mackness, “Emergent learning and learning ecologies in web 2.0,” International Review of Research in Open and Distance Learning 12(3), pp. 1-21, 2011.
2. T. Ozturk, Hayriye, and H. Ozcinar, “Learning in multiple communities from the perspective of knowledge capital,” The International Review of Research in Open and Distance Learning 14.1 (2013): pp. 205-221. March 2013.
3. R. Boyatt and J. Sinclair, “Meeting learners' needs inside the educational cloud,” Published by International Journal of Learning Technology, Vol.8, No.1, pp. 61–85, 2013. DOI: 10.1504/IJLT.2013.052827.
4. K. Gerd, B. Arosha, S. Neil, R. Michael, and P. Marian, “Educating the Internet-of-Things generation,” Published by Computer, 46(2), pp.53–61, 2013. ISSN:0018-9162
5. A. Mc Auley, B. Stewart, G. Siemens, and D. Cormier, “The MOOC model for digital practice,” 2010. Online: http://www.elearnspace.org/Articles/MOOC_Final.pdf.
6. A. Fini, “The technological dimension of a massive open online course: the case of the CCK08 course tools,” The International Review of Research in Open and Distance Learning, North America, 10, nov. 2009.
7. Google Introduces Course Builder, an Open Source Project Targeted at MOOCs. Online: http://mfeldstein.com/google-introduces-course-builder-an-open-source-project-targeted-at-moocs-but-the-real-competitor-might-be-amazon/ <accessed 9 December 2013>
8. Coursera, “Coursera hits 1 million students across 196 countries,” Online http://blog.coursera.org/post/29062736760/coursera-hits-1-million-students-across-196-countries Published on 9 August 2012.
9. K. Worlock, “MOOCs: cutting through the hype,” Published by Outsell on 27 March 2013. Online: http://www.smarthighered.com/wp-content/uploads/2013/04/MOOCs-CUTTING-THROUGH-THE-HYPE.pdf <accessed 19 December 2013>
10. B. Wickremasinghe, R. N. Calheiros, and R. Buyya, “CloudAnalyst: a CloudSim-based visual modeller for analysing cloud computing environments and applications,” Proceedings of the 2010 24th IEEE International Conference on Advanced Information Networking and Applications. 2010. pp. 446-452. ISBN: 978-0-7695-4018-4.

37.018.43:004

A PERSONALIZED E-LEARNING SYSTEM[10]

Aleksandar Kotevski, MSc
Partizanska B.B., Faculty of Law Kicevo, Bitola,
aleksandar.kotevski@uklo.edu.mk

Abstract

Using e-learning systems without modules for giving suggestions and recommendation to the users, although they contains useful and practical learning materials, are not effective and useful for the users. Searching the most adequate learning content in the large dataset of learning materials, without some techniques for filtering, is not effective way of using e-learning systems. That's why, there is a practical need for modules in e-learning systems that offer system personalization based on the user needs and goals, habits and learning style. Furthermore, users have different learning styles, different prior knowledge and goals. It means that the e-learning systems need to integrate modules that provide system personalization.
The main goal of this research is to propose a prototype of intelligent system for e-learning that will suggest the most useful learning materials and deliver the learning material based on the most adequate learning style to the users.

Keywords: intelligent, recommendation, filtering, learning style, tags

INTRODUCTION

Today, the computer technology takes a great part of the learning process, beginning from the first computer-based system until to web based intelligent application, games, simulation and etc. Its known that the Internet is the large dataset of learning materials. It is the same for e-learning systems. They can contain a large data set of resources from different learning areas. On the other hand, users have very specific needs. So, the system need to offer some tools for filtering the learning materials and give recommendation to the users.

[10] original scientific paper

Intelligent e-learning systems can improve and update the computer learning process by filtering the most adequate learning materials based on users learning style, goals and requirements. Based on McCalla 2005, the intelligent e-learning systems need to motivate the users to archive the goals on effective and efficient way.
To be more effective, intelligent learning systems are using a model of individual characteristics for the users (their goals, parameters, knowledge) in order to adapt their operations. The user's model can be modeled based on user's review via several tests, polls, using history and etc.
The main goal of this research is to propose a prototype of intelligent system for e-learning that will suggest the most useful learning materials and deliver the learning material based on the most adequate learning style to the users. The proposed system includes user modeling, based on several tests for user knowledge level as well as the most adequate learning style. Additional, we are going to propose a combination of algorithms that should be used in this intelligent model.
As a result of this research, we are going to answer to following questions:
- How we can determinate the most adequate user's learning style
- How we can organize and group the users based on their knowledge level
- How we can develop the user model and what model contains
- What logic will be used in manner to get decision about the most adequate learning materials

RELATED WORK

There are a huge number of researchers (Brusilovsky, 1999; Brusilovsky, Eklund, & Schwarz, 1998; Brusilovsky & Maybury, 2002; Graf & Kinshuk, 2006; Sessink, Beeftink, Tramper, & Hartog, 2003) that are working in the e-learning section and using artificial intelligence in manner to make them more effective. Some of them are directed to adaptation of learning materials based on users knowledge level, some of them are using material adaptation based on the most adequate learning style. There, the most adequate learning style has been determinate by using several methods, like Peter Honey and Alan Mumford's, Anthony Gregorc's model, Sudbury model of democratic education, NASSP Learning Style Model, VARK and etc). In addition, there are papers that made research about collaborative filtering in order to suggest the most adequate materials to the users.
The authors in [1] propose using a poll for determination the most adequate user learning style. The results of the poll are the criteria for delivering style of the learning materials. Similar idea proposes the authors in [2], but they

are separate the process in the two phases: first they made determination the algorithm for separate the materials and then made decision about delivering style. In [3], the authors propose a model for automatically user's modeling in goal to determinate the most adequate learning style. The paper [4] includes analyzing on user answers on several quizzes and polls, in goal to determinate the user's needs. In that content, the authors are especially focus on the answers with negative connotation and adverbs that are related with disagreement, in order for fix that suggestions and make system for efficient. In paper [5], the authors are working on the algorithm for data mining in order to analyze the user actions and user-system interaction. By using the algorithm, the system defines a template that helps in the process of suggestion the most adequate learning materials. The authors in [6] suggest using the AriorіAll, Apriorisome and DynamicSome algorithms for suggesting the most adequate learning materials. The paper [7] proposed a system prototype for automatically recommendations based on user profiles and their history. The same idea is the topic in the paper [8] where authors are using user's history and searching keywords in order to select the learning materials. The paper [9] intend using Vector Space Model for giving recommendations to the users, by comparing the similarity of the materials that have been used from the users with other available materials in the system. The similar research is given in paper [10], where the authors are focused on determination the similarity between learning materials in the system and propose the most adequate content to the users.

There are several papers that are focused on using tags in order to make the system more effective. In that manner, the authors in [11] propose a method that uses tags in combination with collaborative filtering with limitation of three-dimensional relation into two-dimensional and then using method for fusion in order to update the co-relation between the new relations. In the same papers, the authors gave an overview of all effects from using tags in combination with different algorithms for collaborative filtering. In paper [12], the authors are oriented to a model for giving recommendation based on the tags that are used from the users. In additional, they present results from their investigations about a positive effects from using the tags. In the focus of paper [13] is a system that uses an agent that follows the user navigation and behavior in the system and make decision which learning material should be recommend to that user.

LEARNING STYLE DETERMINATION

It is common question from a lot of authors if students learn on the right way. It means does the learning materials that are suggest to the students are

in the adequate style and format. It's clear that every student has different learning style. Some students want only to read a lot of test, others love to watch video tutorials. Some of them prefer to using audio materials in contrast of some other students which practice to learn from practical examples and real situations. In that manner, the learning style can be define as a indication of how students learn and how they want to learn (Gregorc & Ward, 1977; Keefe, 1987; Tseng, Chu, Hwang, & Tsai, 2008). There are a several models and algorithms for determination the most adequate learning style (Dunn, Dunn, & Price, 1984; Felder & Silverman, 1988; Keefe, 1987; Kolb, 1984, VARK). In the proposed system, we are going to use the VARK model. It uses questionnaire with 26 questions what gave answer for the most adequate user learning style and make user categorization in one of following four categories:

- Visual – this kind of learners want to learn by watching some video tutorials, diagrams, images, presentations and etc
- Aural – this type learners want to use audio materials
- Reading and writing – reading learning materials are preferred learning style for this kind of learners
- Kinesthetic – are focused on learning by using practical realization and using examples

In the proposed system, the student will have to give answer to all 26 questions, so the system will know the most adequate learning style for the users and make adaptation to the materials based on the learning style. Preferred learning style is only one part from the user model in the proposed system. The other important part in the user profile is determination of the user knowledge level. That information will affect in grouping the students in virtual learning groups based on their knowledge level.

USER MODEL

From all available information collected from sign up process and from student activity, the system is going to define and update the student model. It's very important aspect for the system operability because it contains important information that has impact to system decision for recommendation and materials suggestion.

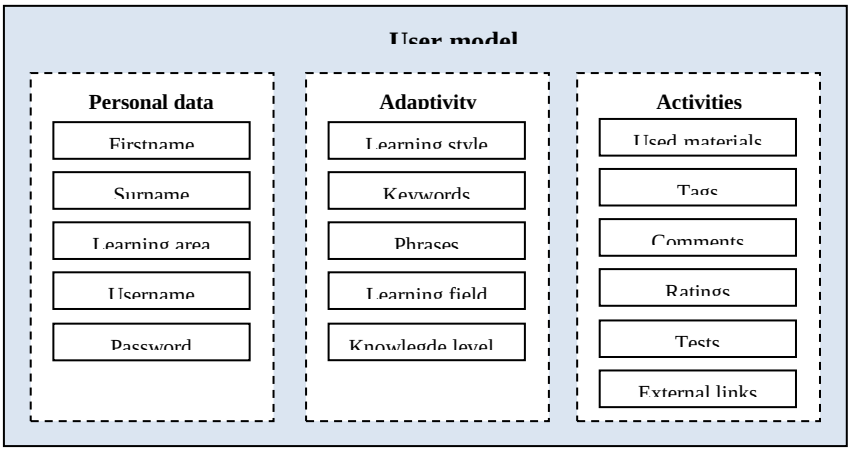


Image 1: User model components

In general, the student model will contain following sections:
- General information (Name, Surname, Learning field, file number, username, password)
- Adaptive information (learning style, keywords, phrases used while searching, knowledge level)
- Activity information (used learning materials, added tags, ratings and comments, used additional learning material and links)

FILTERING LEARNING MATERIALS

One of the most useful functionality of the proposed system is giving recommendation to user based on their needs. In the proposed paper, we are going to use a combination of several algorithms, like PageRank, Vector Space Model and Simple Collaborative Filtering. Pearson correlation coefficient will be used in order to detect the similarity between user profiles, based on their common characteristics, knowledge level, participation in learning group and etc.
Second important aspect for filtering the most adequate learning materials are tags. The most used tags from the students are stored in student model. On the other site, each learning material has list of tags. By using Vector Space Model, we are going to compare both lists. The result of that function will generate the list with the most adequate learning materials that should be recommend to the user.
As last, we are going to implement the PageRank algorithm in order to calculate the most popular learning materials, based on other user's experience. By using the results from PageRank algorithm execution, the system is going to reorder the suggested learning materials find out after execution of the Simple Collaborative Filtering and the Vector Space Model algorithms.

SYSTEM ARCHITECTURE

Proposed system will contain several modules:

- Module for generating user profile: the main goal of this module is to generate the user profile based on the information that students insert while sign up process; based on student activities and using the system and etc. The Image 1 presents the components of the student model
- Module for determination of student requirements: the goal of this module is to determinate the student knowledge level, the most adequate style and format for delivering the learning materials, to generate the list of keywords important for the student
- Recommendation module: this section aim to filter the most adequate learning content for the student, based on:
  - Tags posted from students and teachers for the learning contents
  - The rating posted from student
  - Search keywords

Image 2 shows the architecture of the proposed system.

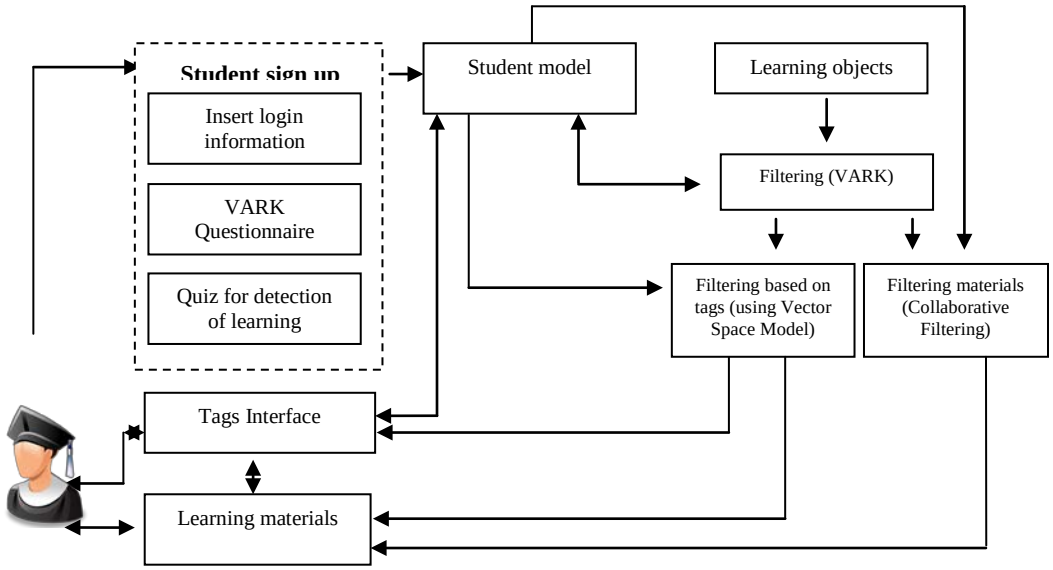


Image 2: System architecture

CONCLUSION

The efficient intelligent system for e-learning is the system that can filter and recommend the most adequate content, suggest it to the users and deliver it in the format and style that is the most adequate for the users.
Tag using in the process of recommendation learning material in the e-learning systems results with more effective e-learning process and gain to successful personalization of e-learning systems.
Instead of the systems that already exist and were discuss in section related works, the proposed system has several advantages. Some of them didn't make student separation based on their learning style, so they deliver learning content in the same format to each student, regardless the most adequate student learning style. Our proposed system is going to deliver learning materials in format based student learning style. Student knowledge level has impact in the content filtering in our system, which is not practice in the reviewed systems.
The proposed system will have positive effect in the process of education because if will produce the learning process more efficient and will contribute in increasing the motivation of students. Delivering the most adequate learning materials in format based on student learning style will results will highest productivity in the educational process.

REFERENCES

[1] An intelligent e-learning system based on learner profiling and learning resources adaptation, National Technical University of Athens, School of Electrical and Computer Engineering, Athens, Greece, 4 May 2007
[2] Personalized E-learning System by Using Intelligent Algorithm, 2008 Workshop on Knowledge Discovery and Data Mining, Mingmin Gong
[3] Implementation of Affective States and Learning Styles Tactics in Web-based Learning Management Systems, 2010 10th IEEE International Conference on Advanced Learning Technologies, Farman Ali Khan, Sabine Graf, Edgar R. Weippl, A Min Tjoa
[4] Opinion Mining in e-Learning System, 2007 IFIP International Conference on Network and Parallel Computing – Workshops, Dan Song, Hongfei Lin, Zhihao Yang,

[5] Real-time Learning Behavior Mining for e-Learning, IEEE/WIC/ACM International Conference on Web Intelligence (WI'05), Yen-Hung Kuo, Juei-Nan Chen, Yu-Lin Jeng, Yueh-Min Huang
[6] Automatic Recommendations for E-Learning Personalization Based on Web Usage Mining Techniques and Information Retrieval, ,Eighth IEEE International Conference on Advanced Learning Technologies, Mohamed Koutheaïr KHRIBI, Mohamed JEMNI, Olfa NASRAOUI
[7] Building a Recommender Agent for e-Learning Systems,International conference on Computers in Education (ICCE'02), , Osmar R. Zaiane
[8] A Markov-based Recommendation Model for Exploring the Transfer of Learning on the Web, (2009), Educational Technology & Society, 12 (2), 144–162, Huang, Y.-M., Huang, T.-C., Wang, K.-T., & Hwang, W.-Y
[9] Social Navigation Support in a Course Recommendation System. 4th International Conference on Adaptive Hypermedia and Adaptive Web-based Systems. Dublin, (2006). 91-100, Farzan, R., Brusilovsky, P.
[10] Item-Based Top-N Recommendation Algorithms, Mukund Deshpande and George Karypis,University of Minnesota
[11] Tag-aware Recommender Systems by Fusion of Collaborative Filtering Algorithms, Karen H. L. Tso-Sutter, Leandro Balby Marinho and Lars Schmidt-Thieme, Information Systems and Machine Learning Lab (ISMLL), University of Hildesheim
[12] Tagging, communities, vocabulary, evolution, Shilad Sen, Shyong K. (Tony) Lam, Al Mamunur Rashid, Dan Cosley, Dan Frankowski,Jeremy Osterhouse, F. Maxwell Harper, John Riedl,GroupLens Research, University of Minnesota
[13] Building a Recommender Agent for e-Learning Systems. Osmar R. Zaıane

37.018.43:004

USING RECOMMENDATION SYSTEMS FOR LEARNING MATERIALS[11]

Josif Petrovski
University St. Kliment Ohridski, FAMIS, PhD candidate
josif.petrovski@yahoo.com

Abstract

Recommendation systems are becoming more attractive today in electronic commerce, where algorithms are developed to determine with high precision the desires of customers. However, despite the rapid development of these systems and their use in the Internet environment, there is a small number of cases where these systems are adapted and used in the learning process. System recommendations complements the natural process of relying on friends, classmates, teachers and others who participated in the selection of learning materials. In this paper we review the aspects of creating a system for recommending documents, and one crucial question: how exactly to find learning materials that suit the needs of the student.

Keywords: Learning, System recommendations, Utility matrix, Recommendation model;

INTRODUCTION

E-learning systems are becoming more popular in educational institutions. The rapid development of e-learning has changed the traditional approach to learning and created new challenges for educators and students. Educators have difficulty choosing the appropriate learning materials for the growing number of materials online. Students have a problem when they decide which material is adequate for them and their needs. Therefore, the educator need an automated way of getting feedback from students in order to better

[11] original scientific paper

guide their learning process. Students, on the other hand, would benefit when an electronic system could suggest activities, and in intelligent way to select and recommend materials and documents for learning, which would improve the knowledge of students.

First attempts to develop recommendation system are made and applied in the field of e-commerce. The basic principle of the system is to use feasibility of creating a list of recommended items and to verify that the user likes the recommended items. This validation may arise directly by customers, or caused by the use of data that represent the previous activities of users. Such systems are called Recommendation System (Ricci, Rokach & Shapira, 2011). Recommendation systems are using many different techniques that will be discussed later, and depending on the techniques they use there are two types of Recommendation System:

- *Collaborative filtering systems*, which focus on the relationships between users and items. The similarity of two items is determined by the familiarity of ratings that were set by users and evaluated both items.

- *Content-based systems*, where first come the characteristics of items. The similarity of objects is determined by comparing their features.

- *Hybrid systems*, combination of both systems above.

COLLABORATIVE FILTERING SYSTEMS

The main goal of collaborative filtering is to predict or provide recommendation for products based on the activities of users who are like-minded. The assistance comes in the form of a top list where items are listed according to their importance for the buyer. Activities, opinions and ratings of the products in the system can be obtained solely by the users. Each user has a list of items where he has given his opinion. It is in form of rating, usually expressed on a numerical scale with values from 1 to 5, with 5 being the highest. For some items there may be no value. In this case the user is called *active user* and the system tends to set rating for that item in two ways:

- *Forecast*, a numerical value showing the forecast whether the active user would like the subject.

- *Recommendation*, Top N list with items that would be favor of the active user. This list contains items that have not been reviewed and evaluated by the user and is called Top recommendation.

The system consists of a crossed data for users and items represented in a matrix, called Utility matrix. Each data is in the form of rating, which represents the user's opinion on that subject. Some values can be 0 or blank, indicating the fact that the user is yet to rate that item.

Collaborative filtering systems do not always succeed in connecting items to users. In case of introduction of new users or new items a problem may appear called Cold Start, because there will be no data the system can process and bring the correct decision. Another problem that arises in these systems is Data Sparsity. In practice, many commercial systems have large databases. As a result, the Utility matrix will be large and mostly empty, thus creating obstacle for proper recommendation. This is often related to the previous problem, because the system tends to make recommendations based on past actions of the user, so for new users the system can’t make a wish-list.

CONTENT-BASED SYSTEMS

First thing these systems do is to create a profile for each item that is offered. Profile is a record or set of records that represent main features of that item. Usually profile consists of features that are easily visible. For example, features of a textbook are *authors, publishers, year of publication* and *classes* where is used.

These systems are of great importance to our paper, because they can discover features of documents or learning materials that should be recommended.

There are items where features are not immediately visible. This is often the case with written documents, intended for students to read. Recommendation system can offer titles that we would have interest in, but how will find out which are the right ones. Unfortunately, when we have documents it is not easy to reveal their main features. As a substitute for the main features we identify words

that describe the topic of the document. For example, if an article is written about IT technology it will have words like computer, Internet, multimedia, data etc. Once a document is classified under the topic IT technology we will easily note that these terms, called *keywords*, appear frequently, but until the classification is done these words are not counted as keywords yet.

Classification begins with reviewing the documents and finding keywords. At first glance it appears that the most words in the text are the keywords. But this assumption is wrong. Most of the repeating words are conjunctions and prepositions (and, or, if, that) or other words that help to build idea, but have no relevance to the topic. These words are called Stop words and are rejected during document classification. In fact, the keywords are relatively rare words. On the other hand, not all rare words may be keywords. There are certain words that rarely appear in the text, and again belong to the Stop group. The difference between the rare words that have significance and those who don't is located in the concentration of useful words in only a few documents.

