

# **Austrian Journal of Technical and Natural Sciences**

**Nº 9–10 2021  
September – October**

# Austrian Journal of Technical and Natural Sciences

Scientific journal

№9 – 10 2021 (September – October)

ISSN 2310-5607

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Typeset in Berling by Ziegler Buchdruckerei, Linz, Austria.

Printed by Premier Publishing s.r.o., Vienna, Austria on acid-free paper.

## Section 1. Information technology

<https://doi.org/10.29013/AJT-21-9.10-3-7>

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### RECOVERY MISSING VALUES AND LENGTHENING THE DATA SERIES

**Abstract.** This work presents six ways of filling the missing values using the values of similar data series. Test of the considered models was carried out on the series of hydrological attribute. Modified models were developed and implemented, which include adjustment to the mean values of the series that requires filling in the gaps, which allowed to increase the quality of renewal of missing values.

**Keywords:** missing values, information technology, data series lengthen.

Many works are devoted to the renewal of missing values, lengthening the data series, analysis of the impact of gaps, development of methods and approaches to the analysis of data series with gaps in the data series, because the integrity and completeness of the data are important for the analysis. The presence of gaps in the data series makes it impossible to use a large number of powerful methods and algorithms for data analysis. Moreover, the presence of incomplete data affects the quality of the analysis and the decisions made based on the results of the analysis.

There are several variants of possible solutions, including [1]:

- excluding “incomplete” objects from the set;
- recover missing values in data series.

In addition, if there are missing values in the data series, it is possible to use special mathematical methods for analyzing incomplete data (EM-algorithm, maximum likelihood method, etc.).

The most accessible, widespread and simple methods for renewal of missing data are: filling the gaps by the average value of the series, interpolation

by the neighboring points, average by N-neighboring points, median of N near values of the series, filling the gaps by using regression models, etc. However, all of the above methods give good results when a small number of gaps are restored.

The use of more complex methods, algorithms, and approaches are described in the works [2–5].

**The goal of the work.** Develop a technology for filling the missing values of large lengths and lengthen data series using similar data series.

**Materials and methods.** Introduce the notation:  $T$  – data series with gaps;  $S$  – similar data series;  $k = \overline{1, N}$ , where  $N$  – number of similar data series;  $\bar{T}$  – the average value of the series with gaps for the period of the joint observations;  $\bar{S}_k$  – the average value of the some  $k$  data series for the period of the joint observations;  $i = \overline{1, M}$ , where  $M$  – number of recovery values;  $w_i \in [0; 1]$  – the value of the components of each similar series, calculated according to the formula:

$$w_i = \frac{\sum_{i=1}^N MSE - MSE_i}{\sum_{i=1}^N MSE} \quad (1)$$

where,  $\sum_{i=1}^N w_i = 1$ .

This work realizes and presents ways of renewing missing values by:

1) values of similar data series:

$$T_i = S_{k,i} \quad (2)$$

2) the average values for a group of similar data series:

$$T_i = \frac{S_{1,i} + S_{2,i} + \dots + S_{N,i}}{N} \quad (3)$$

3) weighted values by a group of similar data series:

$$T_i = S_{1,i} * w_1 + S_{2,i} * w_2 + \dots + S_{N,i} * w_N \quad (4)$$

4) values of similar series with correction for the average value of the data series with missing values:

$$T_i = \frac{S_{k,i}}{S_k} * \bar{T} \quad (5)$$

5) the average values of a group of similar data series with a correction to the average value of the data series with missing values:

$$T_i = \frac{\frac{S_{1,i}}{S_1} + \frac{S_{2,i}}{S_2} + \dots + \frac{S_{N,i}}{S_N}}{N} * \bar{T} \quad (6)$$

6) weighted values for a group of similar data series with a correction to the average value of the data series with missing values:

$$T_i = \left( \frac{S_{1,i}}{S_1} * w_1 + \frac{S_{2,i}}{S_2} * w_2 + \dots + \frac{S_{N,i}}{S_N} * w_N \right) * \bar{T} \quad (7)$$

To recover the data according to formulas 2–4, we will search for similar data series on the data in its original representation, and for formulas 5–7 – on the normalized relative to the average value.

**Computational experiment.** The computational experiment is carried out on a hydrological

data series represented by daily indicators of water levels. In hydrological calculations, filling of gaps in the data is carried out according to values of object-analogues, but the main requirement is availability of strong correlation link between the post, for which data updating is carried out, and the post-analogues. But this approach does not guarantee the similarity values of the data series, and therefore to determine the similarity for values of the data series we use both values of correlation coefficients and values of distances between the data series.

For the analysis we will take daily values of water levels in the period from 01.01.2000 to 31.12.2014. For post 79403 r. Vizhivka, smt. Stara-ya Vizhivka, Volodysk region, Ukraine. We will programmatically delete the data for the period from 01.01.2000 to 31.12.2004 and from 01.01.2013 to 31.12.2014. As a result of the calculation scheme it is necessary to identify the best way of following the data series of post 79403 to the left and right (programmatically extracted periods) in the period of joint observations.