The formal measure for determining the concentration of a given keyword in a relatively small number of documents is called TF.IDF, short from Term Frequency times Inverse Document Frequency. Basically, TF.IDF determines the relative frequency of a particular word in the document compared with inverse proportion of that word in a set of documents. This calculation determines how relevant a given word is in the specified document. Words that are common in a document or a small group of papers tend to have a higher TF.IDF value versus general words, such as conjunctions and prepositions. It is calculated as follows. We assume that we have a set *D* of documents. Choose a document *d* from the group and word *Z* to compare:

$$Z_d = f_{Z,d} * log\left(\frac{D}{f_{Z,D}}\right)$$

where $f_{Z,d}$ represents the number of repetitions of the word *Z* in document *d* and $f_{Z,D}$ is the number of documents from the set where the word *Z* is repeating (Berger, 2000). Depending on the values of the variables we usually have two situations.

If we assume that |D|~$f_{z,D}$, i.e. the number of documents is approximately equal to the repetition of the word Z over all documents in D. Then $0 < log\left(\frac{|D|}{f_{z,D}}\right) < 1$, Z_d will have lesser value then $f_{z,d}$ but still positive value. This indicates that the requested word, though often to be found in the documents, has significance. This would be the case when we search the set of documents associated with the topic *education* for the words "teacher" or "student." But these words are too common, unless the user specifies that the document should contain exactly those words. These common words lead to a low index of TF-IDF and the system might omit these words in the search.

On the other hand, we assume $f_{z,d}$ is high and $f_{z,D}$ is low. Then the value of $log\left(\frac{|D|}{f_{z,D}}\right)$ will be very high and so will the value of Z_d. This is our case because word with high Z_d points to the fact that this word is keyword in the stated document and not just a common word. This word has high discrimination power (Ramos, 2003). When searching with this word, the user would be satisfied with the results offered.

Finally, when we leave out STOP words and perform classification with TF.IDF method, each document will get a set of keywords, by which will become recognizable and now Recommendation system can easily notice its main features and make an accurate recommendation.

Here we see that TF.IDF a simple but effective algorithm for determining keywords of written documents. But despite this TF.IDF has its limits. His algorithm is not developed enough to resolve the grammar of the language. First example are synonyms, where words with same meaning are considered as different. Also, when words change their structure in plural are classified as different. This might be a problem if we have large database of documents. However TF.IDF remains as the basis for development other algorithms that surpass its disadvantages.

RECOMMENDATION SYSTEMS IN EDUCATION

Recommendation systems allow users to share their opinions and therefore to use the gained experience. They can be defined as "systems that provide individual recommendations as a result or lead the participant through a series of interesting and useful items separated from a large group of possible options" (Burke, 2002). These systems are made up primarily to support web users as support in decision making in certain situations, in terms of preparing the information that would be useful in those situations where the user does not have enough experience or knowledge of the environment (Adomavicius & Tuzhilin, 2005).

In the education process systems often recommend documents with specific content by keywords or according to the curriculum. Earlier we saw how a system can extract those keywords if they are not manually entered by the author. After efficient extraction of keywords, next step is to start the Recommendation system and offer Top-N list of documents that are in the interest of the student. This method compares the profile of the student with certain characteristics and predict ratings for papers that student hasn't assessed. We will be presented hybrid system, because it can recommend documents that have not yet received a rating (disadvantage of collaborative filtering), while allowing the recommendation of documents with different content (enrichment of content- based systems).

When a student selects a document to read, a group of related documents will be proposed. The user has the opportunity to evaluate the proffered documents by relevance or interest. On one hand the system for collaborative filtering examines the similarities between the students and their interests. On the other hand, the system for content-based filtering process similarities between the documents and the results are placed in the matrix. The system predicts ratings for all documents that are not rated by users and offers opportunity to be evaluated by the users. Results of the forecast are compared to actual ratings of the user that determines the accuracy of the assessment.

This system is a combination of several similar systems being used and still being updated. According to this model there are four basic matrices involved: User-User, Document–Document, User-Document and Rating-Difference. User-User matrix contains

similarities between users, Document-Document matrix contains similarities between documents, User-Document contains actual or anticipated user ratings and last matrix has the differences between actual and predicted values of the ratings.

Document-Document Matrix contains all the values of the similarity between documents and is filled after all documents are entered into the system. When a user give rating of a particular document, it will be saved in User-Document Matrix and at the same time the User-User Matrix will be updated. At that time predicted rating values will fill the User-Document Matrix. Once users give their rating to a document, it will replace the predicted rating. Then, the difference between actual and predicted ratings are stored in the Rating-Difference Matrix and the predicted values are analyzed again for the remaining documents.

To determine similarities between users technique of collaborative filtering applies, which calculates the similarities of users according to their assessment of documents. All values entered by users are considered as a vector of dimension N, where N is the number of documents in the system. First the algorithm calculates the distance between two users using Taxi geometry (Candillier and others, 2007) and then normalizes distance values between 0 and 1, thus limiting similarity to values from 0 to 1. This way the User-User Matrix is filled with values shown as an example in Table 1:

	User1	User2	User3	User4	User5
User1		0,25	0,62	0,77	0,56
User2			0,09	0,88	0,36
User3				0,21	0,12

Table 1. *Similarity matrix for users*

The number of documents that are rated by many users have major impact on the accuracy of determining the similarity between users. The following equation calculates the similarity:

$$sim(user(i), user(j)) = \frac{(N * R_{\max}) - \sum_{x=1}^{N} | r_i(x) - r_j(x) |}{N * R_{\max}} \qquad [1]$$

where N is number of documents normally assessed, R_{max} is the highest value (usually 5), $r_i(x)$ and $r_j(x)$ are values given for document x from users i and j.

For calculating the similarity between documents is used a method that not only compares keywords as main features of the documents, it takes their authors name and titles (Sarwar and others, 2001). It calculates the importance of keywords with TF/IDF and the similarity is determined by the equation:

$$sim(document(i), document(j)) = \sum_{x=1}^{N} w_x * \frac{a_x(i,j)}{b_x(i,j)} \qquad [2]$$

where N in number of attributes (three in this case – author, title, keywords), w_x is significance of x, a_x is number of common type of x attributes for documents i and j, b_x is the lowest number of x attributes for documents i and j. By determining the values for each pair documents the Document-Document Matrix is filled with values. By adding a new document in the system, this method will compare it with all other documents and will re-enter the values in the Document-Document Matrix.

As previously said Recommendation system stores user ratings for documents in the User-Documents Matrix. This matrix has two types of ratings: real and predicted. The real rating is set by the user depending on how much he liked the document. The predicted rating is set by the system in places where the user has not yet assessed documentation, and it will automatically change if the user enter a rating at any time. The system tends not to leave empty fields in the matrix, because according to these ratings the system makes recommendation. To predict ratings for $User_i$ for $Document_j$ we follow these steps:

1. Generate Top-N list of users similar to $User_i$ who have set ratings for $Document_j$
2. Generate Top-N list of documents similar to $Document_j$ that have received a rating from $User_i$
3. Determine prediction by the similarity of users (Equation 3)
4. Determine prediction by the similarity of the content of the documents (Equation 4)
5. We determine final rating prediction with combining values obtained in steps 3 and 4 (equation 5)

When predicting user ratings, the value of similarity between users will be used as constant. The system uses collaborative filtering where Top-N similar neighbors to $User_i$ will be selected from User-User Matrix. The calculation of the predicted rating PR_user is calculated as follows:

$$PR\_user = \frac{\sum_{n=1}^{N} S_{i,n} * R_{j,n}}{\sum_{n=1}^{N} S_{i,n}} \quad [3]$$

where $S_{i,n}$ is a similarity between $User_i$ and $Neigbor_n$, $R_{j,n}$ is the rating of $Neigbor_n$ for $Document_j$.

Next step is to select top-N similar documents from Document-Document Matrix that are rated by users. The calculation is done as follows:

$$PR\_document = \frac{\sum_{n=1}^{N} S_{i,n} * R_{j,n}}{\sum_{n=1}^{N} S_{i,n}} \quad [4]$$

where $S_{i,n}$ is similarity between $Document_i$ and $Neigbor_n$ of the Document, $R_{j,n}$ is rating of $User_j$ for the $Neigbor_n$. By this equation the system gives a prediction based on content-based filtering. To make correct prediction according to the content, user must have rated at least one similar document. The system will update the forecast every time the user gives new rating for the document.

The last step is combination of results through ponder average. The number of neighbors is used as measurable factors. The equation for calculating prediction P is

$$P = \frac{PR_{user} * N_1 + PR_{document} * N_2}{N_1 + N_2} \quad [5]$$

where N_1 is number of selected neigbors of the user and N_2 number of selected neigbors of the document. This equation calculates the predicted rating for $User_i$ and $Document_j$ with combination of predicted values of ratings based on document contents and the similarity in the activities of users. All the ratings are stored in the

Rating – Difference matrix, as shown on table 2, so the system can use the values all over again.

Real Rating	Predicted Rating	Difference	User	Document
R1	P1	R1-P1	U1,4	D1,5
R2	P2	R2-P2	U2,4	D2,5

Table 2. *Model of Rating – Difference matrix*

DOCUMENT RECOMMENDATION

As mentioned before, the purpose of the system is, as the student reads a document, to recommend a series of similar documents. Recommendation should meet two conditions. First, the user must see the recommended document for the first time. Second, the recommended documents have to be related to the content of the students document. To enforce these conditions, the document is pulled from User- Document Matrix, according to the predicted values for rating, i.e. documents that have not received rating from the user, but are high on the Top-N list according to predicted rating. So, **the recommendation of documents is done only by predicted rating.**

CONCLUSION

In this article a model was presented of a hybrid system for recommending documents to read. The aim was to describe Recommendation system that can be used in the educational process, a system that recommends learning materials. Searching for appropriate learning materials can be hard and long, and often without success. The combination of collaborative and content- based filtering helps students to improve their learning process. This system can not only be an improvement of the institution itself, but can also be the basis to create a Learning Management System which nowadays are becoming increasingly popular in educational environments.

These systems are further explored and are improved in order to increase their intelligence. And to achieve this they need to accurately identify students preferences, to follow their steps and fully

adapt to their needs. Therefore, this systems can use additional tools offered by the education itself. As educators use series of questions and tests to determine the level of knowledge of students, same way the system can obtain additional information that will help build a profile of each student. Next step would be connecting these systems with other similar systems on the Internet, making a global system with learning materials from many areas that would be easily available.

REFERENCES

Adomavicius, G., & Tuzhilin, A. (2005). Toward the next generation of recommender systems: A survey of the state-of-the-art and possible extensions. *Knowledge and Data Engineering, IEEE Transactions on, 17*(6), 734-749.

Berger, A et al (2000). Bridging the Lexical Chasm: Statistical Approaches to Answer Finding. In *Proc. Int. Conf. Research and Development in Information Retrieval*, 192-199.

Bobadilla, J., Ortega, F., Hernando, A., Alcalá, J. (2011) Improving collaborative filtering recommender system results and performance using genetic algorithms, *Knowledge Systems, 24*: 1310–1316.

Burke, R. (2002). Hybrid recommender systems: Survey and experiments. *User modeling and user-adapted interaction, 12*(4), 331-370.

Candillier, L., Meyer, F., & Boullé, M. (2007). Comparing state-of-the-art collaborative filtering systems. In *Machine Learning and Data Mining in Pattern Recognition* (pp. 548-562). Springer Berlin Heidelberg.

Emadzadeh, E., Nikfarjam, A., Gauth, K.I., Why, N.G. (2010) Learning materials recommendation using a hybrid recommender system with automated keyword extraction. *World Applied Science, 9(11)*: 1260–1271.

Rajaraman, A., & Ullman, J. D. (2012). *Mining of massive datasets*. Cambridge University Press.

Ramos, J. (2003). Using tf-idf to determine word relevance in document queries. In *Proceedings of the First Instructional Conference on Machine Learning*.

Sarwar, B., Karypis, G., Konstan, J., & Riedl, J. (2001, April). Item-based collaborative filtering recommendation algorithms. In *Proceedings of the 10th international conference on World Wide Web* (pp. 285-295). ACM.

Tang, T.Y., McCalla, G. (2003) Smart recommendation for an evolving e-learning system. In *Proceedings of the Workshop on Technologies for Electronic Documents for Supporting Learning, International Conference on Artificial Intelligence in Education, AIED 2003*.

651.142.08(497.713)

PEDESTRIAN SAFETY TREATMENT IN THE CITY OF VELES[12]

Associate prof.dr. Ile Cvetanovski
Associate prof.dr. Verica Dančevska
Postgrad. studies student Cvetanka Cvetanovska

Technical Faculty - Bitola
Technical Faculty , Ivo Ribar Lola bb - Bitola, Macedonia
ile.cvetanovski@tfb.uklo.edu.mk
verica.dancevska@tfb.uklo.edu.mk

Abstract

As transport grows globally, cyclists and pedestrians also known as a " vulnerable road users", are becoming victims in traffic accidents, especially in countries where legal traffic measures are not respected. Many countries, however, develop and invest in innovative strategies in order to enable safe movement in the "urban jungle" for all road users.

The topic of this research is the municipality of Veles and pedestrian crashes occurred in the period of year 2010- May 2013. The number of accidents, and the critical months of the year are also analyzed, weather and visibility conditions, the accidents' spatial, daily and hour distribution.In the end, adequate comments and countermeasures to improve the current situations are given.

Keywords: pedestrian safety, vulnerable road users, risk, safety countermeasures.

INTRODUCTION

Pedestrians and bicyclists are often labeled as 'vulnerable road users'. This is because – once they are involved in a crash - they have two distinct disadvantages:

[12] professional paper

- they are totally exposed, having no shield at all to protect them in case of a collision (except for the bicycle helmet that is worn by some cyclists), and
- the difference in mass between them and motorized vehicles is very large.

These two factors make their likelihood of being seriously injured or killed in collisions much higher than that of vehicle occupants.

SCOPE OF THE PROBLEM

As a category of road users, pedestrians are poorly discussed and analyzed in terms of their behavior, safety and treatment. Over 5.000 pedestrians worldwide are victims of road traffic accidents. In Macedonia, 38 pedestrians lost their lives in 2012. Most of them are people over 65 years. These negative statistics define the problem that lacks good practices and sharing of experiences that would be applicable in Macedonia in terms of pedestrian safety treatment.
According to international research, nearly 5.000 pedestrians weekly are victims of road accidents worldwide. In Macedonia in 2012, 38 pedestrians lost their lives in traffic accidents, including a little child. The majority of them were individuals over age 65. (Source: Analysis department, DIA Veles, 2013)

Crossing the street involves a complex set of behavior that begin with the decision to cross the street. But despite the standard recommendations to ‘stop-look-cross’, adults often plan their ‘crossing strategy’ the moment they cross the road. They choose the crossing location and speed on their own, so that they don’t have to stand and wait for a convenient time to cross. However, children are faced with major differences and contradictions between what they perceive and what they are taught of.

DRIVER-PEDESTRIAN COMMUNICATIONS

To avoid a collision, pedestrians and drivers have to be aware of each other, i.e. that both are road users. Therefore, they have to

interact-at least partially. This interaction requires at least six consecutive precautions:
1. Determine the route
2.Visual environment estimation in terms of the presence of the other
3. Detect and evaluate its location
4. To predict the intention of the other
5. On-time and appropriate decision
6. Appropriate response in order to avoid collision.

CAUSES FOR PEDESTRIAN CRASHES

Main causes for pedestrian crashes are:

1. Wrong decisions
2. Inappropriate pedestrian behavior
3. Improper intersection crossing
4. Jaywalking/darting out, etc.

The recklessness among drivers refers to the distraction during the process of managing the vehicle, using a cell phone and various communication devices. Other reasons that could lead to accident are:

1. Driving under the influence of drugs
2. Increased speed near intersections, school zones and pedestrian crossings.
3. Illegal left turns
4. Failure to obey stop signs.

The analysis showed that in 55 percent of the accidents, it was the pedestrian's action that was primarily responsible for the accident. The most common cause - characterizing 34 percent of all crashes - was the pedestrian's 'darting out' from a midblock location into the street; too late for the car to stop. The other main crash causes were 'intersection dashes' (9%) that were the same as dart outs, except that they occurred at intersections; 'vehicle turn / merge with attention conflict' (7%) which was characterized by a collision in which the driver was making a turn and attending to traffic in one direction, while the pedestrian was in an unattended location; and 'multiple threats' (3%) which were situations in which the pedestrian was struck by a car after another car stopped to allow him or her to cross, and in

the process created a view obstruction for the car that eventually hit the pedestrian.

The failure of precautions are shown in Table 1.

Factor Group	Number of Times Selected	Percent of Factors Selected	Percent of Crashes Selected
Pedestrian course	1206	30.6	55.9
Pedestrian search	1166	29.4	54.1
Pedestrian detection	238	6.0	11.0
Pedestrian evaluation	158	4.0	7.3
Pedestrian decision	17	0.4	0.8
Pedestrian action	19	0.5	0.9
Driver course	181	4.6	8.4
Driver search	510	12.9	23.6
Driver detection	292	7.4	13.5
Driver evaluation	82	2.1	3.8
Driver control-action	75	1.9	3.5
Driver and pedestrian interaction	9	0.2	0.4
TOTAL	3953	100.0	---

Source*: Shinar, D.,Traffic Safety and human behavior, pp 625*

The results of the studies are enabling us to determine and compare the accidents causes. Thereby, we can propose appropriate countermeasures to improve the pedestrian safety.

PEDESTRIAN AGE

Pedestrian age is also considered one of the reasons for accident occurrence. New researches show that older pedestrians are facing with bigger accident risk, unlike other pedestrians. This is due to decreased vitality and mobility during the aging process.Although they constitute a small percentage, it is more likely that the injuries they are facing would be fatal for their health. Age groups who are facing with the highest risk are pedestrians younger than 10 years of age and pedestrians over the age of 65.

Table 2. The primary pedestrian crash causes for pedestrians at different ages (based on Hunter *et al.*, 1995).

Age	Primary Pedestrian contributing factors
0- 9	Ran into street, ran from between parked vehicles, playing in street.
10-14	Ran into street, ran from between parked vehicles, failed to obey signal, unsafe skateboard or rollerblade maneuvers, unsafe entering or exiting, Safe movement violation
15-19	Failed to obey signal, unsafe skateboard maneuver, walking/running in wrong direction, leaning/clinging to vehicle
20-24	Alcohol impaired, walking/running in wrong direction, talking/standing in road, lying in road, jogging in road.
25-44	Alcohol impaired, working on car in parking lot, talking/standing in road, lying in road.
45-64	Jaywalking, lack of conspicuity, alcohol impaired.
65+	Jaywalking, stepped into street, failed to yield

Source: *Shinar, D.,Traffic Safety and human behavior, pp 628*

DEFINING THE AREA OF RESEARCH
(2010- May 2013)

For the city of Veles, statistics show that over a period of almost 4 years 2010- May 2013) occurred 1223 traffic accidents, of which 110, or 9% involved pedestrians. Most of them occurred in May, October and December, the most abundant during the years analyzed (50%) 1% of the accidents were fatal after the pedestrians' life.
On Diagram 1 is presented the number of occurred pedestrian accidents, seen annually.

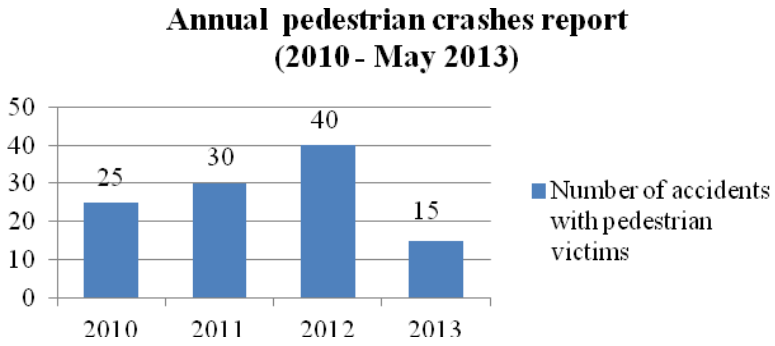


Diagram 1: Annual pedestrian crashes report (2010-May 2013)
Source*: From the authors*

RESEARCH DATA ANALYSIS

Travelling at night withdraws higher accident risk,as a driver and a pedestrian. However, practice shows that the majority of the accidents occur in daily conditions, good visibility and optimal road conditions, or in conditions where there is almost no risk at all. (T.3)

Table 3: Weather and visibility conditions

Weather conditions	%
Clear	73.7%
Cloudy	11.8%
Rain	12.7%
Snow	1.8%
Visibility	%
Day	
Good visibility	73.4%
Poor visibility	2.7%
Night	
Good luminance	13.8%
Poor luminance	8.3%
No luminance	1.8%

Source: *From the authors*

SPATIAL ACCIDENT DISTRIBUTION WITH PEDESTRIANS IN THE CITY OF VELES

As mentioned above, in the city of Veles in the past 4 years, 110 accidents. In table 4 it is separately shown the number of accidents for each characteristic area of the ciy.

T.4. Number of accidents according to zones

Број на зона	Назив на реон	Број на незгоди
1.	Suburb Tunel-Blagoj Gjorev	46
2.	Roundabout-Bus station-city bazaar	33
3.	City pool,Bauman monument	22
4.	Surroundings: Gradsko, Cashka, Buzalkovo,Jabolchishte,Izvor	9
Вкупно		110

Source: *From the authors*

On the following map are displayed the locations where traffic accidents have occurred in in the past 4 years (where „ “ presents the accident location, distributed in the aforementioned areas)

Picture 1: Area 1-SuburbTunel-Blagoj Gjorev
Source*: www.earth.google.com, authors*

PEDESTRIAN ACCIDENTS TIME DISTRIBUTION

Analyses show that most of the pedestrian accidents occur on days when there is increased mobility and transport of goods.
On Diagram 2 are shown the accidents distributed in the days of the week

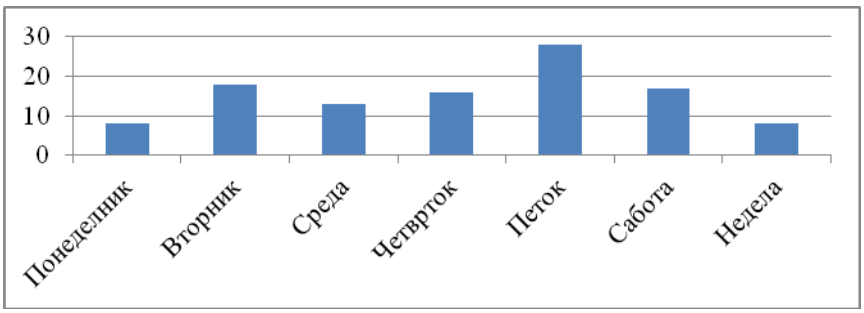


Diagram 2: Day distribution of accidents occurred in the period of 2010-May 2013
Source: From the authors

Statistics show that there is an increasing number of accidents on Tuesday and Friday. During this period are the market days and the migration of the population.

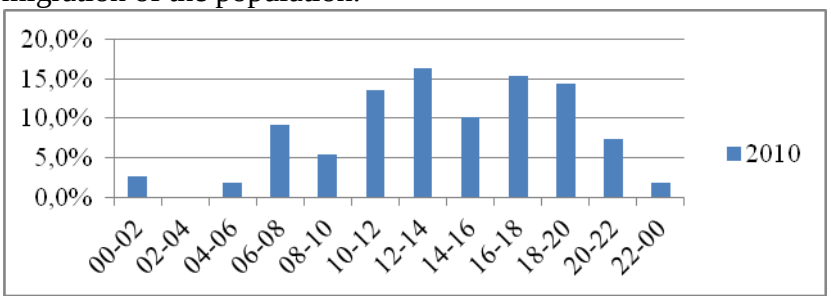


Diagram 3: Hourly distribution of accidents for the period of 2010-May 2013
Source: Developed by authors

MEASURES FOR IMPROVING THE PEDESTRIAN SAFETY

Institutions and experts dealing with pedestrian safety issues over the past few years, seem to favor the engineering measures. However, the improvement of the pedestrian safety requires a balanced approach that includes both perspectives.
Many of the pedestrian problems cannot be solved only referring to one of the three E-factors (Education,Enforcement,Engineering). Engineers, law enforcement, planners, educators and citizens need to identify and implement effective measures to improve the pedestrian safety.
Below are listed the proposed measures :

- Removing the illegally parked vehicles on sidewalks
- Arranging the green areas and trees that are beside the sidewalks.
- Regular horizontal and vertical signaling restoration, using higher quality materials with greater duration and reflectiveness.
- Proper placement of billboards and signboards, because at night they create so called ”dark curtains“, and exists a danger that the pedestrian cannot be observed.
- Proper placement of the equipment (vertical signaling and electric lighting poles) on and around the sidewalks.

- Introducing the school patrols and adequate person training who would assist to the youngest to properly cross the streets.
- Running a campaign that would affect citizens' awareness regarding the pedestrian safety in traffic.
- Construction of pedestrian islands
- Pavement dimensioning according to Rules of urban planning.
- Special regime movement for heavy vehicles in certain days and periods of the day.
- Proper pavements preparation and leveled areas providing on-time drainage during rainy periods.
- Building sidewalks from accumulating heat material (paving tiles are not suitable for construction of pedestrian paths, especially in winter. .
- Bicycle paths and deposed pavement to ease the movement of persons with disabilities.
- Street lighting recovery and maintenance, using an alternative source of energy.

CONCLUSION

According to the analyzed data from the past four years, the number of traffic accidents where pedestrians have been killed or injured is increasing. This is due to many factors, including the increased speed of the vehicles,disregard of traffic regulations, improper signaling, lack of education and campaigns that would affect the citizens' awareness, whether you are in the role of a driver or a pedestrian.

It's time to see the things from another perspective. With commitment, intervention and investment, this security measures will effect on the pedestrian safety, and will be a positive example for other cities in Republic of Macedonia.

REFERENCES

1. Shinar, D.,Traffic safety and human behavior. Israel, Beer Sheeva, 2007
2. Richard A., RettingSusan, A., FergusonAnne T. McCartt. A Review of Evidence-Based Traffic Engineering Measuresto

Reduce Pedestrian-Motor Vehicle Crashes**.**Insurance Institute for Highway Safety. Glebe Road, Arlington, VA,2003
3. Forbes, T. W., *Human Factors in Highway Traffic Safety Research.* New York, Wiley-Interscience, 1972
4. Sivak, M., How common sense fails us on the road: contribution of bounded rationalityto the annual worldwide toll of one million traffic fatalities. Transportation Res. F 2002.
5. Koepsell, T., McCloskey, L, Wolf, M., Mouden, A.V., Buchner, D., Kraus, J.,Patterson, M., CrosswalkMarkings and the Risk of Pedestrian-Motor Vehicle Collisions in Older Pedestrians. Journal of the AmericanMedical Association, 2002.
6. Polus, A. Katz, A., An analysis of nighttime pedestrian accidents at specially illuminated crosswalks, 1978.
7. Pedestrian fatalities data in the period of 2010-may 2013, Occurred traffic accident report, Analytics department, Police station of Veles,2013

637.12’639.07

THE IMPACT OF THE STAGE AND SEQUENCE OF LACTATION ON THE NUMBER OF SOMATIC CELLS IN GOAT MILK[13]

M.Sc. Tatjana Kalevska
Faculty of Technology and Technical Science - Veles
Dimitar Vlahov Street 57
tatjana.kalevska@uklo.edu.mk

ABSTRACT

The purpose of this study is to determine the impact of the stage and sequence of lactation on the number of somatic cells in goat milk. The research includes 75 goats which were cross-breeds of Alpine and Saanen race, of which 25 are in first, 25 are in second and 25 are in third lactation. From the analyses of the goat milk, it was determined that there are certain variations in the number of somatic cells, which depend on the stage and sequence of lactation. On the first control the number of somatic cells in the milk from the first lactation is 826.000/ml, 868.000/ml in milk from the second lactation, and 996.000/ml in milk from the third lactation. On the seventh control a highest number of somatic cells is determined and it equals to 1.550.000/ml in milk from the first lactation, 1.790.000/ml in milk from the second lactation, and 2.042.000/ml in milk from the third lactation. The determined difference of somatic cells on the first and seventh control of milk from the first, second, and third lactation is statistically significant ($p<0,01$). The average number of somatic cells in goat milk from the third lactation is statistically significantly ($p<0,05$) higher than the number of somatic cells in milk from the second lactation, and statistically significantly ($p<0,01$) higher than the number of somatic cells in milk from the first lactation.

Key words: goat milk, stage and sequence of lactation, somatic cells

[13] original scientific paper

INTRODUCTION

The basic pointer for the hygienic quality of milk is the number of somatic cells, which as biological structural elements of milk move during the normal secretory process. Determining the number of somatic cells in milk is important in confirming its hygienic and technological properties, as well as the health condition of the udder (Osteras, 1990). The number of somatic cells varies depending on infection on the milk gland, stage and sequence of lactation, the season, milking etc. (Antunac et al. 1997). The number of somatic cells in 1ml cows' milk is between 50.000 and 250.000 (Kalit, 1999), while the number of somatic cells in goat milk from a clinically healthy udder is 800.000/ml (Pettersen, 1984). In goat milk the number of somatic cells is rarely under 1.000.000/ml, especially at fall when the goats are at the end of lactation (Antunac et al.1997). The increasing of the number of somatic cells with progression of the lactation is more apparent in goat milk compared to cow's milk (Kosev et al.1996). A high number of somatic cells results in a decrease in milk quantity, as well as changing the physicochemical composition and technological properties of the milk (Antunac et al.1997).

MATERIAL AND METHODS OF RESEARCH

The research included 75 goats, which were cross-breeds of Alpine and Saanen race, of which 25 are in first lactation, 25 are in second lactation and 25 are in third lactation. The goats were raised in a combined barn system with grazing on the goat farm of ZK Kicevo.

Control on the milk was done over the course of seven months, from weaning of the goat kids at the end of April, up until the end of lactation at the end of October. The samples for determining the number of somatic cells were taken from the collective milk from the first, second and third lactation in regular time intervals of 30 days. The number of somatic cells was measured with a fluoro-optical-electronic counter Fossomatic.

RESULTS AND DISCUSSION

According to the data in table 1 and chart 1, the lowest amount of somatic cells in the amount of 826.000/ml is found in the first control of the goat milk from the first lactation, 868.000/ml in milk from the second lactation, and 996.000/ml in milk from the third lactation. While analyzing the impact of the stage of lactation on the number of somatic cells in goat

milk, a tendency of constant increase of the number of somatic cells corresponding to the progress of lactation is noticed, whereupon in the seventh control the number of somatic cells in milk from the first lactation is 1.550.000/ml, 1.790.000/ml in milk from the second lactation, and 2.042.000/ml in milk from the third lactation.

Beginning with the second and up until the seventh control, a statistically significant higher ($p<0,05$) number of somatic cells has been established in milk from the third lactation in comparison with milk from the second lactation, and a statistically significant higher ($p<0,01$) number of somatic cells in comparison with milk from the first lactation.

Table 1. Number of somatic cells (SCC x1000) in goat milk, depending of the stage and sequence of lactation.

Stage of lactation	first lactation	second lactation	third lactation
I	826.000	868.000	996.000
II	879.000	965.000	1.220.000
III	982.000	1.136.000	1.480.000
IV	1.013.000	1.390.000	1.640.000
V	1.286.000	1.540.000	1.790.000
VI	1.420.000	1.680.000	1.990.000
VII	1.550.000	1.790.000	2.042.000

The results from this research match the ascertainment of Raynal-Ljutovac et al. (2006) that the stage and sequence of lactation significantly impact the number of somatic cells in milk. Zeng et al. (1996) ascertained an increase in the number of somatic cells with progress of the lactation of goats. Almost identical are the results of Gajdusek and associates (1996) of 831.000/ml for the number of somatic cells in the first control.While researching the impact of the stage of lactation on the number of somatic cells in goat milk, Pavliček et al. (2007) in the first control found the number of somatic cells to be 712.000/ml, and 2.180.000/ml somatic cells in the sixth control. The number of somatic cells determined by Anifantakis,

(1993) which were 900.000/ml at the start of the lactation, and 1.900.000/ml at the end of lactation correspond with the results from this research.
Kosev et al. (1996) were researching the impact of the sequence of lactation on the number of somatic cells in goat milk and found the following results: the number of somatic cells in milk from the first lactation is 363.000/ml, 460.000/ml in milk from the second lactation , and 618.000/ml in milk from the third lactation. These results do not correspond with the results from our research.

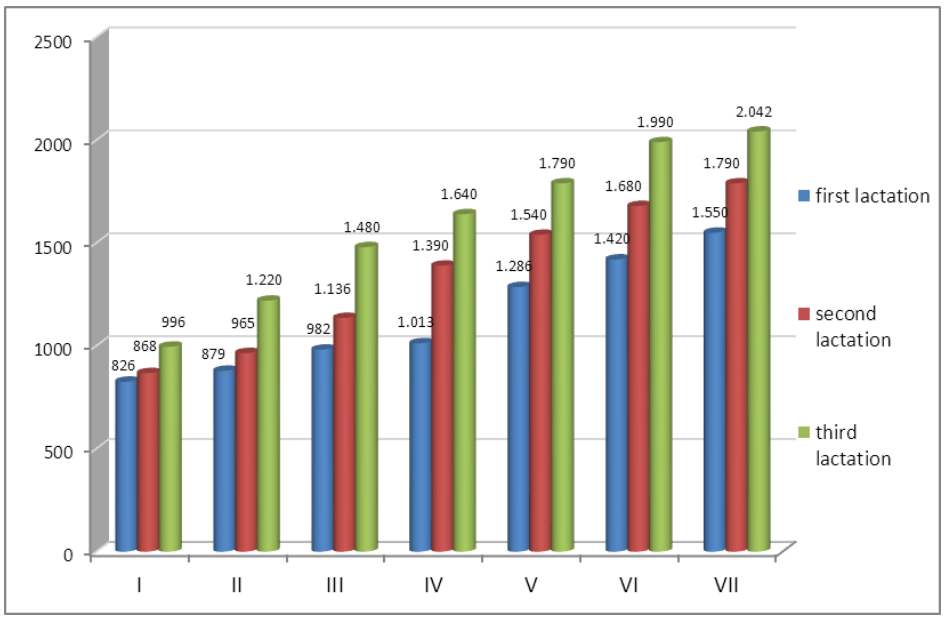


Chart 1. Number of somatic cells in goat milk, depending of the stage and sequence of lactation (SCC/ml x1000)

CONCLUSION

Based on the results from this research, it can be concluded that the stage and sequence of lactation have a significant impact on the number of somatic cells in goat milk. The number of somatic cells in goat milk from the third lactation is statistically significantly ($p<0,05$) higher than the number of somatic cells in milk from the second lactation, and statistically significantly ($p<0,01$) higher than the number of somatic cells in milk from the first lactation. In milk from the first, second and third lactation, the number of

somatic cells is determined to be the lowest on the first control, and in the following controls a constant rise of the number of somatic cells can be observed, reaching the maximum amount on the seventh control.

REFERENCES

1. Anifantakis, E.M., Kandarakis, J.G., (1980.): Contribution to the study of the composition of goat's milk. *Milchwissenschaft, 35,* 617-619.
2. Antunac N., Havrenek J., Samaržija D. (1997): Somatske stanice u kozjem mlijeku. *Mljekarstvo,* 47 (2), 123-134.
3. Antunac N, Samaržija D, Havranek J.,(2000): Hranidbena i terapeutska vrijednost kozjeg mlijeka*Mljekarstvo 50 (4) 297-304, 2000.*
4. Božanić R, Tratnik Lj, Drgalić I.(2002):Kozje mlijeko: karakteristike i mogućnosti *Mljekarstvo 52 (3) 207-237.*
5. Boroš, V. (1987): Influence of the lactation period on variations in the levels of certain components of bulked goats milk. Dairy Sci. Abstracts, 49: 5.
6. Gajdušek, S., Jelinek, P., Hampl, A. (1996): Somatic cell counts in goat milk and their relation to milk composition and properties. Zivocisna Vyroba 41(1): 25-31.
7. Kalit S., (1999): Somatske stanice i njihov utjecaj na proizvodnju i zrenje sira Podravca. Magistarski rad, Agronomski fakultet Sveučilišta u Zagrebu.
8. Kosev, K., Tzolov, S., Denev, S., Michailova, G., Koleva, M., (1996.): Influence of lactation and type of milking on the somatic cell count in goat milk. In: Somatic cells and milk of small ruminant. Proceedings of an International Symposium, Bella, Italy, EAAP Publication, No. 77, 227-229.
9. Osteras, O., (1990.): Somatic cell count in goat milk. *Meieriposten, 79, {1),* 192-196.
10. Pavliček J., Antunović Z., Senčić D., Šperanda M.,(2006): Proizvodnja i kemiski sastav kozjeg mlijeka o ovisnosti o redoslijedu i stadiju laktacije. *Poljoprivreda, Vol.12No.2 Prosinac*
11. Pettersen, K.F., (1984.): Cell count's in goat *milk. Acta Veterinaria Scandinavia, 22,* 226-237
12. Raynal-Ljutovac, K., Pirisi, A., de Cremoux, R., Gonzalo, C. (2006): Somatic cells of goat and sheep milk: Analytical, sanitary, productive and technological aspects. Small Ruminant Research, in press.
13. Zeng, S.S., Escobar, E.N., Popham, T. (1997): Daily variations in somatic cell count, composition, and production of Alpine goat milk. Small Ruminan Research 26: 253-260.

637.12.07:614.31

IMPROVING MILK QUALITY BY USING INDIVIDUAL MILK CONTROL[14]

Makarijoski Borche, MSc
Ljupche Kochoski, PhD
Biljana Trajkovska, MSc
University "St. Kliment Ohridski" Bitola,
Faculty of biotechnical sciences – Bitola,
makarijoski.borce@gmail.com;

Abstract

By using individual milk control, it is examined the influence of individual milk control on milk quality. The examination took place at one little farms, which is located near Bitola. Milk examples were taken from each cow on the farm, and also one milk example from all of the cows on the farm (group milk example). We also wrote down the amount of day milk production and number of lactation for all cows. All examination process lasted three months. Each month were taken milk examples from the examined farms. The goal of this examination was to find out the cows (individuals) which milk has negative influence on the milk quality produced from all cows on the farm.

Key words: individual control, somatic cells, quality, milk;

Introduction

The aim of each farmer is to improve the milk quality (primarily to improve its chemical composition and to reduce the number of somatic cells and microorganisms found in milk). By improving the milk quality, it is also improved the financial profitability of milk production. Poor milk quality reduces the purchase price of milk, so producers have lower incomes, which do not satisfy them. Individual milk control represents a significant part in the process of production of high quality and hygienic correct milk.

[14] original scientific paper

Material and methods

Milk examples were taken from each cow on the farm, and also one milk example from all of the cows on the farm (group milk example). We also wrote down the amount of day milk production and number of lactation for all cows. All examination process lasted three months. In this part it is very important to properly perform the process of taking the milk examples. Taking milk examples incorrectly it affects the correctness of the results. The number of somatic cells were examined using microscopic referent method and fluoro-opto-electronic method ISO 13366-3:199 using the appliance SOMASCOPE, DeltaInstruments-Holland.

Results and discussion

The farm that was examined in this study had ten cows and each of them during the quarterly survey was in lactation. In the following table No.1 are the results from the first examination.

Table No.1: Results of examined parameters on the farm (first examination)

Cow (No.)	Number of somatic cells SCC/ml	Number of lactation	Amount of milk (daily)
1	1 801 000	1	17.8
2	601 000	2	12.3
3	439 000	1	24.1
4	374 000	3	10.6
5	367 000	2	13.2
6	352 000	3	19.3
7	293 000	1	19.1
8	282 000	2	22.4
9	135 000	2	17
10	114 000	1	19
Total: 10 cows	Group milk example (SCC/ml):	Average of lactation:	Total amount of milk (daily):
	473 000	1.80	174.80

From the Results of examined parameters on the farm in the first examination, we can see that from ten cows, three of them (cow No.1, No.2 and No.3) had higher number of somatic cells in ml than the limit of somatic cells of 400.000/ml. The group milk example from all cows had value of 473 000 somatic cells/ml. By using individual milk control, all milk

producers can detect all individuals from the herd which cause an increase in the average number of somatic cells

We've detected clinical mastitis (cow No.1). We've immediately began a process of healing with cow No.1. We've also detected subclinical mastitis (cow No.2 and cow No.3). We've also began process of healing with this two cows.

In one week period, we took milk examples again from each cow, and we've got positive result from the treatments of mastitis (reduction in somatic cells, as shown in the following table No.2).

After treating the three critical cows we had changes in the number of somatic cells in the milk form all cows (from 473 000 SCC/ml, before treatment, 308 000 SCC/ml after treatment.

Table No.2: Hygienic condition of milk after treatment of critical cows

Cow (No.1)	Number of somatic cells SCC/ml	Number of somatic cells after treatment of critical cows	Average value of SCC after treatment of critical cows
1	1 801 000	383 000	Cows: No.1, No.2 and No.3 are successfully cured
2	601 000	415 000	
3	439 000	391 000	
4	374 000	365 000	
5	367 000	379 000	
6	352 000	353 000	
7	293 000	288 000	
8	282 000	271 000	
9	135 000	133 000	
10	114 000	111 000	
Total: 10 cows	Group milk example (SCC/ml): 473 000		Group milk example (SCC/ml): 308 000

In the following table No.3 are written the results from the second examination that was made in the farm.

Table No.3: Results of examined parameters on the farm (second examination)

Cow (No.)	Number of somatic cells SCC/ml	Number of lactation	Amount of milk(daily)
1	371 000	1	19.3
2	427 000	2	13.8
3	383 000	1	22.3
4	368 000	3	13.5
5	699 000	2	12.7
6	795 000	3	18.2
7	336 000	1	19.5
8	321 000	2	21.3
9	233 000	2	17.9
10	215 000	1	19.8
Total: 10 cows	Group milk example (SCC/ml):	Average of lactation:	Total amount of milk (daily):
	405000	1.80	178.30

The results form the second examination showed that the treatment of cows No.1, No.2 and No.3 was successful. The number of somatic cells which they produced is within the permissible with the exception of cow No.2. During the second examination in this farm was noticed an increase of somatic cells – cow No.5 (699 000 SCC/ml) and cow No.6 (795 000 SCC/ml). These cows haven't got any signs of visible mastitis, except increased number of somatic cells. We assumed presence of subclinical mastitis at these cows (No.5 and No.6). The dairy producer had no idea that these two cows have mastitis and milk produced from them, they've mixed it with whole milk, thereby decreasing its quality, and increasing the average number of somatic cells in milk produced from all cows. We've began process of healing with this two cows (No.5 and No.6). In one week period, we took milk examples again from each cow, and we've got positive result from the treatments of mastitis (reduction in somatic cells, as shown in the following table No.4).

After treating the three critical cows we had changes in the number of somatic cells in the milk form all cows (from 405 000 SCC/ml, before treatment, 335 000 SCC/ml after treatment.

Table No.4: Hygienic condition of milk after treatment of critical cows

Cow (No.)	Number of somatic cells SCC/ml	Number of somatic cells after treatment of critical cows	Average value of SCC after treatment of critical cows
1	371 000	368 000	Cows: No.5 and No.6 are successfully cured
2	427 000	411 000	
3	383 000	389 000	
4	368 000	359 000	
5	669 000	281 000	
6	795 000	385 000	
7	326 000	333 000	
8	282 000	290 000	
9	233 000	221 000	
10	215 000	212 000	
Total cows: 10 (ten)	Group milk example (SCC/ml):		Group milk example (SCC/ml):
	405 000		335 000

In the following table No.5 are written the results from the third examination that was made in the farm.