Using the previously developed technology for identifying similar data series, we will identify similar hydrological series, which in the future will be used for renewal of missing values. Period of joint monitoring from 01.01.2005 to 31.12.2012. As a result of the work of the calculation scheme for identification of similar data series found that the most similar to the data series for post 79403: when normalized by the average are the data series of posts 79407, 79424; and by the input values are the data series of posts 79405, 79424.

Table 1.– Errors in restoring data series

Recovery model	Posts	For period of joint observations from 01.01.2005 to 31.12.2012		For the recovery period			
				From 01.01.2000 to 31.12.2004 p.		From 01.01.2013 to 31.12.2014	
		MSE	MAPE,%	MSE	MAPE,%	MSE	MAPE,%
1	2	3	4	5	6	7	8
Model 1 (formula 2)	79405	485.94	8.8	295.77	5.62	977.32	14.28
	79424	239.08	5.78	254.18	6.59	244.41	5.93

1	2	3	4	5	6	7	8
Model 2 (formula 3)	79405 79424	210.5	5.65	148.32	4.63	431.87	9.00
Model 3 (formula 4)	79405 79424	134.3	3.99	140.40	4.64	166.75	4.47
Model 4 (formula 5)	79407	183.03	4.47	251.24	5.67	267.73	4.84
	79424	205.93	5.08	204.83	5.79	206.11	5.03
Model 5 (formula 6)	79407 79424	118.24	3.75	135.36	4.40	168.34	4.36
Model 6 (formula 7)	79407 79424	186.1	5.25	155.93	4.99	327.85	7.56

Color palette: ■ – the maximum value for the corresponding error (by column), ■ – the minimum value for the corresponding error (by column), others – mediate values between the maximum and minimum (by column)

In the (table 1) presents the errors approximation of the values by the appropriate model for the period of joint monitoring from 01.01.2005 to 31.12.2012,

as well as for the renewed values for the periods from 01.01.2000 to 31.12.2004 and from 01.01.2013 to 31.12.2014.

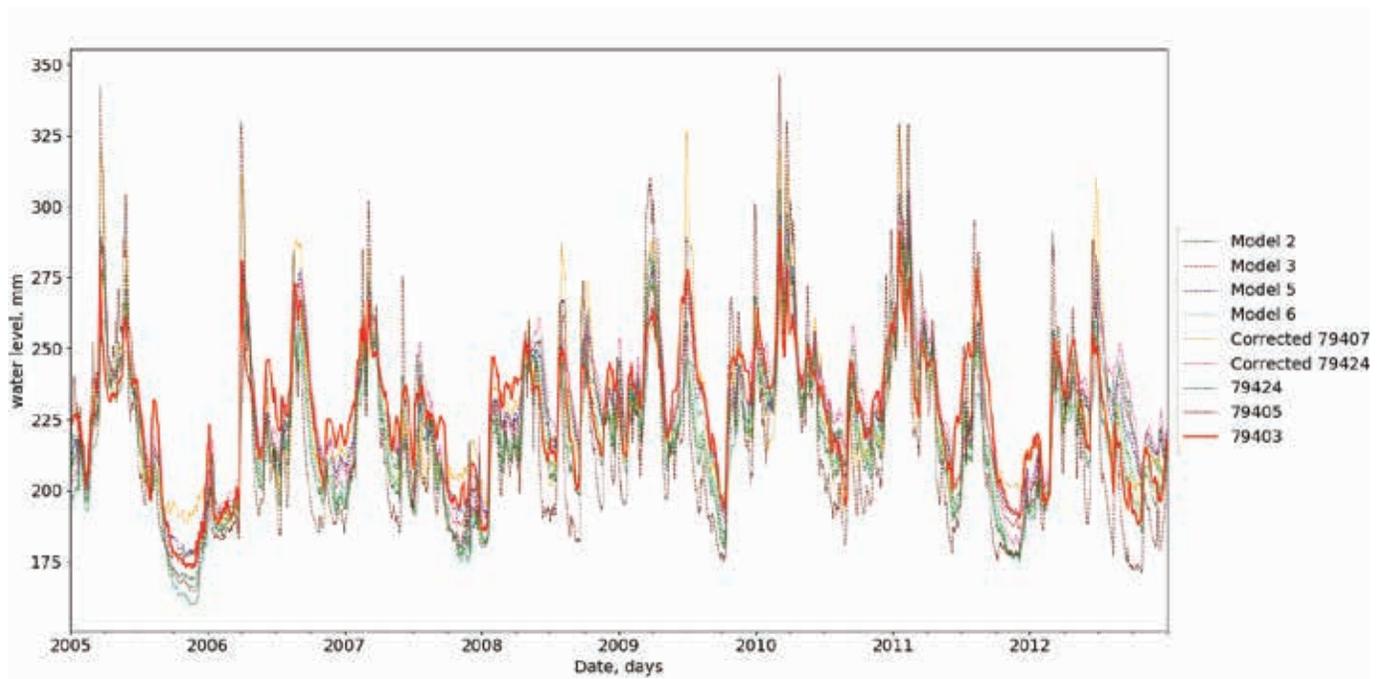


Figure 1. Data series 79403 and data series created with the use of models

In (fig. 1) presents the results by all models and data by the original series for the period of joint observations.