Table No.5: Results of examined parameters on the farm (third examination)

Cow (No.)	Number of somatic cells SCC/ml	Number of lactation	Amount of milk (daily)
1	335 000	1	19.5
2	378 000	2	14
3	372 000	1	23
4	283 000	3	14.7
5	239 000	2	14.5
6	391 000	3	19.3
7	333 000	1	20
8	299 000	2	22
9	315 000	2	17.5
10	311 000	1	20.3
Total: 10 cows	Group milk example (SCC/ml):	Average of lactation:	Total amount of milk (daily):
	331 000	1.80	184.80

The results form the third examination showed the health of the herd is significantly improved compared to the previous month. Cows No.5 and No.6 was successfully cured and that improve the quality of milk produced from all cows. The last month the number of somatic cells in group milk example was 335 000 SCC/ml, but after curing cows No.5 and No.6 the number of SCC/ml was reduced to 331 000/ml.

The condition of all dairy cattle in this farm in the third month of this examination was stable and all cows were in good health. Milk that has been produced was with good quality and had levels of somatic cells under the limit of 400 000 SCC/ml. In this situation we didn't took any measures, because we had no potential indication. In continuation hygiene in farm must to be maintained at high levels in order to produce milk with high quality. Hygiene is also important for the health condition of the herd.

The results are made according to the method that applied William L. Crist and his associates at the University of Kentucky, College of Agriculture. The results which they obtained in their investigation, corresponds with our results.

These presented data demonstrated the condition of the farm for a period of three months of research. We also found out the cows (individuals) which milk has negative influence on the milk quality produced from all cows on

the farm. By improving milk quality all diary producers get more money per liter produced milk.

Conclusion

Using this individual milk control, in this examined farm we found out four cows with subclinical mastitis and one cow with clinical mastitis. We can see the positive site of using this individual milk control from the results which we've got during our process of examination:

In this farm, at the beginning the number of the somatic cells in the milk group example was 473 000/ml, and after three months that number was reduced to 331 000 somatic cells/ml.

By reducing the number of somatic cells in milk, respectively, is increased the amount of produced milk per cow. In the first month of the the examination, the daily amount of milk production was 174.8 liters, but after completion of individual milk control program, in period of three months, the daily amount of milk production was increased for 10 liters. With these presented information we can see the correlation between somatic cells number and the amount of milk production.

According to that individual milk control represents a significant part in the process of production of high quality and hygienic correct milk.

References

1. Makarijoski, B. The influence of individual milk control on milk quality, Faculty of biotechnical sciences-Bitola, pages 53-61, 2012.
2. Miljkovic, V. Higijena i tehnologija mleka, Beograd, 1992.
3. Мицковски, Г. и Мицков,Љ.Заболувњата на млечната жлезда кај животните(33-83).Скопје.2010.
4. Cacic Z., Kalit S., Antunac N., Cacic M. Somatske stanice i cimbenici koji utjecu na njihov broj u mlijeku. Mljekarstvo 53 (1) 23 – 36, 2003.
5. Crist,L.W.1997.Mastitis and its control
6. Axelsson, A. 2004. A comparison between bulk tank milk samples and individual milk samples from dairy herds in Uruguay;
7. Douglas VL, Holmes CW, Williamson NB, Steffert IJ. Use of individual cow somatic cell counts, electrical conductivity, and the rapid mastitis test on individual quarters to diagnose subclinical mastitis in early lactation, with an economic assessment of antibiotic therapy. In: *Proceedings of the Milk Quality Conference,* Ministry of Agriculture and Fisheries, New Zealand, 1997:1-11

8. Stojanovic, L. i Katic,V.1998. Higijena mleka.Beograd
9. Duranec, V. и сор. 2008. Проект: „Higijena mleka od krave do trzista”.

637.523

THE INFLUENCE OF COTTAGE-CHEESE ADDITION ON THE PHYSICS, CHEMICAL AND SENSORY CHARACTERISTICS OF COOKED SAUSAGES[15]

Elena Joševska, PhD
Mitre Stojanovski, PhD
Gordana Dimitrovska, PhD
Dejan Trajanovski

University St.''Kliment Ohridski''- Bitola
Faculty of Biotechnical sciences – Bitola
elena.josevska@uklo.edu.mk

ABSTRACT

In this paper, the physic–chemical and sensory characteristics of reduced–fat cooked sausage, made with addition of 10% and 15% cottage-cheese, (sausages B and C) were examined and compared with those of conventionally cooked sausage (sausage A).

With the addition of cottage-cheese noted increase in protein content after heat treatment in the production of sausages groups B and C (29.31 % : 34.02 %) .

The lowest score of all tested sensory properties of the sausages have control group A (3.17) produced by standard recipe.

Based on this conducted research at "huntsman" sausage can be concluded that the addition of cottage-cheese in the production is justified, not only to improve the nutritional and biological value, but for the sensory quality that is an important factor to greater demand for these types of sausages.

Key words: cooked sausages, cottage-cheese, physic-chemical composition and sensory characteristics

[15] original scientific paper

INTRODUCTION

Meat products play an important role in the modern diet. The production of cooked sausages comprises an important segment in the complex meat industry. Cooked sausages are manufactured from a mixture of chopped meat (pork or beef), pork fat, ice water, soy proteins, starch, salt, additives and spices (Official Gazette of the RM No.63/2013).

Fat, as a food component, contributes to the taste, texture and appearance, increases the feeling of satiety during meals. From a physiological standpoint, fat is a source of energy and essential fatty acids. However, fat intake is associated with increased risk of obesity, some types of cancer, high blood cholesterol and coronary heart disease. For these reasons, several health-related organizations (American Heart Association, American Cancer Society and World Health Organization) have proposed to limit total fat intake to no more than 30% of total calories (4).

In order to protect health of consumers and to improve sensory characteristics of sausages, fat tissue or meat is replaced by other supplements such as soy, cheese, cottage cheese, flour, dietary fibers such as inulin, carrot fiber, etc. Cottage cheese is a product obtained by boiling the whey, rich in albumin and globulin, proteins that are essential and easily digestible for the human organism. It is used as a fat substitute because of its contribution mouth feel and low caloric value (1kcal/g).

With these beneficial effects in mind, this study was designed with the aim to determine the effect of cottage cheese addition to the physic–chemical and sensory properties of fat reduced cooked sausages by comparing these sausages with the product prepared with the standard fat levels used in the industrial production.

MATERIAL AND METHODS

The tests were performed in three groups of “huntsman” sausage, produced by a standard recipe at the meat industry ‘’Marfil’’- Prilep.
Sausages from the production group A were made from 40% pork meat, 20% beef meat, 30% pork fat, 5% ice water and 5% of a commercial mixture of spices and additives. In sausage B, the percentage of pork fat was reduced by approximately 40% compared to the control, and formulation was the following: 40% pork meat, 20% beef meat, 15% pork fat, 10% ice water, 5% of the commercial mixture of spices and additives, and 10% cottage cheese. Sausage from the production series C was added 15% cottage cheese. After

homogenization the mixture was stuffed into artificial casings (Ø22) and sausages were kept in the bath until the geometric center of each chub which corresponds to the thickest part of the product reached 72°C. Both groups of sausages were stored at 8 °C for 12 days until analyzed.

Moisture content is investigated by the method of drying at 105 ° C for 24 hours to achieve both consequential measurements. The content of fat was examined by the method of Soxhlet. The total nitrogenous substances are tested by the method of Kjeldahl. The minerals contents (ash) was examined by a method of combustion of the sample at the temperature of 550 ° C and measurement of the residual ash, expressed in percent. Nitrate and nitrite contents of samples were determined according to the methods of Nessler & Hehner. The overall sensory quality of sausages was evaluated according to method of scoring - pointing Radovanović-Rajlić & Popov, (2000/2001).

All measurements were performed on seven sausages from each group. The results were evaluated statistically using the ANOVA test.

RESULTS AND DISCUSSION

The chemical composition of cottage cheese–added sausage (sausage B, C) and control (sausage A) before and after heat treatment are shown in Table 1.

Table1 Chemical composition of control and cottage cheese-added sausages

Groups of sausages	Before heat treatment (%)					
	moisture	fat	protein	nitrate	nitrite	ash
A	62,37	17,48	17,59	0,0065	0,020	2,60
B	56,00	15,78	25,71	0,0105	0,032	2,51
C	55,57	13,03	29,00	0,0132	0,042	2,53
After heat treatment (%)						
A	56,76	20,34	20,37	0,0061	0,019	2,67
B	49,57	19,32	29,31	0,0100	0,030	2,53
C	45,82	17,53	34,02	0,0129	0,038	2,51

From the performed tests can be seen that moisture content in the control group A (62.37% - 56.76%) before and after heat treatment was significantly higher ($P < 0.01$) compared to reduced–fat sausages from group B (56.00% - 49.57%) and C (55.57% - 45.82%). On the other hand, the fat content in sausage C (13.03%) was significantly ($P < 0.01$) lower compared to sausage A (17.48%) and B (15.78) before heat treatment. After heat treatment fat content reach values from 17.35 to 20.34%. These results are in agreement with results of (1), (2), (5), (6).

Protein content in sausages with cottage cheese (25.71 %: 29.00 %) increased after heat treatment in both groups (29.31% : 34.02%) as a result of reduction of the moisture content and increase the dried matter. results are in agreement with results of (5),(9). Ash content in sausages of all groups during all manufacturing period did not differ significantly ($p > 0.05$). Nitrates and nitrites not show statistically significant differences ($p> 0.05$).

The obtained values of chemical composition are typical for cooked sausages and are in agreement within the standard defined by Macedonian legislation.

Sensory evaluation of cottage cheese–added sausage (sausage B, C) and control (sausage A) are shown in Table 2.

Table 2 Sensory evaluation of "huntsman" sausages

Selected sensory properties	A	B	C
External appearance	2.2	3.3	3.4
Appearance of cut surface	3.6	4.0	4.1
Consistency	2.7	4.5	4.7
Color	2.5	4.3	4.4
Odor	3.8	4.3	4.3
Taste	3.2	4.2	4.2
Average rating	**3.17**	**4.19**	**4.27**

Results of the sensory evaluation are presented in Table 2. External appearance did not differ significantly ($P > 0.05$) between B and C groups, while average score for the appearance of cut surface in sausage A was significantly lower ($P < 0.05$) compared to other two groups.

Score of color for sausage A was significantly lower than reduced–fat sausages ($P < 0.05$). Also, sausage A had significantly lower ($P < 0.05$) score for odor and taste than sausage B and C. This seems to indicate that fat

reduction and cottage -cheese addition had improved the odor and taste of the sausage.

Based on the obtained results it can be seen that the lowest score of all tested sensory properties have control sausages A (3.17) manufactured by standard recipe. The highest scores for sensory characteristics of the sausages have reduced–fat sausages from group C (4.27) produced with 15 % of cottage-cheese.

From the evaluation and results of sausages, we think that the obtained average scores are very good, especially at the reduced–fat sausages with 10 and 15 % cottage -cheese. Similar results for this type of meat products were reported by several authors (7-9).

CONCLUSION

Results from the investigation show that the cooked sausages derived from pork and beef meat , fat tissues of pigs and addition of 10% and 15% cottage –cheese have appropriate chemical composition which agreement within the standard defined by Macedonian legislation.

Sensory quality of reduced–fat sausage with added cottage-cheese was significantly better than of control. Cottage-cheese in amount up to 15% improved the odor and taste of the sausage and does not affect negative to color.

Favorable composition and the presence of cottage-cheese made this type of sausage quality foods with high biological values, with significant potential to positively impact on human health.

REFERENCES

1. Babić S.: Aditivi u proizvodima od mesa i njihov uticaj na konzumente, Institut za higijenu i tehnologiju mesa, Beograd, (2008),(1-2, 45-46)
2. Busboom R. J. and F. A. Ray: Homemade Meat, Poultry and Game Sausages. Washintong State University, (2003)
3. Macedonian Regulations, Quality requirements for meat products, Official Gazette of the R.M (2013) (in Macedonia)
4. Cáceres, E., García, M.L., Toro, J., Selgas, M.D: The effect of fructo-oligosaccharides on the sensory characteristics of cooked sausages. Meat Sci. (2004),68 p: 87-96
5. Radovanoviš, R., Popov-Raljic, J.: Sensory analysis of food, Faculty of Agronomy, Belgrade-Zemun Serbia, Faculty of Technology, Novi Sad, Serbia (2001) p.331

6. Sutton, D.S., Hand, L.W. and Newkirk, K.A.: Reduced fat, high moisture beef frank-furters as affected by chopping temperature. J. Food Sci. 60 (1995) 580-582
7. Selgas D. M., Caceres E., Garcija L. M.: Long-chain soluble dietary fiber as functional ingredient in cooked meat sausages. Food Science and Technology International, (2005), 11 (1), 41-47
8. Savić I., Milosavljević Z.: Higiena I tehnologije mesa. Privredni pregled, 1983. Beograd
9. Varman H. A. and Sutherland R. J. Meat and meat products. Tehnology, Chemistry and Microbiology, Chapman & Hall, London, (1995), 314-354
10. Vukovic I.: Osnove tehnologije mesa. Univerzitet u Beogradu, Fakultet veterinarske medicine, Beograd, (1998)

637.12’62.07

CHANGES IN CHEMICAL COMPOSITION AND SOMATIC CELL COUNT IN BOVINE MILK DURING COLOSTRUM PERIOD[16]

Trajkovska Biljana, MSc
Kochoski Ljupche, PhD
Makarijoski Borche, MSc
University st. "Kliment Ohridski" - Bitola, Faculty of biotechnical sciences – Bitola
e-mail: bile.petkovska@yahoo.com

Abstract

The aim of the paper was to evaluate the bovine colostrum quality and changes in composition during the first five days postpartum. Researches were carried out on a dairy farm with Holstein –Friesian heifer and multiparous cows. Samples of colostrum milk were collected at 1, 6, 12, 24, 48, 72, 96 and 120 hours postpartum. Samples were analyzed for chemical composition using an infrared spectrometer (fat, protein, lactose and dry matter), and for somatic cell count using a fluoro-optic-electronic method.

In the first colostrum the concentrations of milk fat, protein and dry matter were high (7.07%, 20.86% and 30.19% respectively) with significant reducing after 12 hours postpartum. Lactose concentration was low at the beginning (1.23%) and increased slowly until the fifth day postpartum to 3.76%. Somatic cell count was high in the first milking (1,163,330 cells/ml) and decreased after that.

Key words: colostrum, chemical composition, somatic cell count, Holstein – Friesian, cow

Introduction

Colostrum is the secretion of the mammary gland produced immediately after parturition and is vital food for the newborn of all mammals within the

[16] original scientific paper

first 5-7 days (Gerogiev P.I., 2008; Abd El –Fattah et al., 2012) or in a period of 6-10 days after parturition (Kochoski Lj., 2011). Colostrum differs greatly in composition of mature milk and meets the nutritional requirements of the newborn (Ontsouka et. al, 2003).

Bovine colostrum contains higher amounts of fats, proteins and peptides, fat soluble vitamins, and various enzymes, hormones, growth factors, cytokines, minerals and nucleotides than mature milk, and except for lactose, the levels of these compounds rapidly decrease during the first three days of lactation to those typical to mature milk (Blum J.W, Hammon H., 2000). This is the first food for neonates after the parturition that provides them with all necessary nutrients (Gerogiev P.I., 2008).

Breed, age, nutrition, and health status of the cow are well known to influence milk composition (Ontsouka et. al, 2003). Also, management practices could have an important influence on colostrum quality, and herd size influences the colostrum management and quality at the farm level (Kehoe et. al., 2007)

Milk constituents change during milking of colostrum, which need to be considered if milk samples are taken for analysis and to evaluate the health of the udder (Ontsouka et. al, 2003).

Material and methods

The objectives of this study were to evaluate the colostrum quality and changes during the first five days of lactation in Holstein –Friesian cows. Researches were carried out on Holstein –Friesian multiparlous cows during the summer. Samples of colostrum milk were collected immediately after calving after 1, 6, 12, 24, 48, 72, 96 and 120 hours after parturition, by hand milking. Milk was placed in sterile pots and carried at the laboratory at refrigeration temperature. Samples were immediately analyzed for chemical composition and somatic cell count.

The analysis of the chemical composition of the milk means determining milk fat content, proteins, lactose and dry matter using infrared analyzer Milkoscan in accordance with the IDF 141C:2000 standard.

The cell count was determined with Fossomatic 5000 and milk-enumeration of somatic cell was done according to ISO 13366/2:2006

standard. The working principle of Fossomatic 5000 consists of staining and electronic counting of somatic cells.

Results and discussion

The results in Table 1 show that the average milk fat is 6.04 (min. 4.66 up to max.7.07), proteins 10.24 (min.3.70 up to max.20.86), lactose 2.84 (min. 1.23 up to max.3.95), total dry matter 19.99 (min. 13.12 up to max.30.19) and somatic cell count 767.90 (min. 299.50 up to max.1163.33).

Table 1: Composition of bovine colostrum during the first five days after calving

	Milk fat %	**Proteins %**	**Lactose %**	**Dry matter %**	**SCC/ml x 1000**
after calving	7.07	20.86	1.23	30.19	1163.33
1h	6.87	20.00	1.44	29.33	733.38
6h	6.93	17.40	1.81	27.15	963.10
12h	5.49	13.69	2.37	21.28	504.33
24h	5.48	8.20	3.00	17.71	1054.92
48h	5.73	5.08	3.65	15.44	511.18
72h	5.52	4.07	3.66	14.25	1022.25
96h	6.38	3.86	3.95	15.15	299.50
120h	4.66	3.70	3.76	13.12	661.00
x	6.04	10.24	2.84	19.99	767.90
min	4.66	3.70	1.23	13.12	299.50
max	7.07	20.86	3.95	30.19	1163.33

The greatest percentage of milk fat, protein, total dry matter and somatic cells were detected immediately after partus (7.07%, 20.86%, 30.19% respectively), after that they fall significantly, while the lactose have opposite results it is lowest after partus (23.1%) and then gradually increased (3.76%). This is in accordance with (Abd El Fattah et al., 2012) where concentrations of total dry matter, protein and fat after partus was 24.19%, 13.45% and 8.04% respectively, while the quantities of lactose was 1.89% with its increase until the fifth day after parturition. While the results from

Kehoe S.I., et al., (2007) indicate the following average concentrations of fat protein and lactose in colostrum 6.7%, 14.9% и 2.5% respectively. Low values of lactose match the physiology of the newborn calf, where lactose is found in low concentrations, and gradually increases (Kehoe S.I., et al., 2007). The high lipid content of colostrums allows the newborn calf to rapidly gain strength (Fisher H., 2000).

Protein and total dry matter are highly correlated (r=0,99) also positively correlated fat and proteins (r=0.75), and positively correlated fat and total dry matter (r=0.82). Protein was highly correlated negatively with lactose (r=-0.99), and also highly negatively correlated fat and lactose (r=-0.72). Among other parameters correlative dependence is very small.

Compared to milk, colostrum contains higher levels of proteins (Gerogiev, P.I., 2008), − lactalbumins, lactoglobulins and especially immunoglobulins (Ig), peptides, hormones, growth factors, prostaglandins, enzymes, cytokines, acute-phase proteins, nucleotides, polyamines, minerals, vitamins etc., and therefore the greatest changes have been in proteins which are heights after parturation (20.86%) and after the first day postpartum they starting decreased (8.20%), on the third day was 4.07%, while on the fifth day was 3.70%. The most consistent changes occur in milk protein content that is reduced more than twice by the 3rd post partum day compared to initial values (Ontsouka et al., 2003). This is mostly due to the sharp decrease in Ig fractions, whose concentration, was the highest in the first colostrum portions

Parity. stage of lactation and the month of calving were all associated with SCC. (O'Brien B., 2009). Mean percentage of somatic cell count after partus was 1163.33/ml x 1000, and decreased after that and on the fifth day after parturition the mean percentage was 661.00/ml x 1000. Elevated SCC may occur in milk in late gestation and for a few weeks following calving, regardless of infection status (Duane N.R, Bodman R.G., 1993). This SCC elevation appears to be part of a cow's natural immune system response in preparation for calving, to enhance the mammary gland defense mechanisms at this critical parturition time. Quarters with no infections generally have a rapid decline in SCC within a few weeks postpartum. Also the existence of intramammary infection (mastitis) is a real risk that colostrum may contain high amounts of somatic cells (Quigley J., 2010).

The researchers Ferdowski Nia et al., (2009), assume that very high counts of SCC were indicative of mastitis in the cows even in colostrum. In

our research there was only one mastitis cow which was treated promptly with antibiotics. The high SCC could have been caused by a stress situation during cows' birth, as a consequence of increased susceptibility to the udder infection, especially with the animals whose birth was difficult, even in situations with no particular risk (Sgoiforossi *et al*., 2009). Secretion of colostrum is responsible for very high levels of somatic cells and immunoglobulins in milk for only the first 5-7 days after calving. Beyond this point, high SCC is due to intramammary infections (Fisher H., 2000).

The health of calves may be affected by the quality of colostrum. It's possible that cows with mastitis may produce colostrum containing pathogens which may cause scours in newborn calves (Quigley J., 2010). Increased colostral SCC may affect the highly sensitive and neonate small intestine, by depressing nutrient assimilation and causing diarrhea (Ferdowsi N., et al 2009).