In (fig. 2) presents are graph of the data series of post 79403 in the period from 01.01.2000 to

31.12.2014 and data series created by using the model number five for the test period from 01.01.2000 to 31.12.2004.

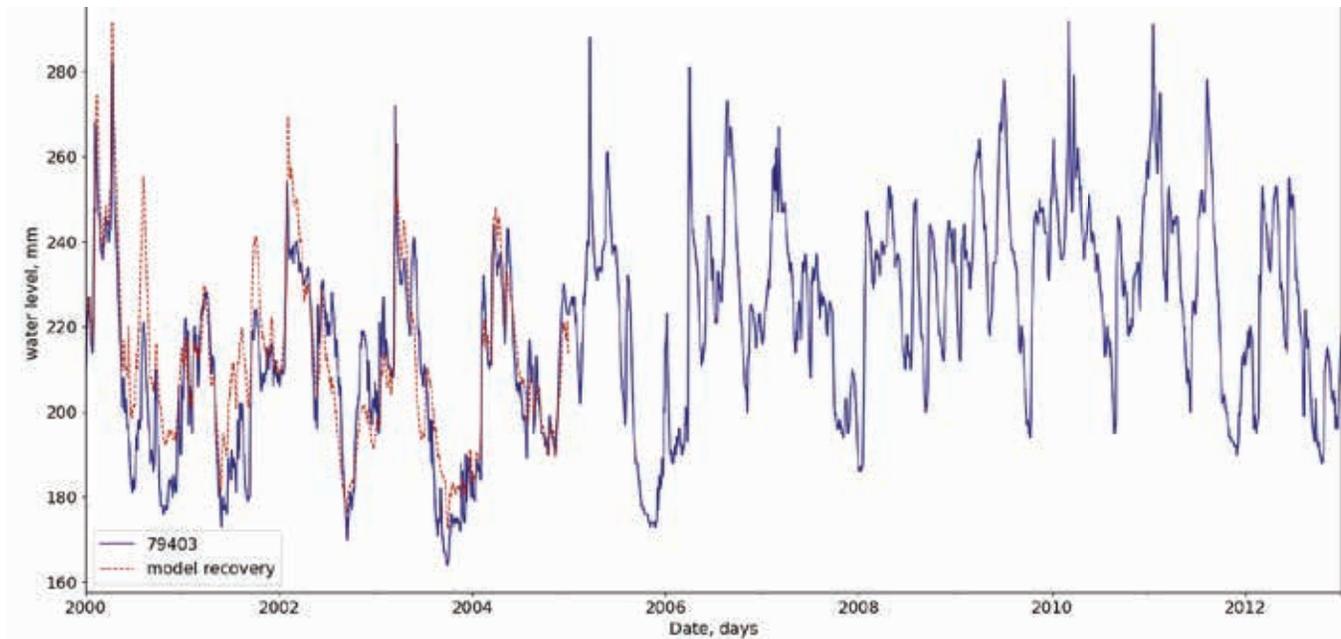


Figure 2. Graph of the data series of post 79403 and the series of simulated values

**Evaluation of results.** Analyzing the results obtained, presented in Table 1, we can see that the best results were obtained using model 3 and model 5 (formulas 4 and 6), while the worst results were obtained when filling in the input values of similar data series (model 1, formula 2).

As for the evaluation of the recovery results, in that case, the best results were obtained, as for the period joint observations, using the models recovery missing values by the average values the group similar series using corrective the average value of the data series, which has missing values, as in the period 01.01. 2000 to 31.12.2004, and in the period 01.01.2012 to 31.12.2014.

As can be seen from the graph in Fig. 1, all the simulated series mostly repeat the behavior the series of post 79403, but at the same time they do not give the same results.

In fig. 2 presents data series of the post № 79403 (from 01.01.2000 to 31.12.2012) and a number of data is built on the average value of a group of similar series with adjusted to the average value of the series with missing values (formula 6), which has the lowest value of error MSE – 118.24, and the value of the MAPE error is only 3.75%, which means that the

simulated data series is similar to the series of post 79403 by 96.25% in the period of joint observations. Considering the recovery period, this model was able to ensure the quality of recovery at 95.6% in the period from 01.01.2000 to 31.12.2004 and 95.64% in the period from 01.01.2013 to 31.12.2014.

**Conclusions.** Recovery of data lost or unreceived for various reasons (device failure, inability to take samples, etc.) is the most effective approach to analyze data with missing values.

The developed technology allows replenishing data series with missing values ensuring the possibility of analysis and selection of the most accurate model.

The advantage of filling missing values in the data series using similar data series, especially the models implemented in this technology, is the possibility to recover the missing data of large periods of the data series in both directions (before and after the period of the join observations).

If we evaluate the models as a whole with correction by the mean value over the period of the join observations of the series with missing values, we can say that this correction improves the accuracy of value recovery.

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<https://doi.org/10.29013/AJT-21-9.10-8-16>

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## EXPERT SYSTEM OF DIAGNOSIS OF ERRORS IN THE OPERATION OF REMOTE NODES OF THE DISTRIBUTED SYSTEM OF THE BANK

**Abstract.** Due to log files coming to the main office from the bank's branches, analysts have the opportunity to receive information about the correct operations of customers, as well as failures in the software and hardware of the nodes. The developed expert system, under the control of the LogHelper program, allows to build clear and exact inquiries for the analysis of log files, automatically find and offer the decision for correction of the found errors, classify unknown errors.

**Keywords:** log files, expert diagnostic system, MongoDB.

### I. Formulation of the problem

In distributed systems, in particular in banking systems, failures during important transactions lead to a loss of bank profits and a decrease in customer confidence. The problem was a huge number of log files from remote offices, which had to be sorted by date, to find the place where something was supposed to indicate the reason for failure, and it took a lot of time and nerves. At that time, it was decided to write a software product that will help to analyze log files faster and more efficiently, which is necessary both for testing the bank's IT system and for its technical support. Subsequently, this program became the basis of the diagnostic expert system. When developing a diagnostic expert system, it is obvious that two aspects are important:

1. The diagnostic expert system should provide a quick search in the log file of messages about failures in the system, identify the causes of failures and suggest ways to solve the problem. This problem can be represented as an objective function:

$$\sum_{i=1}^n L_i t_i + \sum_{j=1}^m L_j t_j + T_n + T_\beta \rightarrow \min, \quad (1)$$

where  $L_i$  –  $i^{\text{th}}$  log file object,  $n$  – the number of objects in the log file,  $1 < i < n$ ,

$t_i$  – the time of viewing the  $i^{\text{th}}$  log file object,

$L_j$  –  $j^{\text{th}}$  log file object, in which an error message was found,  $m$  – the number of objects in the log file in which errors were found,  $1 < j < m$

$t_j$  – the time of processing the  $j^{\text{th}}$  object of the log file, identifying the cause of the failure and the formation of proposals for its elimination,

$T_s$  – the time of transmission of the log file with messages about ways to eliminate errors,

$T_c$  – time for correction errors sent in the log file.

The diagnostic system cannot affect the response time to the client ( $T_s$ ) and the error correction time ( $T_c$ ). The system should reduce the time to find the causes of failures and the time to find solutions to eliminate them.

Restrictions have to be imposed on the components of the objective function.

$$\sum_{i=1}^n L_i t_i < T_v, \tag{2}$$

where –  $T_v$  – time to view the log file without the use of programs;

$$\sum_{i=1}^m L_j t_j < T_g, \tag{3}$$

where –  $T_g$  – time for searching a solution using Google and other search engines.

2. The developed system should provide service for identifying errors which are not in the knowledge base, ie, should be constantly updated with new knowledge.

Accumulation of statistical information from log files allows to select a set of  $N$ -states of normal system operation,  $Z$ -states corresponding to failures of various kinds.  $Y$  is a set of states that have not yet been determined. Then,

$$X = N \cup Z \cup Y, \tag{4}$$

where  $X$  – the set of all possible states of the bank’s IT system.

It was supposed that  $X$  can have a finite number of states  $x_1, x_2, x_3 \dots x_i \dots x_n$ , which correspond to both the correct functioning of the system and work with the presence of deviations,  $p_1 p_2 \dots p_i \dots p_n$  – the probabilities of the system to be in states  $x_1, x_2, \dots x_i \dots x_n$ , respectively. Then the entropy (a measure of uncertainty) of such a system will be calculated by the formula:

$$H(X) = -\sum_{i=1}^n \rho_i \log_2 \rho_i, \tag{5}$$

where  $\sum \rho_i = 1$

For a distributed bank system consisting of  $s$  independent systems, the total entropy will be the sum of the entropies of all systems:

$$H(X_1, \dots, X_s) = \sum_{k=1}^s H(X_k). \tag{6}$$

In the case when the bank’s branches operate IT systems identical in terms of hardware and software

they can be expected to have the same indicators of correct operation by their nature, as well as failures and errors. In this case, it can be assumed that formula (3) will turn as follows:

$$H(X_1, \dots, X_s) = s \cdot H(X_k). \tag{7}$$

As can be seen from formula (7), the tasks of control and diagnostics are to reduce the entropy of a typical node system by detecting known errors and identifying unrecognized situations in the operation of nodes (remote offices) of the banking system.