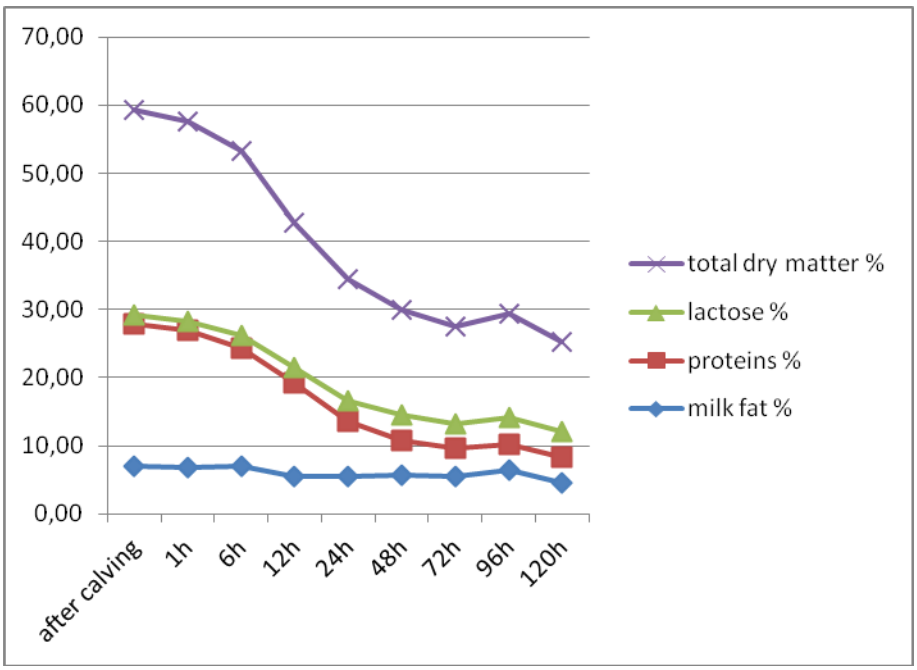


Figure 1: Fat, protein, lactose and total dry matter content evolution during the first five days after calving

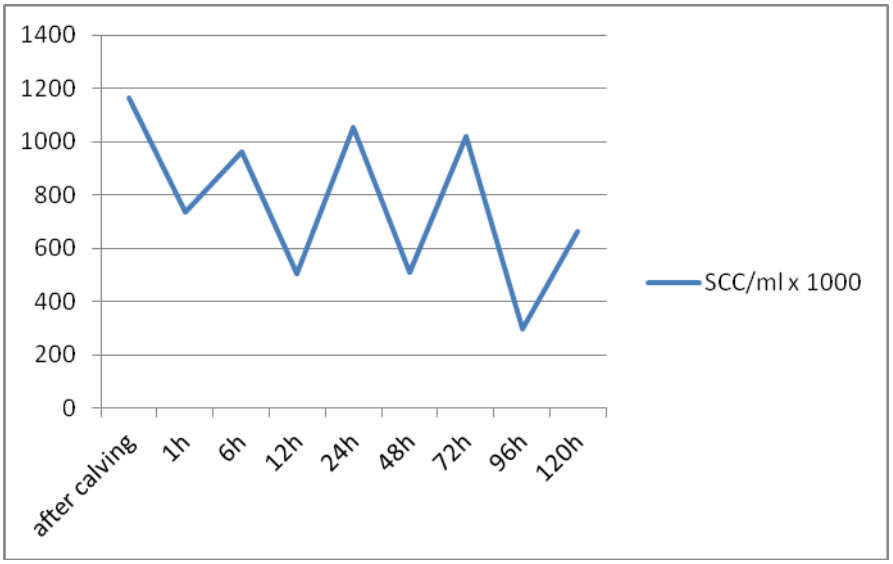


Figure 2: Somatic cell count (SCC/ml x 1000) evolution in milk during the first five days after calving

Conclusion

Results showed significant changes in colostrums composition from the first milking right after calving until fifth day postpartum. In the first colostrums the concentration of milk fat, protein and dry matter were high (7.07%, 20.86% and 30.19% respectively) and were almost half in the second milking, after hours. Lactose concentration was low at the beginning (1.23%) and increased slowly until the fifth day postpartum (3.76%). SCC were high in the first milking (1,163,330 cells/ml) and decreased after that. SCC continually oscillates due to the physiological condition of the cows. Protein and total dry matter are highly correlated (r=0,99) also positively correlated fat and proteins (r=0.75), and positively correlated fat and total dry matter (r=0.82). Protein was highly correlated negatively with lactose (r=-0.99), and also highly negatively correlated fat and lactose (r=-0.72). Among other parameters correlative dependence is very small.

References

1. Abd El Fattah et al., *Changesin composition of colostrums of Egyptian buffaloes and Holstein cows*, Veterinary research, 2012
2. Duane N.R, Bodman R.G., *The somatic cell count and milk quality*, University of Nebraska-Lincoln, 1993
3. Ferdowsi Nia, E., G. R. Ghorbani, H. R. Rahmani, M. Alikhani, M. Mohammad Alipour and A. Nikkhah, *Increased colostral somatic cell counts reduce pre-weaning calf immunity, health and growth*, Journal of Animal Physiology & Animal Nutrition. 94:628-634, 2009
4. Fisher H., Colostrum: *Properties, Functions, and Importance The Relationship Between the Immunoglobulin Concentration in Holstein Colostrum and the Total Senlm Protein in Holstein Heifer Calves*. Washington State University Libraries, 2000
5. Georgiev, I.P. , *Differences in chemical composition between cow colostrum and milk*, Bulg. J. Vet. Med., 11, No 1, 3−12, 2008
6. J.W. Blum , H. Hammon, *Colostrum effects on the gastrointestinal tract, and on nutritional, endocrine and metabolic parameters in neonatal Calves,* Livestock Production Science 66 pp 151–159, 2000
7. Kehoe S.I., et al., *A survey of bovine colostrums composition and colostrums management*, J.Dairy Sci, 2007
8. Kochoski Lj., *Hygiene, control and monitoring of animal product*, University st. Kliment Ohridski, Faculty of biotechnical sciences, Bitola, 2011
9. O'Brien, Donagh P. Berry, P. Kelly, William J. Meaney and Eddie, *A study of the somatic cell count (SCC) of Irish milk from herd management and environmental perspectives*, Bernadette J. O'Callaghan, Moorepark Dairy Production Research Centre, Fermoy, Co.Cork, 2009
10. Ontsouka, C. E., R. M. Bruckmaier & J. W. Blum, Fractionized *Milk Composition During Removal of Colostrum and Mature Milk*, Journal of Dairy Science Volume 86, Issue 6 , pp 2005-2011, 2003
11.

664.641.12(497.7)

EFFECT OF MILLING TO ZN AND FE CONTENT OF SOFT WHEAT FLOUR FROM MACEDONIA[17]

M. Menkinoska[1], I. Gorgoski [2], V. Pavlova[1], S. Manasievska-Simic[3], V. Stamatovska[1], T. Blazevska[1]
Faculty of Technology and Technical Sciences - Veles. University "St. Kliment Ohridski" - Bitola[1], R. Macedonia
Institute of Biology. Faculty of Natural Sciences and Mathematics, University "Ss. Cyril and Methodius"in Skopje [2], R. Macedonia
Faculty of Agricultural Sciences and Food, University "Ss. Cyril and Methodius"in Skopje[3], R. Macedonia
e-mail:**marija_menkinoska@yahoo.co.uk**

Abstract

Wheat is one of the major cereals which are processed by milling into flour. The aim of this research is to examine the degree (percentage) of milling will affect the concentration of Fe and Zn in obtained flour of two soft wheat varieties (Triticum aestivum). Analyses were performed by flame atomic absorption spectroscopy. Ascertained higher concentrations of Fe and Zn were found in seeds of two wheat varieties "treska" Fe -44(mg / kg) and Zn-29 (mg/kg) and "radica" Fe - 47 (mg/kg), Zn -19 (mg/kg) compared with concentrations in their flour, the "treska" Fe -10.5 (mg/kg) and Zn-9.8 (mg/kg) and "radica" Fe – 10.3 (mg/kg), Zn -9.2 (mg/kg).
We can conclude that the process of milling the wheat grain by reducing the percentage of milling leads to a loss of important micronutrients and acquire flour with lower nutritional value.

Keywords: treska, radica, wheat, Fe, Zn, milling

[17] original scientific paper

INTRODUCTION

Although a small country, the Republic of Macedonia is in abundance of a great variety in relation to both the herbs (vegetation) kinds and the agricultural cultures. The climatic characteristics of the Republic of Macedonia range the wheat cultures as daily present in the people` life and on their dining table in most heterogeneous products.The impact of this group of culture on the nutrition is global one while the modernization of the nutrition-related way is imaginable without them. (1)

Any type of a food, regardless of whether or not it is obtained from vegetative or animal sources, is rarely suitable for a direct consumption and therefore an additional processing is needed. Throughout centuries, different methods for food processing were developed with a view to making the final product more attractive according to its taste, appearance, steadiness and longevity. (2)

The wheat like vegetation as a basic food for the man is only little used as a grain but it is processed through milling into the mill products: flour, groats, snowflakes, junk foods / bran (trici) and so on. While milling, different parts are separated from the grain while the final product - the flour, is the milted core of the grain with a smaller or bigger portion of the other structural parts of the very grain. Since the contents of the wheat grain is being changed in quantitative and quality senses moving from the middle towards the periphery depending on the degree of the grain-related usage, flours of different chemical contents, bakery characteristics and different nutritious value may be obtained..(3),(4)

To a certain degree, the wheat grain`s basic ingredients also pass into the flour. The variations in relation to the quantities of substances in the flour does not depend only on the milled wheat-related traits and composition but also on the very way of milling, that is the percentage of milling. By increasing of the wheat milling there is also an increase of the ashes-related contents, the proteins, the fats and the plant fibers, while the starch`s contents is being decreased.(3)

The wheat` s form and texture (both depend on the type) as well as the milling-related technical conditions have also a great impact in determining the degree of loss of minerals. Nevertheless, even when these variables would be fixed ones, the distributions of minerals in different fractions of milling would depend ultimately on the uneven distribution within the grain`s core. There is a little data on the milling`s effect on the mineral contents in a soft wheat. This information is needed for the purposes of assessing the impact of the loss of minerals in the people` nutrition as a consequence of the conventional methods of milling with a view to ensuring

basic data necessary for determining the need of fortification, bio-fortification or any other method for completion, as well as at what level of the lost microelements in the flour.(5) This research was conducted with a view to determine the effect of conventional milling over the iron and zinc in two types of soft wheat.

MATERIALS AND METHODS

Two samples of soft wheat were used as material for examination (*Triticum aestivum*). The examinations were conducted on samples taken from a pre-basic seed from the breed "*Treska*" and C2 breed "*Radika*" produced во 2011/2012 in different parts of Macedonia.

METHOD

The examinations were conducted in the Laboratory of Chemistry Institute of the Natural-Mathematics Faculty within the University "*St. Cyril and Methodious*".
The determination of zinc and iron in both the grain and the flour was conducted by means of blazing atomic absorbent spectrometer type *Termo*. The examined sample is prepared for an analysis with the moist mineralization. During this procedure a destruction and removal of organic substances from the food are being made, so that only the mineral substances remain in the mixture. 0,5g. homogenized sample of the wheat (flour) is being placed in teflon bowl in which 7 ml. concentrated HNO_3 and 2 ml. H_2O_2 is added; this is then being left one night following which it is warmed up. The warming up lasts several hours at a low temperature until the organic substances disappear completely and a clear mixture is obtained. It is then filtered and removed into a flask, in which a distilled water is added in volume up to 25 ml. The absorbency is being noted on the prepared mixture through the previously calibrated atomic absorbent spectrometer.
The contents of proteins, ashes as well as the wheat milling are produced in the Laboratory of the Factory "*Zito Luks*" A.D. Skopje.
The proteins were analyzed by means of the *Kjedalh method*. The quantity of ashes was determined through a gravimetric method.
The wheat`s hectoliter mass was measured by a Shoper scale.
The wheat milling was done by a laboratory mill from the company BRABENDER.
The computer program *Microsoft Excel 2007* was used for statistical analysis of the data.

RESULTS AND DISCUSSION

The contents and distribution of biogenic elements in the wheat`s grain was a subject of examination by several authors, especially during the last 30 years. Most data are found in relation to the contents of inc, phosphor and potassium since these three elements most frequently limit есто го ограничуваат both the yield and the quality of grain. In more recent time, more attention is being paid on both the microelements and hard metals in the grain, taking into account the increasing actuality in relation to their harmful impact on the organisms because of their anthropogenic accumulation in the biosphere.(6)

The conventional agricultural methods are more focused on the usage of chemical fertilizers with microelements while the importance of the zinc, iron, manganese and others is neglected. Consequently, there is decrease of the wheat`s quality and an occurrence of micro-nutritive lacks in the cultures.(7). The increase of the concentration of *Zn* and *Fe* in the plants is resulting in improvement of the wheat`s quality and thus also improvement of the people` health (8).

Table 1 shows the results of our examinations.

Table 1.Contents of zinc. iron, proteins ,ashes, hectoliter mass and the mass of 1000 grains in two breeds of wheat.

	Wheat Radika	*White flour Radika*	*Wheat Treska*	*White flour Treska*
Fe (mg/kg)	47	10,3	44	10,5
Zn (mg/kg)	19	9,2	29	9,8
ash %	1,83	0,48	1,62	0,45
protein	10,9		12,1	
mass of 1000 grains(g)	32,6		35,2	
hectoliters (kg/hL)	70,5		75,5	

The contents of iron in the dry substance with the plants ranges from 50 to 1000 mg/kg (7) and it is mostly found in the leaf , then in the trunk and at least in the grain (the fruit). The lack of iron may appear at a high doze of phosphoric fertilizers.

The concentration of iron with the wheat from the breed "*Radika*" cultivated in Probishtip is 47 mg/kg, while with the wheat from the breed "*Treska*" cultivated in Skopje is 44 mg/kg.

The contents of zinc in the dry substance of the plants most frequently varies from 20 to 100 mg/kg, and under that it is a critical value. (6)
The quantity of zinc in our researches with the grain of "*Radika*" is 19 mg/kg while with the wheat of the breed "*Treska*" it is 29 mg/kg. From the bellow results as presented in Table 1 and graphic 1 one may observe that there are not great variations in relation to the concentration of iron in the aforesaid two breeds of wheat. However, the difference in the contents of zinc is significant breed "*Radika"* has 10 mg/kg less zinc as compared to the breed "*Treska*". This difference may be a result of a number factors such as weather conditions, the breed`s quality, the used agricultural measures, the soil type, etc. .
From the consulted literature we found data provided by the Macedonian researchers who have determined the impact of a certain concentration macro (*N,P,K*) and microelements (*Cu* and *Co*) in the fertilizer over the concentration of hard metals in the wheat`s grain, of the breed "Radika", that is, that part which is used in the people`s nutrition. Their two years lasting research shown that the zinc`s contents in the grain of the breed "Radika" cultivated under conditions of "Ovche Pole" on the soil type poorly carbonate varies within the limits from 22 to 38 mg/kg, while the concentration of iron is 50-98 mg/kg. All examined hard metals are placed within the limits of the normal values as mentioned in the literature on the wheat.(6)
Although the values from our examinations on the zinc and iron are close to the ones established by the abovementioned Macedonian researchers , they are nevertheless under the limits of normal values as mentioned in the literature on the both breeds of wheat.
The refining of wheat products leads to losing of important minerals and fibers and it may have significant consequences for the people` health, that is, it may generate a cancer of the colon, diabetes mellitus and heart difficulties. The lack of zinc is mentioned as one of the key risk factors for the people` health and as one of the reasons for the death at a global level. According the report of the World Health Organization – WHO (2002) related to factors responsible for developing diseases, the lack of *Zn* is ranged on the 11^{th} place among the twenty most important factors in the world and on the 5^{th} place from among the most important factors in the underdeveloped countries..
Also, two billions people, that is more than 30% of the world population are anemic which is due to the lack of iron .(10) The biggest part of *Zn* in the wheat is located in the embryo and the aleura-related aleurone layer 150 $mg.kg^{-1}$ while *Zn*`s concentration in the endosperm is much less, that is, 15 mg/kg.(11).

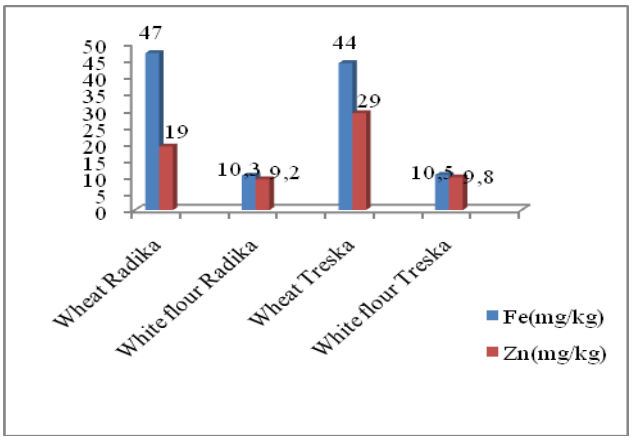


Fig. 1. Effect of Milling on the level of Trace metals.

The parts being rich with zinc are removed during the milling process, and it results in decreasing of its (Zn) in the flour. Also, if the wheat contains about 33 mg/kg iron before the milling process, this quantity is decreased to 11 mg/kg after the very milling.

From the results as shown in Table 1 and from the graphic overview, one may note that the milling process has significantly decreased the concentration of the examined elements, with losses ranging from 52,6 % for a zinc and 78,7 % for an iron with the wheat of "Радика" breed and 65,5 % for zinc and 77,3 % iron with the wheat of "*Treska*" breed.

From the reviewed literature we found data related to the effects of both the milling process and the cooking of dough-products produced from a hard wheat over the levels of eight minerals, namely, Ca,Cu,Fe,Mg,P,K,Se and Zn. It is established that the milling leads to a change of the contents of six minerals which initially were present in the hard wheat`s grain.The Selenium had the highest degree of keeping the concentration in groats equal to 77% - 85% from which was in the wheat (dry mass), as accompanied by calcium (54% -60%), copper (49% -53%), potassium and phosphor (42%-47%), iron (36%-38%), magnesium and zinc (32% -36%).

Unlike the milling, the cooking process has generated small insignificant loses of the examined elements, except for the calcium and the potassium.(2)

The results from the research of Jawad I. at al. show that both processes of milling have significant effects over the concentration of the micronutrients.The milling process significantly decreases the level of metals in tracks depending on both the type and the form of the very processing. It is ascertained a significant increase of the level of Cu and Mn

while the bread production which may due to different sources of these metals such as water, soul and other additives which are usually added while the bread production. The increase of the level of Cu and Pb nay be due to both the equipment and the tools being used in the bakeries.(12)
The study of *Wo Ÿniak A. at.all*. confirms that the fertilization with nitrogen has an impact over the concentration of *Fe* and *Zn* in the grain. Their research shown that the application of N with a doze of 90 kg/h significantly increases the contents of Ca,K, Fe and Zn in the wheat in comparison with a doze of 150 kg/h N(13).

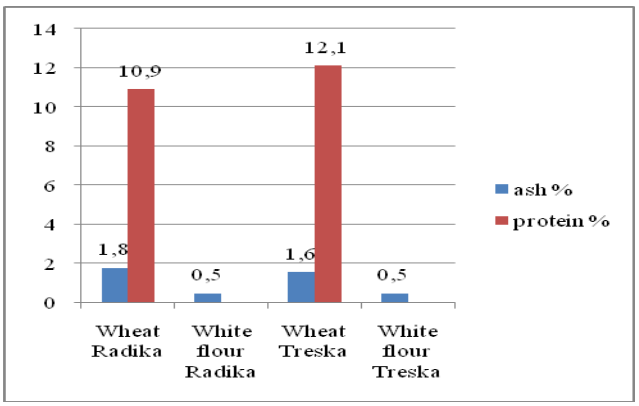


Fig. 2. Protein and ash contents in two varieties of wheat

The contents of mineral substances indirectly shows the relationship of anatomic parts of grain in the flour, they are mostly located in the aleurone layer, while little less in the endosperm, so that the flour which would contain more from of external parts of grain, will contain more ashes.
The wheat flours from mineral substances contain mostly phosphor and calcium, then magnesium chlorine and potassium. The remaining elements are represented in micro-quantities (4). According to the rule book on quality, the wheat flour is characterized in 3 types: type 400, type 500 and type 850. According to the regulations in the Republic of Macedonia, the flour of type 400 should have a relative moistness up to 14%, ash from 0,50 to 0,55%, proteins minimum 12,5% and moist gluten minimum 30%.(14)
In the light of the results we obtained in our study in relation to the contents of ash in the flour (graphic 2) compared with the mentioned regulations, we may characterize the produced flour as a type 500.It also contains periphery parts, which gives to it a little dark color, increased contents of mineral substances, proteins, fats and vitamins while decreasing the starch which

makes it nutritive-ly more favorable from the flour type 400 with a degree of milling at the most to 40-45%.

It may also note from the graphic 2 that the contents of ashes in grain from the breed "*Radika*" is higher for 10.4 % than the one from the breed "*Treska*". Despite that, the concentration of zinc in the flour from "*Radika*" is less in comparison with "*Treska*".

According to *Araus et al.* the variation and the negative relationships of ashes with the yield and other parameters may be due to the fact that the ash is higher with those genotypes which are more affected by drought during the wheat ripening (15).

One of the other important component for the wheat quality is the percentage of proteins. The contents of proteins as measured by the *Kjeldahl*-method has shown that there is a higher level of proteins in the breed "Treska" 12,1% as compared with the breed "Radika" 10,9%. In general, the proteins which are contained in the wheat vary between 8% and 17%, depending on both the genetic characteristics and the external factors connected with the culture-related cultivation.

The mass of 1.000 grains depends on the very grain`s size, its fulfillment and health situation. That`s why the mass of 1.000 grains constitutes an indicator of the seed`s size. The seed with bigger mass has usually a more developed "*embryo*" and provides better developed and more resistant plants in the early stages of the development.(16)

The mass of 1.000 grains in our examinations is 32,6g for the breed "Radika" and 35,24 g for the breed "Treska".

Hectoliter mass means a mass of one hectoliter of wheat as expressed in kilos. The high hectoliter mass indicates small and round grains with a soft surface, compact endosperm and small mass of moistness, while a low hectoliter mass are given by the big and long grains with uneven surface and bigger contents of moistness. According to the rule book.on the minimal conditions for quality, traits and classification of the wheat and the rice, the hectoliter mass of the wheat designed for production of flour should beat least 67 kg/hl.(17). Our results on the hectoliter mass of the both breeds of wheat (Table 1) are within the limits of the normal values as mentioned in the aforesaid rule book.