This goal can be achieved by studying and analyzing set of messages (log files) which come from remote nodes from the bank’s branches to the central office or a special diagnostic center.

That is,

$$H(X) = -\sum_{i=1}^n \rho_i \log_2 \rho_i \rightarrow \min_Z H, \tag{8}$$

Provided  $\sum \rho_i = 1$ .

According to formula (8), the entropy will decrease due to the reduction of the set  $Z$ , which consists of unrecognized situations recorded in the log files.

To solve these problems, the most suitable is expert system, based on the knowledge base, which can store the contents of log files, quickly process them, find the right solution and have a mechanism to replenish the knowledge base.

There is a number of software products at the market which perform log file processing functions. The study and comparison of existing parsers of log files, presented in [3], showed their unsuitability for solving the tasks. The results of the comparison of four systems, which are designed to solve search problems in log files, according to the specified criteria, are shown in (Table 1).

Table 1.– Comparison table of Parsers of log objects

Log Parser 2.2	Logstash	Web Log Explorer	Web Log Storming	Tasks
<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
–	–	+	+	Interface
+	+	+	–	Support for various formats
–	–	–	–	Failure sustainability, impact on resources

1	2	3	4	5
+	-	-	-	The presence of a database
-	-	+	+	Clarity in settings
-	-	-	-	Data analysis

As it can be seen from (Table 1), none of these programs provides data analysis, which is essential for the diagnostic system.

## II. Selection of database for expert system and log file structure development

As it was shown in [1; 2; 7], the non-relational MongoDB database has a number of advantages over relational databases, namely:

- is convenient for storing documents of variable length;
- scales much better than a relational database, which is important when processing very large amounts of data;
- is effective for analytical data processing.

### Log file structure model

Since it is possible to specify the format of log files, their structure, it was proposed to save all failures registered in the log files of the system in the JSON document format, which is used in the MongoDB database.

An object in a NoSQL MongoDB database is a document which has its own ID and attributes. The number of attributes is not regulated, but the total volume of the document cannot exceed 16 Kv. Documents are collected in such way, which is a prototype table in a relational database. Communication among documents is provided by means of identifiers. In view of the above, the document in the MongoDB database can be described as a tuple of the form:

$$D = \{ \langle f_0 : e_0 < f_1 : e_1, f_2 : e_2 \dots, f_n : e_n, f_n + 1 : d_1, f_n + 2 : d_2, \dots, f_n + 1 : d_1 \rangle \}, \quad (9)$$

where  $f_0$  – id of the document;

$f_1 \dots f_n$  – document attributes;

$e_1 \dots e_n$  – atomic values of document attributes;

$d_1 \dots d_1$  – links to other documents.

Formula (9) corresponds to the case where the parent document contains references to child documents through their id.

There is another case of providing a link among documents, when the parent document contains a subsidiary document with its ID and attributes.

Then the model of the document as a database object will look like:

$$D = \{ \langle f_0 : e_0 < f_1 : e_1, f_2 : e_2 \dots, f_n : e_n, < f_n + 1 : d_0, f_n + 2 : ed_1, \dots, f_n + 1 : ed_1 \rangle \}, \quad (10)$$

$\Delta e f_0 : e_0$  – id of the document;

$f_1 \dots f_n$  – document attributes;

$e_1 \dots e_n$  – atomic values of document attributes;

$f_n + 1 : d_0$  – id of subsidiary document;

$ed_1 \dots ed_1$  – atomic values of subsidiary document attributes.

The structure of the log file object as a MongoDB document

To control the correct operation of each node of the bank's corporate system, the log file is created every day, in which all user actions are recorded. The software product is a client-server, and therefore records everything that the client sent to the server and that the client received from the server. The structure of the log file object was considered as the following example:

```
<<=> BarsScheduler at 5/8/2016 7:17:45 AM:
from 10.7.73.12; RequestType = POST; Content-
Type = application/json; charset=>UTF-8;>>
```

```
Input = { "sessionId": "slxctezudkzyv0di3ymysxyd",
"method": "CloseSession", "params": null, "message_
id": "BARS-MESS-6735248" }
```

```
<= BarsScheduler at 5/8/2016 7:17:45 AM: to
10.7.73.12
```

```
Output = { "status": "OK", "RESULT": { "sessionId":
"slxctezudkzyv0di3ymysxyd", "message_id": "BARS-
MESS-6735248", "responce_id": "1", "current_
timestamp": "2016-05-08T07:17:45" } }>>
```

The following parts can be selected in the structure of the log file object:

- 1) Date and information about the request.

- Server title, date and time of the received request (BarsScheduler at 5/8/2016 7:17:45 AM);
- IP- address from which the request came (from 10.7.73.12);
- Request type (RequestType = POST);
- Content type (ContentType = application/json);
- Unicode conversion format (charset="UTF-8");
- 2) Request body.
- Input = { ... };
- 3) Date and information about the answer.
- Server title, date and time of sending a response (BarsScheduler at 5/8/2016 7:17:45 AM);
- IP - addresses to which the response is sent (to 10.7.73.12);
- 4) Response body.
- Output = { ... }.

The description of the structure of the log file in the form of a tuple, according to formula (9) was defined as:

$$D = \{F_0, F_1 < P_1: e_1, P_2: e_2, P_3: e_3, P_4: e_4 \rangle, F_2, F_3 < P_1: e_1, P_2: e_2, P_3: e_3, P_4: e_4 \rangle,$$

where

1.  $F_0$  – ID of the document
2.  $F_1$  – Date and information about the request;
3.  $F_2$  – Request body
4.  $F_3$  – Date and information about the answer;
5.  $F_4$  – Response body;
6.  $P_1 - P_n$  – document attributes;
7.  $e_1 \dots e_n$  – atomic values of document attributes.

*The structure of the log file object with attached documents*

A model with attached documents was also developed to save parser-processed log files. The view of the Log class presented in C # language is shown in (Fig. 1).

```
class Log
{
    public ObjectId Id { get; set; }
    public DateTime RequestDate { get; set; }
    public BsonDocument Request { get; set; }
    public BsonDocument Response { get; set; }
    public DateTime ResponseDate { get; set; }
    public ObjectId LogFileId { get; set; }
    public string MessageId { get; set; }
}
```

Figure 1. Description of the Log class in C# language

The type of parent document with attached subsidiary documents was considered as a tuple, according to the formula (10):

$$D = \{F_0, F_1, F_2 < P_1: e_1, P_2: e_2, P_3: [a1: en], P_4: e_4 \rangle, F_3 < P_1: e_1, P_2: [a1: en], P_3: e_3, P_4: e_4, P_5: e_5 \rangle, F_4, F_5 < P_1: d_1 \rangle, F_6\},$$

where

1.  $F_0$  – Id;
2.  $F_1$  – Request date
1.  $F_2$  – Request document;
2.  $F_3$  – Response document;
3.  $F_4$  – Response date;
4.  $F_5$  – Document link;

5.  $F_6$  – Id a message that belongs to one request and one response.

6.  $P_1 - P_n$  – document attributes;
7.  $a_1 - a_n$  – array attributes;
8.  $e_1 \dots e_n$  – atomic values of document attributes;
9.  $d_1 \dots d_l$  – links to other documents.

Therefore, a log file structure model adapted for storage in MongoDB in JSON format was proposed.

#### IV. Processing and analysis of log files in the diagnostic expert system

For easy storage, processing and analysis of log files, a two-tier server architecture was chosen. The database and knowledge base were stored on a separate server.

The object model of diagnostic expert system is shown in (fig. 2). As for the object model, it con-

sists of objects (collections): Log, Error, StatusError, Known Error, Answer, Log Query, Query Config.