CONCLUSION

On the basis of the conducted examinations of the contents of zinc and iron in the grain and flour of the wheat type "*Radika*" and "*Treska*" , the following conclusions may be adopted:

- the milling process leads to a significant decrease of the concentration of the examined microelements which are of essential importance in the people` nutrition;
-from among all of the examined parameters, it was established that the breed "*Treska*" is more qualitative in relation to the breed "*Radika*" since there is a bigger concentration of zinc and iron in the flour, a higher hectoliter mass and it contains more proteins;
Because of the abovementioned, our future researches will be aimed at completing the micronutrients with bio-fortification of the same two breeds of wheat since, although the fortification is efficient approach for the many of the underdeveloped countries, it still seems that that it is expensive and (because of it) it is hardly accessible.
As alternative economically justified solution is the agricultural bio-fortification by means of which there will be an increase of the productivity and the concentration of micronutrients in the wheat, and this would contribute to improving the people` health.

LITERATURE

1. *Zdrava hrana – moznosti za iskoristuvanje na potencijalot na paletata raznovidni kulturi vo R.Makedonija*
http://agrojugozapadmak.com/files/zdrava
2.Y.G.Deosthale *The nutritive value of foods and the significance of some household processes* National Institute of Nutrition, Hyderabad, India
3. Kalugerski G.,Kalugerski S.,Tosic (2006). *Ptrehranbena tehnologija*, Zavod za uzdbenike i nastavna sredstva,Beograd;
4.Žeželj M. (2005). *Tehnologija žita i brašna: prerada brašna*, NIP Glas javnosti doo, Beograd
5.Cubadda F., Aureli F., Raggi A., Carcea M. (2009) *Effect of milling, pasta making and cooking on minerals in durum wheat* Journal of Cereal Science 49 92–97
6.Petkovski D.,Melovski L.,Petkovska R.,(1997) *Sodrzina na nekoj teski metali vo zrnoto na pcenica odgleduvana na Cernozem vo ovce pole* Ekol. Zašt. Život. Sred. Vol.5 No1. pp(35- 40).
7. Ryan E. Nuffield Scholar March (2010) *Nuffield Australia Project No 0911 Trace Element Nutrition* Revitalising Health and Agriculture
8. Habib Maralian (2008) *Effect of foliar application of Zn and Fe on wheat yield and quality* African Journal of Biotechnology Vol. 8 (24), pp. 6795-6798
9. Kastori, R. (1993). Fiziologija bilja, IV izdanje. IP "Nauka", Beogra

10. World Health Organization (WHO) (2002). *The World Health Report 2002 Geneva*: WHO
11. Ozturk L, Yazici MA at.al.((2006*) Concentration and localization of zinc during seed development and germination in wheat.* Physiol Plant 128:144–152
12. Jawad I.and Sadia H.Allafaji (2012) *The levels of Trace Metals Contaminants in Wheat Grains, Flours and Breads in Iraq* Australian Journal of Basic and Applied Sciences, 6(10): 88-92, 2012 ISSN 1991-8178
13. WoŸniak A, Makarski (2013) *Content of minerals, total protein and wet gluten in grain of spring wheat depending on cropping systems* B. J. Elem. s. 297–305 DOI: 10.5601/jelem
14.*Pravilnik za kvalitet na pcenicno brasno(2012)*(Sl. Vesnik na R. Makedonija,br.175/11)
15.Araus JL, Amaro T, Casadesus J, Asbati A, Nachit MN. (1998) *Relationship between ash content, carbon isotope discrimination and yield in drain wheat.* Aust J Agric Res.;25(6):835– 843
16. Ilieva V.,Mitrev S.,Karov I.Markova N.,Todorovska (2011) *Varijabilnost na nekoi kvalitetni svojstva na semeto kaj pcenicata* Godisen zbornik UDK: 633.11-153.1.02
17. *Pravilnik za minimalnite uslovi za kvalitet,svojstva i klasiranje na zitata i orizot (2011)* (Sl.Vesnik na R.M.,br.104 str.2

582.998.16:547.458.88

CHARACTERIZATION OF PECTINS ISOLATED FROM STEMS OF *HELIANTHUS TUBEROSUS L.*[18]

V Stamatovska[1], N. Delchev[2], G. Nakov[3]
Faculty of Technology and Technical Sciences
Petre Prlickov 42, 1400 Veles, Republic of Macedonia
"St. Kliment Ohridski" University, 7000 Bitola[1]
Department of Analytical Chemistry, Technological Faculty,
University of Food Technologies – Plovdiv, Bulgaria[2]
Eng.Technologist, Veles, Macedonia[3]
e-mail:**vikistam2@gmail.com**

Abstract

The pectin content in the stems of Jerusalem artichoke (*Helianthus Tuberosus L.*) was studied. Extraction of the polysaccharide was carried out and their physico-chemical characteristics were determined (degree of esterification, acetyl content, molecular weight, viscosity, etc.). The monosaccharide composition of the isolated pectins was analysed and the presence of 7 neutral sugars (L-rhamnose, D-glucose, D-fructose, D-mannose, D-galactose, D-xylose and L-arabinose) was confirmed.

Keywords: Jerusalem artichoke, pectins, physico-chemical characteristics

INTRODUCTION

Pectins are heteropolysaccharides which are widespread in nature. They can be found in the fruits- cell juice, roots and stems of many plants [1,2]. Main sources of pectin yield are some waste fruit

[18] original scientific paper

materials such as pressed apples, citrus fruit peels, sunflower head residues, sugarfree beet slices, etc. [3,4].

Pectin as a vital ingredient has been used in food industry for a long time due to its functional properties (gelling, thickening, emulsifying, foaming, etc.) [5,6].

In recent years there has been a growing interest in the study of the polysaccharide composition of different unconventional plant sources [1,7]. Previously a characterization of the polyuronide content (PUC) of several types of Jerusalem artichoke growing in Bulgaria was carried out [8]. It was established that all parts of the plant (blossoms, leaves, stems, tubers) contain pectins but the greatest amount was found in the tubers (13.5 %) and the stems (12.4 %).

It was also noticed [9] hat flour made out of Jerusalem artichoke stems shows sorption properties toward some heavy metals which is probably due to the presence of pectin.

The main objective of this paper is to analyse in detail the pectins in stems of Jerusalem artichoke and to give their physical and chemical characterization.

MATERIALS AND METHODS

1. Raw materials

Stems of Jerusalem artichoke were gathered for the purpose of this paper. The stems were picked up during the blossoming season (the beginning of October, 2012) from three different regions in Bulgaria – the Stara Zagora region, near the town of Stara Zagora (sample 1), the Plovdiv region, near the town of Parvomai (sample 2) and the Vidin region, near the town of Vidin (sample 3).

All reagents used for the analyses are classified p.a. (lat. Pro Analysi p.a.).

2. Pectins characterization

The polyuronide content was determined by the method proposed by Mc Cready [8] as follows:

The raw material was ground in advance. Then 100 mL 5 % solution of HCl in ethanol (70 %) was added to 10 g of the ground material and the mixture was stirred for 1 hour with an electromagnetic stirrer. Next the mixture was filtered through a Büchner funnel and washed in turns with ethanol (70 % - to a neutral reaction) and ethanol (96 %). Finally it was dried at 50 °C.

2.2. Determination of the polyuronide content (PUC)

2 g NaCl and 150 mL distilled water were added to 2 g of the washed material. The mixture was stirred for 2 hours with an electromagnetic stirrer and then 50 mL distilled water was added to it. Two check samples were also prepared. 4-5 drops of Hinton reagent were added to each of the samples and they were titrated with 0.1 M NaOH. Then 40 mL 0.1 M NaOH were added to the samples and they were left undisturbed for 2 hours. Finally 50 mL 0.05 M H_2SO_4 were added to the samples. The rest of the acid was titrated with 0.1 M NaOH.

The PUC (%) of the washed material is calculated with the following formula:

$$PUC = \frac{(V_1 \cdot F \cdot 0.01761) + (V_2 \cdot F \cdot 0.01901)}{m} \cdot 100\%$$

where

V_1 – the NaOH volume used in the first titration, (mL);

V_2 – the NaOH volume used in the second titration, (mL);

F – factor of NaOH;

0.01761 - the amount of the non-esterified galacturonic acid residue which corresponds to 1 mL 0.1 M NaOH (g);

0.01901 – the amount of the esterified galacturonic acid residue which corresponds to 1 mL 0.1 M NaOH (g);

m- sample weight, (g).

The following formula was used to determine the degree of esterification (DE, %):

$$DE = \frac{V_2 \cdot F}{V_1 \cdot F + V_2 \cdot F} \cdot 100\%$$

3. Pectins extraction

The extraction is made with ammonium oxalate, because previous findings related to the isolation of pectinc from stems of Jerusalem artichoke using different solvents (hydrochloric acid, nitric acid, oxalic acid, ammonium oxalate) determined that the greatest yields are obtained within ammonium oxalate extraction [10].

100 g of the washed material was covered with 2000 cm^3 of distilled water (85-90 °C) containing 18.8 g (0.075 mol/L) ammonium oxalate. The mixture was extracted by being periodically stirred for 45 min. at 85 °C. It was filtered while hot, the volume of the extracted filtrate was measured and it was cooled at room temperature. Then 20 mL concentrated HCl and 20 mL ethanol (90 %) were added to the filtrate. It was stirred well and left undisturbed for 2 hours. The obtained coagulating agent was filtered, repeatedly washed with ethanol (70 %) to the lack of chloride ions, then washed twice with ethanol (96 %) and dried at 40 °C to a constant weight.

The degree of extraction (R) of the polysaccharide (%) was determined by the formula:

$$R = \frac{A \cdot 100}{N}$$

where A - the amount of the extracted pectin (%)
N - the initial content of the polysaccharide in the raw material (%).

4. Determination of the degree of esterification and purity of pectin isolated from stems of Helianthus tuberosus L.

0.5 g of the material was placed in an erlenmeyer flask and was splashed with 3 mL ethanol. 100 mL distilled water was added and the material was energetically stirred until it dissolved completely. The solution was titrated with 0.1 M NaOH using phenolphthalein as indicator for 20 s until the initial colouring was retained and the released carboxyl groups were determined. 40 mL 0.1 M NaOH were added to the sample for saponification of the ester groups. After 2

hours 50 mL 0.05 M H_2SO_4 were added to the sample, it was stirred and the rest of the acid was titrated again with 0.1 M NaOH. A check sample was also prepared.

The degree of esterification (DE, %) and purity (P, %) of pectin were calculated by the following formula:

$$DE = \frac{b - d}{(a + c) - (b + d)} \cdot 100\%$$

$$P = \frac{(a - c) \cdot F \cdot 0{,}01761 + (b - d) \cdot F \cdot 0{,}01901}{m \cdot \frac{100 - W}{100}} \cdot 100\%$$

where
a – the volume of 0.1 M NaOH used in the first titration of the sample, (mL);
b - the volume of 0.1 M NaOH used in the second titration of the sample, (mL);
c - the volume of 0,1 M NaOH used in the first titration of the check sample, (mL);
d - the volume of 0.1 M NaOH used in the second titration of the check sample, (mL);
F – factor of 0.1 M NaOH;
W – water content of pectin, (%).

5. Physical - chemical characterization of pectins

The methods described in reference [11] were used to determine the main physical - chemical characteristics of the isolated pectins preparations – moisture and ash (quantitatively), reducing substances (the method proposed by Schoorl was used), degree of esterification, acetyl content (determined by the acetic acid liberated from the saponified acetyl groups), molecular weight (determined by the method proposed by Anger) and gelling ability (according to the method proposed by Tarr–Baker).

The water-insoluble substances were determined as follows: 1-5 g pectin were dissolved and diluted with water to 0.5 % concentration. The solution was filtered through a thick filter which was weighed in advance. The precipitation on the filter was washed with warm water and dried at 80-85 °C to constant weight.

The pectin preparations were dissolved in a 0.1 M phosphate buffer with pH 6 in order to determine the intrinsic viscosity [η]. The relative viscosities were determined with a glass Ubbelohde viscosity meter at 25±0.1 °C. The time of draining of the solvent (t_0) is 81.8 s. At least six different concentrations of pectin solutions were used and their time of draining (t_s) had to satisfy the condition $1{,}2\ t_0 < t_s < 2t_0$.

The intrinsic viscosity [η] was calculated with Huggins equation:

$$\eta_{dp}/C = [\eta] + Kn\cdot[\eta]^2\cdot C,$$

where $\eta_{dp} = (t_s - t_0)/ t_0$.

The monosaccharide composition was determined by gas chromatography after a complete acidic hydrolysis and silanization with hexamethyldisilazane in the presence of pyridine and trifluoracetic acid [11].

RESULTS AND DISCUSSION

The results concerning the polyuronide content (PUC) and the degree of esterification (DE) of pectins in the stems of *Helianthus tuberosus L.* are presented in table 1.

Table 1. Polyuronide content and degree of esterification of pectins in stems of *Helianthus tuberosus L.*

Number of sample	PUC, % a.d.m.*	DE, %
№1	11.6	54.1
№2	9.8	53.7
№3	10.3	56.4

*a.d.m. – absolutely dry matter

The table shows that the stems of Jerusalem artichoke have a relatively high content of pectins (№1 – 11.6 % a.d.s.) In comparison, in apples (the main raw material for extraction of pectin) the pectin content is approximately 2 % (‘raw’ pectin) and 18 % (‘dry’ pectin) [3]. The determination of the polyuronide content with the methods used in part 2 of Methods and materials makes it possible to determine the degree of esterification without isolating the pectins. Thus the degree of esterification of pectins in the stems of Jerusalem artichoke can be determined as average [6].

Table 2 shows the results from the extraction of pectins.

Table 2. Extraction of pectin from stems of Jerusalem artichoke

№	Yield*, %	Purity of pectins, %	Pectins content in the isolated product,%	Degree of extraction (R), %
Sample #1	10.9	86.3	9.4	81.0
Sample #2	10.1	85.7	8.7	88.8
Sample #3	11.2	82.4	9.2	89.3

*Pectins yield from the raw material

The results in table 2 show that the extracted pectin preparations have relatively high purity (over 82 %). The existing impurities are probably due to the milder conditions of the extraction process. As far as the degree of extraction (R) is concerned, sample 3 has the highest value (89.3 %).

The initial analyses concerning the physical and chemical characterization of pectin established some general characteristics which give additional information about the purity of the obtained pectin preparations (Table 3).

Table 3. Contents of moisture, ash, insoluble and reducing substances in pectin from stems of Jerusalem artichoke

Pectins isolated from Jerusalem artichoke	Moisture, %	Ash, % a.d.m.	Water – insoluble substances, % a.d.m.	Reducing substances, %
Sample #1	3.4	0.8	0.8	-
Sample #2	2.8	1.1	0.7	0.9
Sample #3	4.6	0.6	1.0	0.6

Table 4 shows the results for the degree of esterification, molecular weight, acetyl content, viscosity and gel strength. It is evident that the extracted pectins in the three samples have very close characteristics.

Table 4. Physical-chemical characterization of pectins from stems of Jerusalem artichoke

	Sample #1	Sample #2	Sample #3
DE, %	52.8	51.4	53.9
Acetyl content, %	1.4	0.8	1.2
Molecular weight, Da	328 000	386 000	354 000
Intrinsic viscosity [η], dl/g	6.12	7.14	7.08
Gel strength, ° TB	230	240	230

The acetyl content gives information about the percent of galacturonic residues esterified with acetic acid in the presence of OH-groups connected with C-2 or C-3. Usually the acetyl groups are of small quantities 0.3 – 0.8 % [11]. The pectin preparations obtained from beet, tomatoes and sunflower heads have higher acetyl content [13]. Regarding the values of acetyl content it can be concluded to be within the range of 0.8 % to 1.4 %

The molecular weight of pectins is an important characterization of their functional properties. Literary sources show that it varies widely [12]. The difference in the molecular weight of various biopolymers is due to the used method of analysis and also to the heterogeneousness and aggregation of some of them in water. Table 4 shows that the molecular weight of pectins obtained from stems of Jerusalem artichoke varies between 328 000 and 386 000 Da.

Table 5 shows information about the monosaccharide composition of pectins isolated from the stems of Jerusalem artichoke. As expected D-galacturonic acid has the highest content (~ 80.4 %) [4,6].

Table 5. Monosaccharide composition of pectins isolated from stems of Jerusalem artichoke

Monosaccharide, %	Sample #1	Sample #2	Smple #3
D-galacturonic acid	79.4	81.4	80.3
L- rhamnose	3.5	3.9	2.8
D-glucose	3.1	2.3	1.8
D-fructose	4.6	3.8	4.1
D-mannose	1.8	2.0	1.3
D-galactose	1.9	1.6	2.0
D-xylose	2.7	2.4	3.1
L-arabinose	1.8	1.1	2.2

Seven neutral sugars were determined in the three samples – L-rhamnose, D-glucose, D- fructose, D-mannose, D-galactose, D-xylose and L-arabinose. In previous papers on the monosaccharide composition of pectinc extracted from the tubers of Jerusalem artichoke the presence of L-fructose was determined [8], but this monosaccharide was not identified in the present study.

CONCLUSION

The stems of Jerusalem artichoke are characterized by high polyuronide content (~10,6 % a.d.m.). The dergree of esterification of pectin is between 50 % and 60 % which is average. The obtained pectin substances are characterized by relatively high purity (over 82

%). The main physico-chemical characteristics of pectins preparations isolated from the stems were determined. The values that were obtained for extracted pectins from the three samples of stems from Jerusalem artichoke are partially identical, considering that stems from Jerusalem artichoke were collected from three different areas. The analysis of the monosaccharide composition of pectins shows the presence of the following neutral sugars – L-rhamnose, D-glucose, D-fructose, D-mannose, D-galactose, D-xylose and L-arabionose.

REFERENCES

1. Ефремов А., Кондратюк Т., *Выделение пектина из нетрадиционного растительного сырья и применение его в кондитерском призводстве*. Химия растительного сырья, №4, 2008.
2. BeMiller N. James, *Carbohydrate Chemistry for Food Scientists*, AACC International, Inc. 2007, Prevod na deloto: Ars Lamina DOO, Skopje, 2011.
3. Крачанов Х., *Функционални храни на основата на пектиновите вещества*. Научни трудове, ВИХВП, Том XLIV, Св. 1, 2000.
4. Coultate T., *Food: The Chemistry of its Components* (5th Edition), RSC Publishing, Royal Society of Chemistry, Cambridge, UK, 2009, Prevod na deloto: Ars Lamina DOO, Skopje, 2011.
5. Нечаев А., Кочеткова А., Зайцев А., *Пишевые добавки* „Колос", „Колос-пресс", Москва, 2002
6. Малчев Е., Моллов П., *Технология на консервирането на плодове и зеленчуци - концентрати и плодово-захарни продукти.* Второ издание. "Контраст", Стара Загора, 2008.
7. Золотарева А., Чиркина Т., Цыбикова Д., Бабуева Ц., *Исследование функциональных свойств облепихового пектина.* Химия растительного сырья, №1, 1998.
8. Делчев Н., Тодорова М. и др., *Върху въглехидратния състав на растението топинамбур (Helianthus tuberosus L.).* Сборник на докладите от седма национална научно-техническа конференция с международно участие „Екология и здраве", Акад. изд. на АУ, Пловдив, 2008.

9. Делчев Н., Прокопов Ц., *Изследване адсорбционните свойства на брашно от Helianthus tuberosus L. спрямо йоните на Cu (II).* Научна конференция, СУБ, Пловдив, 2013.
10. Делчев Н., Денев П., Панчев И., Кирчев Н., *Экстракция пектиновых веществ из различных частей растения топинамбур (Helianthus tuberosus L.).* Бутлеровские сообщения, Т. 18, №7, 2009.
11. Делчев Н., *Изолиране и характеристика на въглехидрати от Helianthus tuberosus L*. Дисертация, УХТ, Пловдив, 2011.
12. Колева М., Колев Д., *Полизахариди*. Наука и изкуство, София, 1985.
13. Kratchanov C., *Polysaccharides in the food industry: chemical, technological and medical aspects.* HIFFI – Plovdiv, Scientific works, Vol. XLVI, 2001.

635.83:547.56(497.7)

CORRELATION BETWEEN ANTIOXIDANT CAPACITY AND PHENOLIC CONTENTS OF SELECTED BOLETS FROM MACEDONIA[19]

Daniela Nikolovska Nedelkoska, MSc
"Petre Prlickov" 42, Faculty of Technology and Technical Sciences,
St. Kliment Ohridski University, Veles, Macedonia
daniela.nedelkoska@uklo.edu.mk
Oliver Tusevski MSc, Katerina Rusevska, MSc
Sonja Gadzovska Simic, PhD, Mitko Karadelev, PhD
"Arhimedova" 5, Institute of Biology, Faculty of Natural Science and Mathematics, Ss. Cyril and Methodius University, Skopje, Macedonia
mitkok@pmf.ukim.mk

Abstract

Considering the global interest for the natural sources of antioxidants, macrofungi have become attractive for research activities. The aim of this study was to investigate the antioxidant properties of three *Boletus* species: *B. appendiculatus*, *B. satanas* and *B. lupinus*. Specimens were collected from Macedonian oak forest on Galichica Mountain in autumn 2011. Antioxidant properties of the selected fungi were assayed using 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging capacity method in the methanolic extracts. The contents of phenolic compounds and flavonoids present in the mature fruiting bodies were also analyzed. A highly significant correlation between antioxidant capacity and phenolic content was found, indicating that phenolic compounds are a major contributor to antioxidant activity in the mushroom fruiting bodies. The highest antioxidant capacity and the lowest effective concentrations of the samples at which DPPH radicals were scavenged by 50% (EC_{50} values) were confirmed in *B. appendiculatus* extracts.

Keywords: *Boletus*, antioxidant activity, total phenolics, total flavonoids

[19] original scientific paper

INTRODUCTION

Antioxidants are molecules that may reverse, prevent or slow oxidative damage, occurring both in the human body and food. With consumers growing awareness and concerns regarding chemically synthesized antioxidant, novel and safe natural antioxidant with no adverse effects have attracted much more attention (Chang, 1999; Saito et al., 2003).