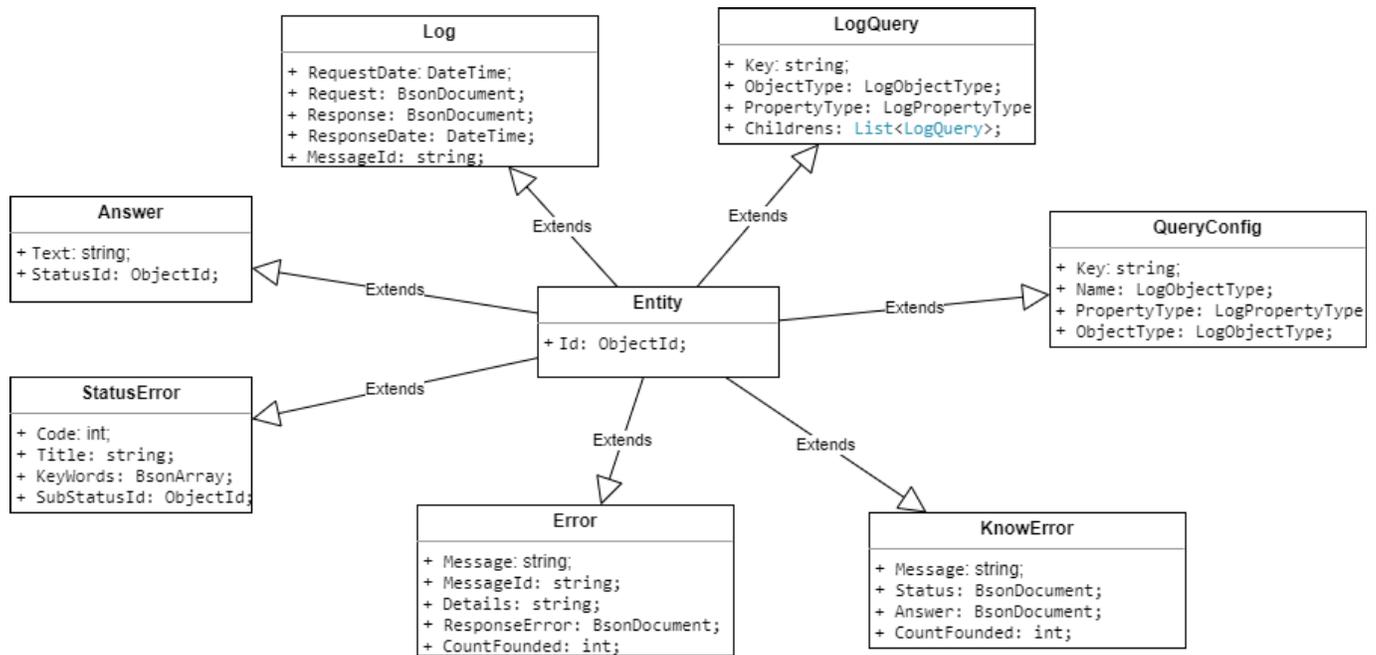


Figure 2. Object model of system data

- In the Error collection all errors unknown to the knowledge base are saved, which will be further processed by the administrator, expert analyst or programmer;
- In the StatusError collection the statuses for the processed errors by means of which there is a classification of errors are saved;
- In the KnownError collection all known to the knowledge base errors which were processed by the administrator, analyst or programmer are saved;
- In the Answer collection variants of the solutions for the processed errors and errors which are in the KnownError collection are saved;
- In the LogQuery collection filter options are saved, by properties, to find the desired log objects;
- In the QueryConfig collection the filtering options already selected by users are saved.

The diagnostic expert system works under the control of the LogHelper software product. The description and detailed algorithm of the program are given in [4]. The structure of the expert system is shown in (Figure 3), which consists of: the database designed to store log files received and processed by the parser; knowledge base, which contains the knowledge of experts about known errors and ways to eliminate them; a mechanism of logical conclusions that allows to identify errors with those saved in the knowledge base, a module of knowledge acquisition, which provides interaction of the system with the expert and a module of advice and explanations, which is the interface between the user and the system.

System administrator, expert analyst and programmer-developer can be users of the system in the process of testing a distributed system.

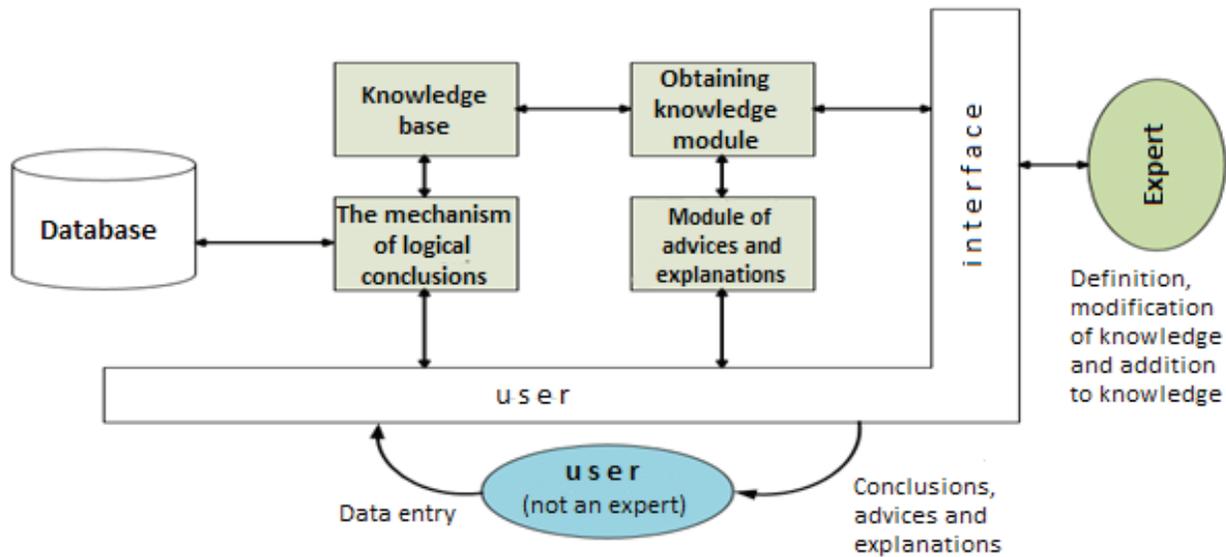


Figure 3. The structure of the expert system

After starting the LogHelper program, the system offers to select log files for analysis, or the user can select from the top menu bar the section «work with log objects», where it is possible to:

1. Construct queries on log objects;
2. View the results of the query;
3. Consider all known and unknown, for the system, errors;
4. Process the unknown error and set the status for it;
5. Suggest existing solutions to the user.