Mushrooms have long been valued as nutritional food by different cultures worldwide due to their high fibre, minerals and protein content, as well as low fat content (Leon-Guzman et al., 1997). On the other hand, extracts of medicinal mushrooms have been an important part of the traditional medicine. In the recent years, the antioxidant properties of the fungi have been extensively studied, and many antioxidant compounds extracted from these sources have been identified.

The antioxidant properties of fungi refer to different antioxidant compounds. Fungi contain a variety of secondary metabolites which have been shown to act as excellent antioxidants. Phenolic compounds are widely distributed secondary metabolites in mushrooms. A correlation between the mushroom antioxidant activity and their phenolic content has been well established (Mau et al., 2002, 2004; Cheung et al., 2003; Barros et al., 2007a). Flavonoids are a group of naturally-occurring mushroom phenolic compounds that in food systems can act as free radical scavengers and terminate the radical chain reactions that occur during the oxidation of triglycerides (Madhavi et al., 1996). In addition, different wild mushrooms species have been reported to have antioxidant activity related to terpenes, pigments, amino acid ergothioneine, tocopherols, ascorbic acid, etc. (Akanmu et al., 1991; Dubost et al., 2007; Kasuga et al., 1995; Mau et al., 2002; Barros et al., 2007b). The antioxidant properties of mushrooms are also derived from the essential trace elements: selenium and zinc (Falandysz et al., 2008; Bauer-Petrovska et al., 2008) that have a key role in some biological processes involved in antioxidant defence (Brenneisen et al., 2005).

According to Ferreira et al. (2009) there are some advantages of using mushrooms over plants as commercial sources of antioxidant compounds: the fruiting body can be produced in much less time, the mycelium may also be rapidly produced in liquid culture and the culture medium can be manipulated to produce optimal quantities of active products. Hence, purification of the mushroom extracts may lead to increased activity of the antioxidant compounds and to the possibility of developing natural antioxidant material for the food and cosmetic industry with safer and better antioxidants.

In this perspective, the aim of our study was to investigate the antioxidant properties of 3 *Boletus* species: edible *B. appendiculatus*, poisonous *B. satanas* and *B. lupinus*, a new species for mycobiota of Macedonia, collected on Macedonian oak forest on Galichica Mountain in autumn 2011. Results from this study are comprehensive part of the systematic research for antioxidant characterization of Macedonian fungi.

MATERIAL AND METHODS

Fruiting body selection. Wild fruiting bodies of the genus *Boletus* (*B. appendiculatus*, *B. satanas* and *B. lupinus*) were collected on Macedonian oak forest on Galichica Mountain, in autumn 2011. Taxonomic identification was made in the Mycological Laboratory at the Institute of Biology, Faculty of Natural Sciences and Mathematics in Skopje, by implementing standard methods of macroscopis, microscopic and chemical techniques (coloring of fruit bodies and spores), as well appropriate literature. The representative voucher specimens were deposited at the Macedonian Collection of Fungi (MCF) at the Institute of Biology.

Preparation of methanolic extracts of mushrooms. The fruiting bodies were cleaned to remove any residual compost/soil and subsequently air-dried in the oven at 40^{o} C. A mushroom powder sample (50 mg) was extracted by stirring with 2 mL of 80% (v/v) methanol in ultrasonic bath for 30 min at 4 ^{o}C, and centrifuged at 12000 rpm for 15 min. Supernatants were used for quantification of total antioxidant capacity and total phenolic and flavonoid content.

Determination of total phenolics. Total phenolic content in the methanolic extract was determined by Folin-Ciocalteu's colorimetric method (Singleton and Rossi, 1965). In 20 µL diluted methanolic extract, 100 µL Folin-Ciocalteu's reagent were added and allowed to stand for reaction. The mixture was neutralized by adding 80 µL of 0.7 M sodium carbonate and kept in dark at room temperature. The absorbance was measured at 750 nm using UV-VIS spectrophotometer (SpectraMAX 190). Quantification was done on the basis of standard curve of gallic acid and the results were expressed as milligrams gallic acid equivalent (GAE) per gram dry weight (DW) of the mushroom material.

Determination of total flavonoids. Flavonoid content in the methanolic extract of mushrooms was determined by using aluminium chloride colorimetric method (Chang et al., 2002). To an aliquot (80µL) of diluted mushrooms extract, 5 µL of 10% (w/v) aluminium chloride, 5 µL of 1 M sodium acetate and 110 µL of distilled water were added. The mixture was allowed to stand at room temperature for 30 min and the absorbance of the

developed color was recorded at 415 nm using an UV-VIS spectrophotometer (SpectraMAX 190). Quercetin was used as standard for the calibration curve. Flavonoid contents were expressed as milligrams quercetin equivalent (QE) per gram dry weight.

Radical Scavenging Activity (RSA). The effect of mushroom methanolic extracts on DPPH radical scavenging was estimated according to the method of Brand–Williams et al. (1995), with some modifications. Various concentrations of mushroom extracts (0.01 mL) were mixed with 0.19 mL of methanolic solution containing DPPH radicals (0.127 mM). The mixture was shaken and left to stand for 30 min at room temperature in the dark. The absorbance of the resulting solution was measured spectrophotometrically at 517 nm. The capability of the mushroom extracts to scavenge the DPPH radicals was calculated using the following equation: $\%RSA = [(A_{DPPH} - A_S) / A_{DPPH}] \cdot 100$, where A_S is the absorbance of the solution when the sample extract has been added at a particular level, and A_{DPPH} is the absorbance of the DPPH solution.

An antioxidant value of 100% indicates the strongest antioxidant activity. The EC_{50} value represents the effective concentration of the sample (milligrams per milliliter) at which DPPH radicals were scavenged by 50%. A lower EC_{50} value corresponds to a higher antiradical activity of mushroom extract.

Statistical analysis. The experiments were independently repeated twice under the same conditions and all analyses were performed n triplicate. The statistical analyses were performed with SPSS statistical software program (SPSS version 11.0.1 PC, USA, IL). All statistical tests were considered significant at $p \leq 0.05$.

RESULTS AND DISCUSSION

Total phenolic and flavonoid content

The total phenolic content, expressed as mg of GAE per gram of dry mushroom, is shown in Figure 1. The highest content of total phenolic compounds was found in *Boletus appendiculatus* (21.24±0.69 mg GAE/g DW), followed by *B. lupinus* and *B. satanas* (17.63±0.36 and 16.25±1.10 mg GAE/g DW, respectively).

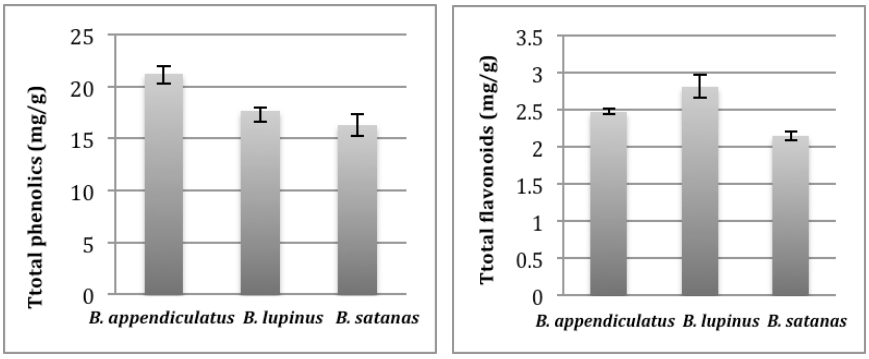


Figure 1 Total phenolic (mg GAE/g) and flavonoid (mg QE/g) contents of methanolic extracts from selected *Boletus* mushrooms.

The amount of total flavonoid compounds in the methanol extracts, expressed as mg of QE per gram of dry mushroom, is also shown in Figure 1. The total flavonoid contents of selected species were ranged from 2.15±0.06 to 2.81±0.15 mg QE/ g DW. It is evident that extracts with a higher phenolic content did not always have higher flavonoid content. Results showed that *B. lupinus* had a higher total flavonoid contents (2.81±0.15 mg QE/g) compared to those of *B. appendiculatus* (2.47±0.03 mg QE/g). On the other side, total phenolic contents in *B. lupinus* were lower (17.63±0.36 GAE/g) compared to those of *B. appendiculatus* (21.24±0.69 mg GAE/g). These results suggested that different mushrooms extracts contained different levels of total flavonoids as a proportion of the total phenolic compounds.

Also, it is obvious that the extracts contained much lower total flavonoid contents than the total phenolic contents. The results suggest that other compounds besides flavonoids are the major phenolic substances present in the tested mushrooms.

Scavenging effect on DPPH radical

In this study, the DPPH scavenging activity was selected to evaluate the antioxidant activity of mushrooms extracts because it is one of the most effective method for estimation the concentration of radical-scavenging materials active by a chain-breaking mechanism (Niki, 1987).Results for DPPH activity in the mushrooms extracts are presented in Figure 2. The scavenging effect of all tested *Boletus* species increased depending of the extract concentrations. This implied that the DPPH radical scavenging of the mushroom extracts was dose-dependent.

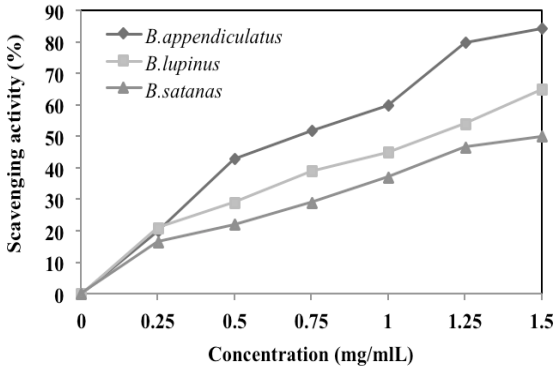


Figure 2 Antioxidant activity of selected *Boletus* mushrooms: Scavenging effect on DPPH radicals (%).

Results from our study showed that *B. appendiculatus* extract (1.5 mg/mL) had the highest scavenging effect (84.65%) compared to *B. lupinus* and *B. satanas* (64.30 and 50.56%, respectively). EC_{50} value was defined as the concentration of antioxidants required for 50% scavenging of DPPH radicals in specified time period. This parameter is widely used to measure antioxidant activity and smaller EC_{50} value corresponds to higher antioxidant activity of the mushrooms extract. EC_{50} values of DPPH radical scavenging in *B. appendiculatus*, *B. lupinus* and *B. satanas* extracts were 0.72, 1.12 and 1.49 mg/mL, respectively. Among the tested extracts, *B. appendiculatus* fruiting body was the strongest DPPH scavenger with the lowest EC_{50} value, followed by the extracts of *B. lupinus* and *B. satanas*.

Correlation between total phenolic content, total flavonoid content and antioxidant capacity

In order to understand the antioxidant activity of the selected mushroom species in terms of their total phenolic content, a regression analysis was performed by Pearson correlation coefficient (R). As shown in Figure 3, significant correlation was found between the antioxidant capacity expressed as EC_{50} and total phenolic content ($R= -0,924$, $p<0.001$). A significant correlation obtained between antioxidant activity and phenolic content indicate that phenolic compounds contribute significantly to antioxidant activity of the investigated mushrooms. These negative linear correlations proved that *B. appendiculatus* showed the highest phenolic antioxidants which is correlated with the lowest EC_{50} value. On the other side, *B. satanas*

contained the lowest amounts of phenolic antioxidants correlated with the highest EC_{50} values.

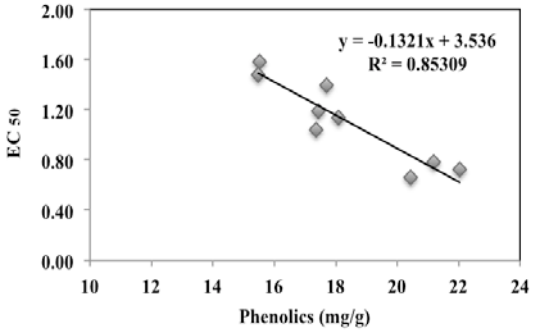


Figure 3 Correlation between total phenolics and scavenging effect on DPPH radicals (EC_{50}).

Correlation coefficients between total phenolic compounds (TFC), total flavonoid content (TFC) and DPPH antioxidant activity determination assay (EC_{50}) are shown in Table 1. There was no correlation between total flavonoids and antioxidant activity (Table 1). This lack of relationship indicates that flavonoids are not main contributors to antioxidant activity of tested mushrooms. In addition, a non-significant correlation coefficient was found between flavonoid content and total phenolic content indicating that flavonoids are no dominant group of the phenolic compounds in tested mushrooms.

Table 1 Correlation coefficients between total phenolic compounds (TFC), total flavonoid content (TFC) and DPPH antioxidant activity determination assay (EC_{50}).

	TPC	TFC
TFC	0.209 (0.044) ns	-
EC_{50}	- 0.924 (0.853)*	- 0.412 (0.170) ns

R – correlation coefficient; the values in parentheses represent the R^2 values.
n= 9; ns – non significant ; * significance level at $p \leq 0.001$.

The results presented in our study are in agreement with those in the literature which showed that the total phenolics are the major contributors to the antioxidant activity of macrofungi (Mau et al., 2002, 2004; Cheung et al., 2003; Barros et al., 2007a, Sarikurkcu et al., 2008). Puttaraju et al. (2006) also found a direct correlation between mushrooms antioxidant activity and total phenolic content and reported correlation coefficient (*R*) of about 0.95

between total phenolics and antioxidant capacity assay for the extracts of 23 species of wild mushrooms.

The present study suggests that selected bolets are a potential source of natural antioxidant and that phenolics are major naturally occurring antioxidant compounds found in their methanolic extracts.

SUMMARY

The current study was undertaken to measure the antioxidant potential of methanolic extracts from fruiting bodies of three *Boletus* species naturally grown on Galichica Mountain. Results from this study showed that analyzed mushroom extracts are rich in phenolic compounds and exhibit strong antioxidant capacities. A highly significant correlation between antioxidant capacity and phenolic content was found, indicating that phenolic compounds are the major contributor to antioxidant activity in the mushroom fruiting bodies. So, it is evident that the selected bolets have potential to be used as natural antioxidants. Regarding the development of natural antioxidants from macrofungal origin, further research could be focused on the identification and quantification of individual antioxidant compounds in selected mushroom extracts.

REFERENCES

Akanmu D, Cecchini R, Aruoma OI, Halliwell B. *The antioxidant action of ergothioneine*. Arch Biochem Biophys 288(1): 10–16, 1991.

Barros L, Baptista P, Ferreira ICFR. *Effect of Lactarius piperatus body maturity stage on antioxidant measured by several biochemical assays*. Food Chem Toxicol 45: 1731-1737, 2007a.

Barros L, Ferreira M-J, Queirys B, Ferreira ICFR, Baptista P. *Total phenols, ascorbic acid, β-carotene and lycopene in Portuguese wild edible mushrooms and their antioxidant activities*. Food Chem 103: 413–419, 2007b .

Bauer-Petrovska B, Karadelev M, Kirovska-Cigulevska O, Sulejmani S, Memisi S. *Selenium in Selected Species of Edible Mushrooms from the Republic of Macedonia*. 5th Conference on Medicinal and Aromatic Plants of Southeast European Countries, Brno, Czech Republic, 2008.

Brand-Williams W, Cuvelier ME, Berset C. *Use of a free radical method to evaluate antioxidant activity*. Food Sci Technol-Leb 28: 25-30, 1995.

Brenneisen P, Steinbrenner H, Seis H. *Selenium, oxidative stress, and health aspects.* Mol Aspects Med 26: 256-267, 2005.

Chang C-C, Yang M-H, Wen H-M, Chern J-C. *Estimation of total flavonoid content in propolis by two complementary colometric methods*. J Food Drug Anal 10(3): 178–182, 2002.

Chang S. *Global impact of edible and medicinal mushrooms on human welfare in the 21st century. Nongreen revolution.* Int J Med Mushrooms I : 1-7, 1999 .

Cheung LM, Cheung PCK, Ooi VEC. *Antioxidant activity and total phenolics of edible mushroom extracts*. Food Chem 81: 249–255, 2003.

Dubost NJ, Ou B, Beelman RB. *Quantification of polyphenols and ergothioneine in cultivated mushrooms and correlation to total antioxidant capacity.* Food Chem 105: 727-735, 2007.

Falandysz J. *Selenium in Edible Mushrooms.* Environ Carcin Eco R 26(3): 256-299, 2008.

Ferreira IC, Barros L, Abreu RM. *Antioxidants in wild mushrooms*. Curr Med Chem 16:1543-60, 2009.

Kasuga A, Aoyagi Y, Sugahara T. *Antioxidant activity of fungus Suillus bovines (L:Fr.) O. Kuntze*. J Food Sci 60: 1113-1115, 1995.

Madhavi DL, Singhal RS, Kulkarni PR. *Technological aspects of food antioxidants*. In: Madhavi, D. L., Deshpande, S. S., Salunke, D. K. (Eds.). In: Food Antioxidants. Technological, Toxicological and Health Perspectives. Marcel Dekker, New York, pp. 242–246, 1996.

Mau J-L, Chang C-N, Huang S-J, Chen C-C. *Antioxidant properties of several medicinal mushrooms*. J Agr Food Chem 50: 6072–6077, 2002.

Mau J-L, Chang C-N, Huang S-J, Chen C-C. *Antioxidant properties of methanolic extracts from Grifola frondosa, Morchella esculenta and Termitomyces albuminosus mycelia.* Food Chem 87: 111–118, 2004.

Niki E. *Antioxidants in relation to lipid peroxidation*. Chem Phys Lipids 44: 227–253, 1987.

Puttaraju NG, Venkateshaiah SU, Dharmesh SM, Urs SMN, Somasundaram R. *Antioxidant activity of indigenous edible mushrooms.* J Agr Food Chem 54: 9764–9772, 2006.

Saito M, Sakagami H, Fujisawa S. *Cytotoxicity and apoptosis induction by butylated hydroxyanisol (BHA) and butylated hydroxytoluene (BHT)*. Anticancer Res 23: 4693–4701, 2003.

Sarikurkcu C, Tepe B, Yamac M. *Evaluation of the antioxidant activity of four edible mushrooms from the Central Anatolia, Eskisehir - Turkey: Lactarius deterrimus, Suillus collitinus, Boletus edulis,*

Xerocomus chrysenteron. Bioresource Technol 99: 6651-6655, 2008.

Singleton VL, Rossi JA. *Colorimetry of total phenolics with phosphomolybdic—phosphotugstic acid reagents*. Am J Enol Viticul 16: 144–158, 1965.

615.214.074:543.544.5.068.7

HPLC METHOD FOR DETERMINATION OF SOME PSYCHOSTIMULATIVE DRUGS USING DERIVATIZATION REAGENT[20]

V. Pavlova[1],T. Blazevska[1], M. Menkinoska[1],N.Gjorgovska[2]
Faculty of Technology and Technical Sciences
Petre Prlickov 42, 1400 Veles, Republic of Macedonia
"St. Kliment Ohridski" University, 7000 Bitola[1]
Ss. Cyril and Methodius University in Skopje, Institute of Animal Science[2],
e-mail: valentina.pavlova@uklo.edu.mk

Abstract

Different alternatives for the rapid and sensitive determination of some psychostimulative drugs (MDA, MDMA, MDEA, MBDB), by High-performance liquid chromatography (HPLC) have been evaluated. The method involved derivatization with 3,5-dinitrobenzoylchloride at ambient temperature and separation of the derivatives formed on a Lichrospher® 60 RP-select B, 5 μm, 250 x 4,6 mm id column protected by appropriate guard column. Conditions for the derivatization have been investigated, including the pH, the reaction time and the derivatization reagent concentration. After optimisation, the best results obtained using buffer with pH 10.0, reaction time 5 min and concentration of derivatization reagent 5 mmol/L.

Key words: determination, psychostimulative drugs, derivatization, High-performance liquid chromatography

INTRODUCTION

Amphetamine derivatives have become trendy drugs of abuse because they are powerful stimulants of the central nervous system. In particular, a dramatic increase in the abuse and recreational use of psychostimulative drugs, detected in many countries, especially among young people, for example, group of methylenedioxylated amphetamine derivatives [1]. The most representative substances in this group are 3,4-

[20] original sctientific paper

methylenedioxyamphetamine (MDA), 3,4-methylenedioxymethamphetamine (MDMA), 3,4-methylenedioxyethamphetamine (MDEA), and *N*-methyl-1-1-(1,3-benzdioxol-5-yl)-2-butanamine (MBDB), which are classified as illicit substances in most countries.

Many analytical methodologies used in toxicological studies and forensic science have been described and the great number of publications on psychostimulative drugs analysis published in the last 15 years indicates that it was necessary to improve the methods of analysis [2-6].

Several methods have been described for the determination of amphetamine derivatives using High performance liquid chromatography (HPLC) but procedures without derivatization reactions have not been widely applied to the analysis of drugs because they show low UV absorbance and very little natural fluorescence [7-9]. In addition, primary and secondary amines often show poor chromatographic performance which could be improved by derivatization. To improve both chromatographic behavior and detectability of the psychostimulative drugs, a great number of procedures involving precolumn or postcolumn derivatization using different reagents have been developed [10-14].

In this paper, we evaluated different alternatives to develop the procedure for rapid and sensitive determination of some psychostimulative drugs (MDA, MDMA, MDAE and MBDB), using 3,5-dinitrobenzoylchloride (DNB) such as derivatization reagent (Fig. 1). The developed derivatization procedure followed by HPLC analysis of DNB-derivatives formed was used for determination of examined psychostimulative drugs on paper and textile inflicted.

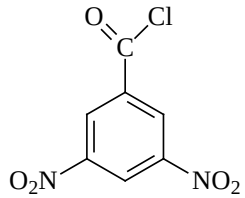


Fig. 1. Chemical structure of 3,5-dinitrobenzoylchloride.

EXPERIMENTAL

The chromatographic system consisted of a ternary pump (Model 9012, Varian) a valve Rheodyne Model 7125 with a sample loop injector of 20 μL and a UV-Diode Array detector (Model 9065, Varian) monitored in the whole UV range. The detector linked to a data system (Varian Star 4.50) for data acquisition and storage. All the assays carried out ambient temperature.

The reagents used were of highest purity (> 99.95 % purity), methanol and acetonitrile HPLC grade (Merck, Darmstadt, Germany), *ortho*-phosphoric acid (Alkaloid, Skopje, R. Macedonia). Authentic samples of MDA, MDMA, MDEA, and MBDB were supplied from the United Nations Drug Control Program (Vienna, Austria).
3,5-dinitrobenzoylchloride (DNB) was obtained from Aldrich (Steinheim, Germany). Stock standard solutions of MDA, MDMA, MDEA, MBDB (1 mg/mL) were prepared in methanol. Working standard solutions of psychostimulative drugs were prepared by dilution of the stock standard solutions with methanol. All solutions were stored in the dark at 4 ^{o}C. DNB solutions were prepared daily by dissolving the pure compound in acetonitrile. A 0.01 mol/L borax buffer was prepared by dissolving the appropriate amount of borax in water and adjusting the pH to the required value with 0.1 mol/L sodium hydroxide solution.

Table I. Conditions used for derivatization and HPLC separation of MDA, MDMA, MDEA and MBDB

Step	Conditons
Derivatization procedure	100 μL of the samples + 100 μL of buffer (0.01 mol/L borax at pH 10.0) + 50 μL of DNB (5 mmol/L) Time of reaction: 5 min Temperature: ambient
Chromatographic separation	Isocratic elution: 13 % acetonitrile : 87 % acidified water with H_3PO_4 (pH = 2.1) Flow rate: 1.5 mL/min UV detection: 200 nm

A LiChrospher® 60 RP-select B, 5 μm, 250 x 4,6 mm id column (Merck, Darmstadt, Germany) protected by a guard column of the same packing, 5 μm, 4 x 4.6 mm id column, (Merck, Darmstadt, Germany) was used for separation of the derivatives formed. The mobile phase was acetonitrile/acidified water with H_3PO_4 (pH = 2.1). The chromatographic conditions used summarized in Table I.
Derivatization with DNB were carried out as follows (see Table I): 100 μL of the samples and 100 μL of the borax buffer were placed in 2 mL glass vials, then 50 μL of the reagent was added and the resulting mixture was left to react for a defined period of time. Finally, aliquots of 20 μL of the

reaction solution into the chromatographic system injected. Derivatizations performed at ambient temperature and each sample assayed in triplicate.

RESULTS AND DISCUSSION

Optimisation of the derivatization procedure of MDA, MDMA, MDEA and MBDB with 3,5-dinitrobenzoylchloride

The effect of the experimental conditions affecting the derivatization with 3,5-dinitrobenzoylchloride (DNB) was investigated using methanol solutions of MDA, MDMA, MDEA and MBDB at a concentration of 25.0 μg/mL. The main parameters affecting the reaction yields being the concentration of reagent and the time of reaction, and the other experimental parameter such as, pH in the reaction medium optimized.

First, the effect of the pH of the buffer in the reaction medium was examined by allowing the derivatization to proceed for pH ranging from 9.2 to 11.0 (for reaction time of 10 min and concentration of DNB 10.0 mmol/L). As shown in Fig. 2, that give the dependence of pH of buffer on peak area of MDA (25.0 μg/mL), the best results were at pH 10.0, where is the maximum of the curve obtained. Higher pHs, resulted in a decrease in the reaction yield. Moreover, and the other drugs showed similar behaviour. Therefore, the pH value of 10.0 was selected for optimal and used for optimisation of other parameters in next experiments.

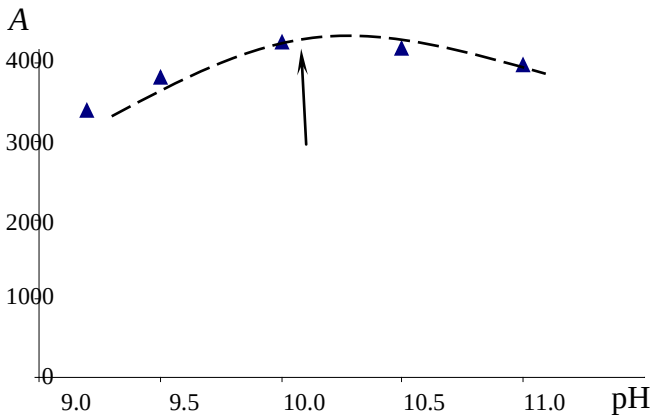


Fig. 2. The dependence of pH of buffer on peak area of MDA (25.0 μg/mL), reaction time 10 min and concentration of DNB 10.0 mmol/L.

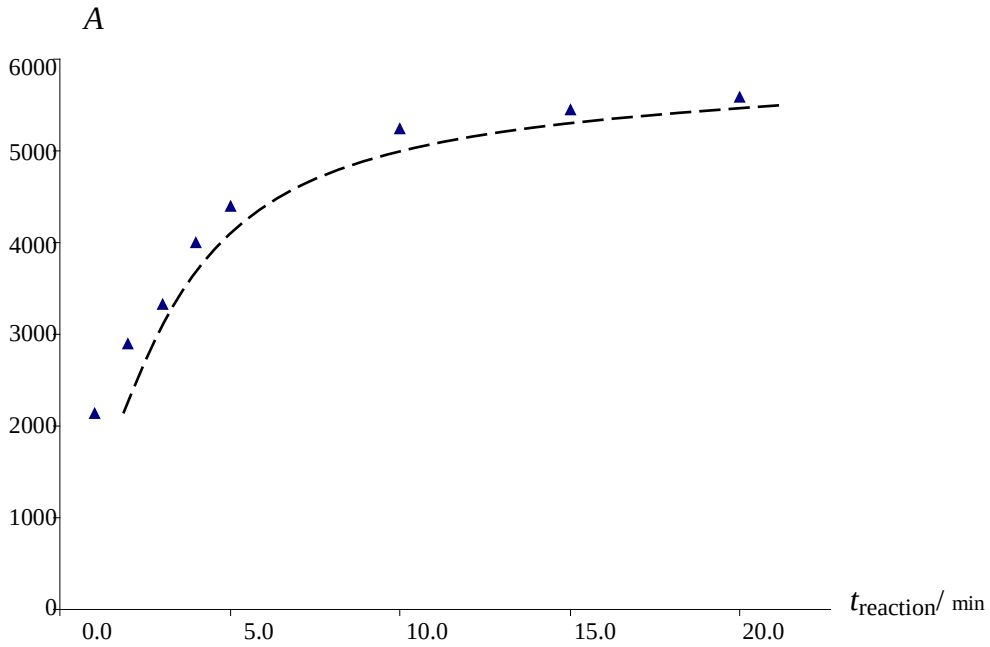


Fig. 3. The effect of reaction time on peak area of MDA (25.0 μg/mL), pH of buffer 10.0 and concentration of DNB 10.0 mmol/L.

For times ranging from 1 to 20 minute, the effect of the reaction time on the sensitivity of the derivatization procedure was tested. In this research, the concentration of reagent was 10.0 mmol/L and the pH of the buffer was 10.0. The results obtained about the effect of reaction time on peak area of MDA, are presented in Fig. 3. As can be observed, the analytical signals (peak areas) increased as the time of reaction increased within the tested interval.

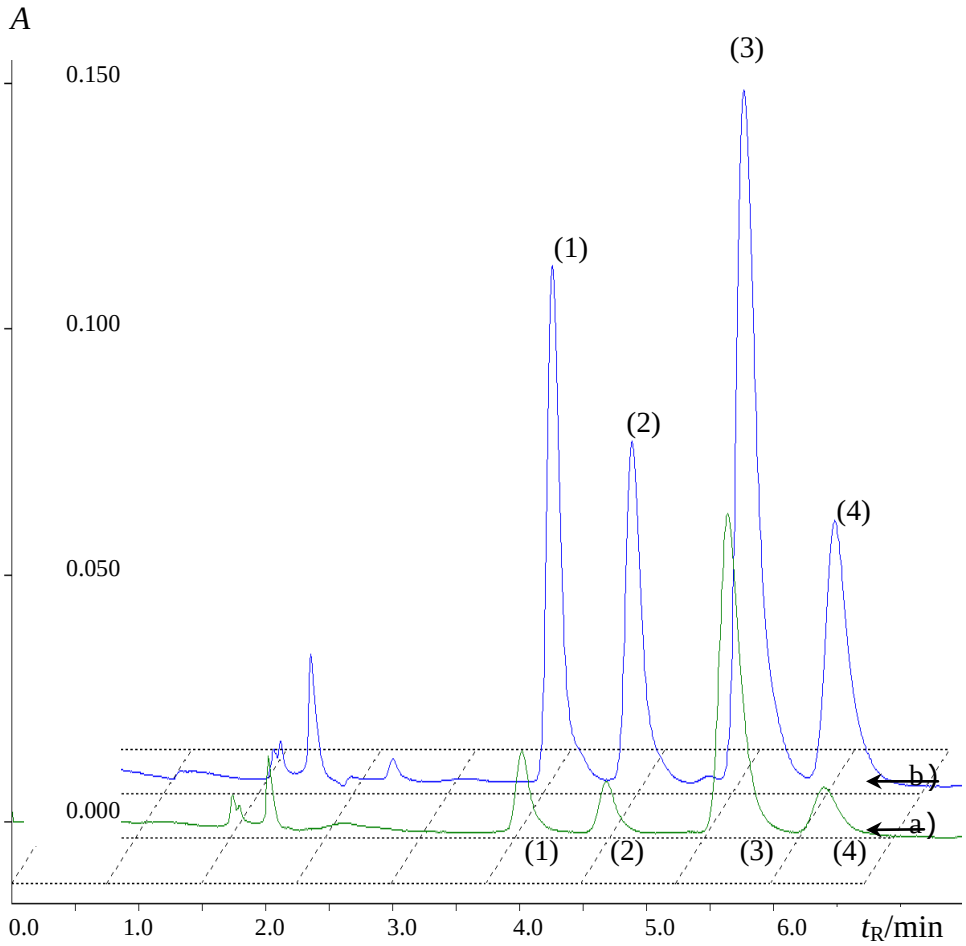


Fig. 4. Chromatograms obtained with derivatization by 3,5-dinitrobenzoylchloride on solution of (1) MDA, (2) MDMA, (3) MDEA and (4) MBDB under reaction time of: a) 0 min; b) 5 min.

Similar behaviour showed and MDMA, MDEA and MBDB (Fig. 4). As a compromise between sensitivity and time of analysis, a time of reaction of 5 min selected for further experiments.

Another parameter affecting the derivatization, is the concentration of 3,5-dinitrobenzoylchloride (DNB). For this reason, the influence of the concentration of DNB are investigated within the range from 1.0 to 15.0 mmol/L, (for reaction time of 5 min and pH of the buffer 10.0). As shown in Fig. 5, the analytical responses increased with increasing DNB concentration up to 5.0 mol/L. A further increment did not significantly improve the analytical signal. Analogous performance showed and MDMA, MDEA and MBDB. Consequently, 5.0 mol/L was the concentration selected as optimal.

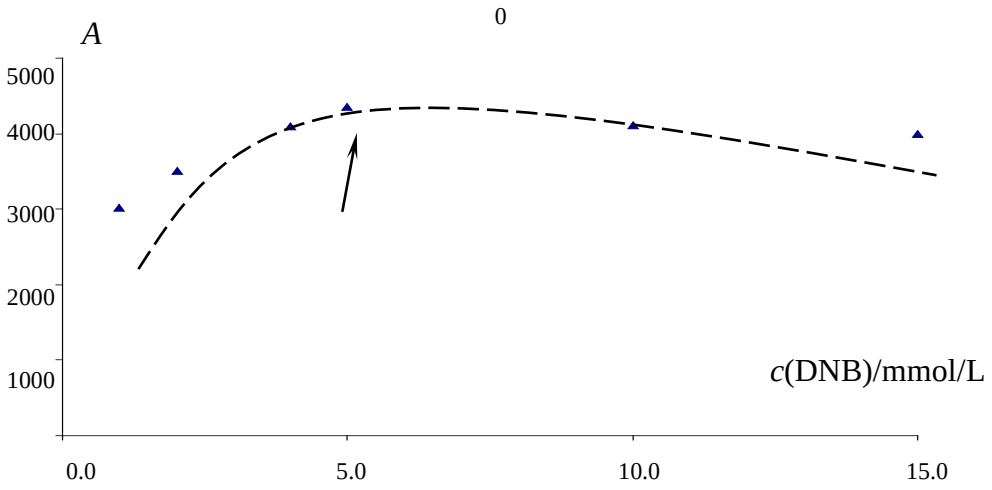


Fig. 5. The effect of concentration of DNB on peak area of MDA (25.0 μg/mL), reaction time of 5 min and pH of buffer 10.0.

Determination of DNB-derivatives of MDA, MDMA, MDEA and MBDB

Based on the above results, the conditions finally selected for the determination of MDA, MDMA, MDEA and MBDB derivatives were those summarized in Table I. Under optimal derivatization conditions, the DNB-derivatives formed have been analyzed using High-performance liquid chromatography (HPLC) method. After chromatographic separation, the obtained retention times (t_R) for DNB-designer drugs were: 3.8 min (MDA), 4.5 min (MDMA), 5.7 min (MDEA), and 6.8 min (MBDB). The chromatogram obtained using this method was shown in Fig. 6.

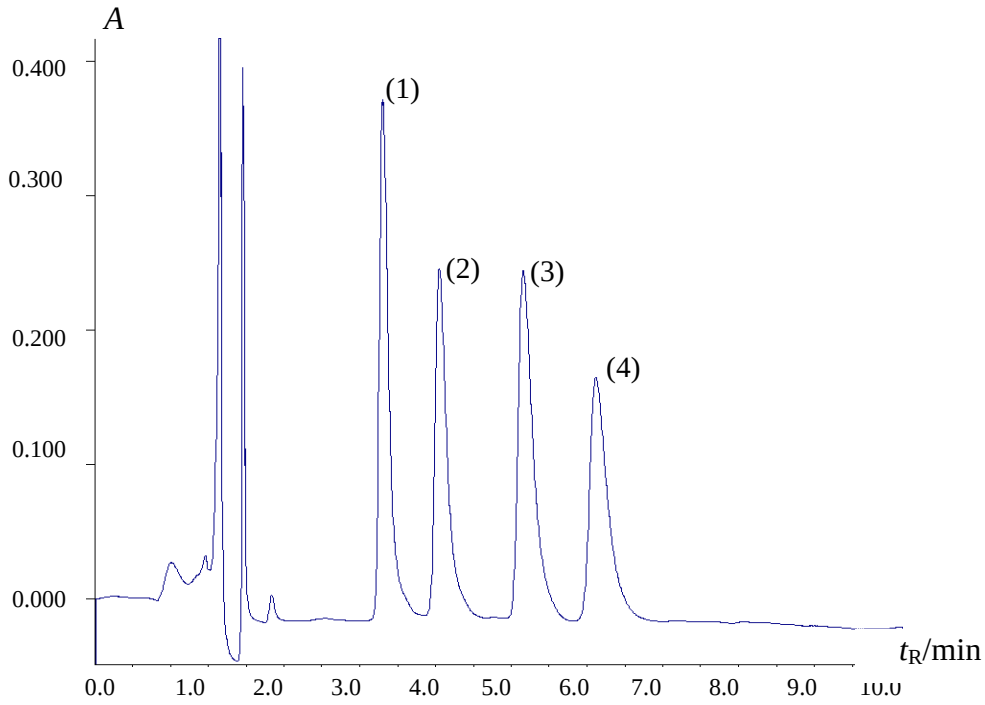


Fig. 6. Chromatogram obtained for standards of: (1) MDA, (2) MDMA, (3) MDEA, (4) MBDB. The concentration of each compound was 100 μg/mL.

The identity of derivatives of MDA, MDMA, MDEA, and MBDB was established by comparing the retention times and UV spectra on peak of interest, with those obtained for standards. The calibration curves for all analytes in the concentration range of 1.0 μg/mL - 100.0 μg/mL, were constructed for quantitative analysis.

The least-squares regression equation obtained of the calibration curves, that give the dependence of peak area (A) and mass concentration (γ) for four drugs were:

MDA $A = 6{,}0231 \cdot 10^3 \cdot \gamma + 4{,}052 \cdot 10^3$; ($n = 6$) $R^2 = 0{,}9986$

MDMA $A = 5{,}8112 \cdot 10^3 \cdot \gamma + 2{,}770 \cdot 10^3$; ($n = 6$) $R^2 = 0{,}9975$

MDEA $A = 5{,}4572 \cdot 10^3 \cdot \gamma + 3{,}069 \cdot 10^3$; ($n = 6$) $R^2 = 0{,}9981$

MBDB $A = 5{,}1432 \cdot 10^3 \cdot \gamma + 3{,}354 \cdot 10^3$; ($n = 6$) $R^2 = 0{,}9983$

The values of the coefficient of correlation were satisfactory ($R^2 > 0.99$).

The limit of detection was calculated as three times the ratio between the *SD* and the slope of the low concentration curve in the concentration range from 0.1 to 5 μg/mL (LOD = 3·*SD/slope*) and the limit of quantification as ten times this ratio (LOQ = 10·*SD/slope*) [15]. Using the suitable equations, the calculated limits of detection (LOD) for analyzed psychostimulative drugs were: MDA (0.018 μg/mL), MDMA (0.032 μg/mL), MDEA (0.008 μg/mL) and MBDB (0.032 μg/mL), whereas, limits of quantification (LOQ) were: MDA (0.054 μg/mL), MDMA (0.096 μg/mL), MDEA (0.024 μg/mL) and MBDB (0.096 μg/mL).

CONCLUSIONS

A HPLC method for determination of some psychostimulative drugs (MDA, MDMA, MDEA, and MBDB) derivatives, using UV detection at 200 nm has been described. The derivatization procedure with 3,5-dinitrobenzoylchloride have been done. After optimisation, the best results obtained using pH value of the buffer 10.0, a reaction time of 5 min and a concentration of derivatization reagent of 5.0 mmol/L. Derivatizations performed at ambient temperature. The proposed derivatization procedure accompanying with HPLC/DAD method is fast, shows good linearity, could be successful used for determination of examined compounds in textile or partially used for paper samples.

REFERENCES

1. C. Giround & all, Ecstasy-the status in French-speaking Switzerland. Composition of seized drugs, analysis of biological specimens and short review of its pharmacological action and toxicity, *Med. Prax.*, **86** (13), 510-523, 1997

2. A. Brettell, R. Saferstein, Forensic Science, *Anal. Chem.*, **69** (12), 123R-143R, 1997

3. T. Kraemer, H.H. Maurer, Determination of amphetamine, methamphetamine and amphetamine-derived designer drugs or medicaments in blood and urine, *J. Chromatogr. B. Biomed. Sci. Appl.*, **713**, 163-187, 1998

4. T.A. Brettell, K. Inman, N. Rudin, R. Saferstein, Forensic Science, *Anal. Chem.*, **71** (12), 235-256, 1999

5. V. Pavlova, S. Gadzovska, S. Petrovska-Jovanović, Simultaneous determination of methylenedioxylated amphetamines in ecstasy tablets by High-performance liquid chromatography, *International Scientific Conference South-West University*, Blagoevgrad, Bulgaria, 2007

6. A. Ivanović, Z. Dekov, V. Pavlova, S. Petrovska-Jovanović, Development and optimization of HPLC/DAD method for determination of MDA, MDMA, MDEA and MBDB, *VIIth Congress of pure and applied chemistry for the students of Macedonia*, O-9, 44-45, Skopje, Macedonia, 2007.
7. R. Backer, D. Tautman, S. Lowry, C. M. Harvey, A. Poklis, Fatal ephedrine intoxication, *J. Forensic Sci.*, **42** (1), 157, 1997
8. O. Al-Dirbashi, J. Qvarnstrom, K. Irgum, K.L. Nakashima, Simple and sensitive high-performance liquid chromatographic determination of methamphetamines in human urine as derivatives of 4-(4,5-diphenyl-1H-imidazol-2-yl) benzoyl chloride, a new fluorescence derivatization reagent, *J. Chromatogr. B Biomed. Appl.*, **712** (1-2), 105-112, 1998
9. B.S. Foster, D.D. Gilbert, A. Hutchaleelaha, M. Mayersohn, Enantiomeric Determination of amphetamine and methamphetamine in urine by precolumn derivatization with Marfey's reagent and HPLC, *J. Anal. Toxicol.*, **22** (4), 265-269, 1998
10. N. A. Santagati, G. Ferrara, A. Marrazzo, G. Ronsisvalle, Simultaneous determination of amphetamine and one of its metabolites by HPLC with electrochemical detection, *J. Pharm. Biomed. Anal.*, **30** (2), 247-255, 2002
11. D. Talwar, I.D. Watson, M.J. Stewart, Routine analysis of amphetamine class drugs as their naphthaquinone derivatives in human urine by high-performance liquid chromatography, *J. Chromatogr. B*, **735** (2), 229-241, 1999
12. C. Cháfer-Pericás, P. Campíns-Falkó and R. Herráez-Hernández, Application of solid-phase microextraction combined with derivatization to the determination of amphetamines by liquid chromatography, *Anal. Biochem.*, **333** (2), 328-335, 2004
13. R. Herráez-Hernández, P. Campíns-Falkó, J. Verdú-Andrés, Sensitive determination of methylenedioxylated amphetamines by liquid chromatography *Analyst*, **126** (5), 581-586, 2001
14. R. Herráez-Hernández, P. Campíns-Falkó, Derivatization techniques for automated chromatographic analysis of amphetamine usingo-phthaldialdehyde: A comparative study, *Chromatographia*, 52 (3-4), 169-174, 2000
15. Varian's Bond Elut Certify Instruction Manual; Varian Sample Preparation Products: Harbor City, CA, 1989.