#### *The mechanism of logical conclusions*

The mechanism of logical conclusions provides a search by complete coincidence or by key words, for information about the error in the log file object processed by the parser (hereinafter – the error). If such information is present in the knowledge base, then the mechanism of logical conclusions transfers control of the module of advice and explanations. If not, the inference mechanism compares the objects processed by the parser with already existing messages similar to the found error, counts the number of similar errors and saves it in the database for further processing.

#### *Knowledge acquisition module*

*Processing of unknown errors.* When analyzing log files, the system checks the generated Logs object for the error property and determines whether the error is known to the system. The check is based on data on known errors from the knowledge base. If the system recognizes the error as unknown, it will be saved in the database and in the future processed by the analyst. Expert Analyst has the opportunity to process the error by setting the status and option or solutions (Fig. 4). In the background it is seen that the error message identifies 'Not found' and indicates the number of errors of this type. The system attracts attention of the analyst-expert to an unknown error, indicating the frequency of its occurrence. The active window lists the events close to the unknown error and their status.

When specifying a status for an unknown error, it is possible to create a new status or select an existing one. With the help of the status it is easy to classify errors and filter data for further analysis of the correctness of the distributed system of the bank.

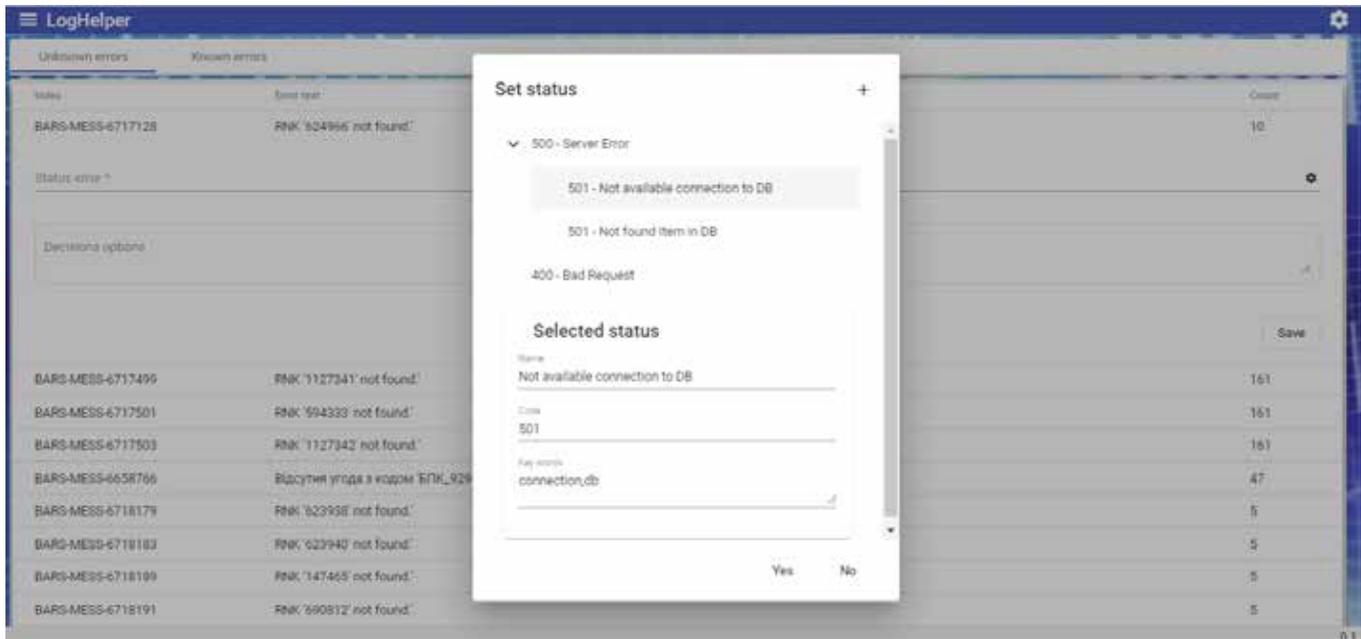


Figure 4. Interface for determining the status of an unknown error

*The module of advice and explanations – the offer of options of decisions for the user*

*Known errors.* This section displays all errors handled by experts which are known to the system and are stored in the knowledge base. The known error, as a result of the logical inference mechanism, (full match search or by keywords) is displayed with the following information:

- Error status, which describes its code and title;
- The answer or solution of this problem;
- Number of similar errors found.

The found information is provided to the user through the user interface (Fig. 5).

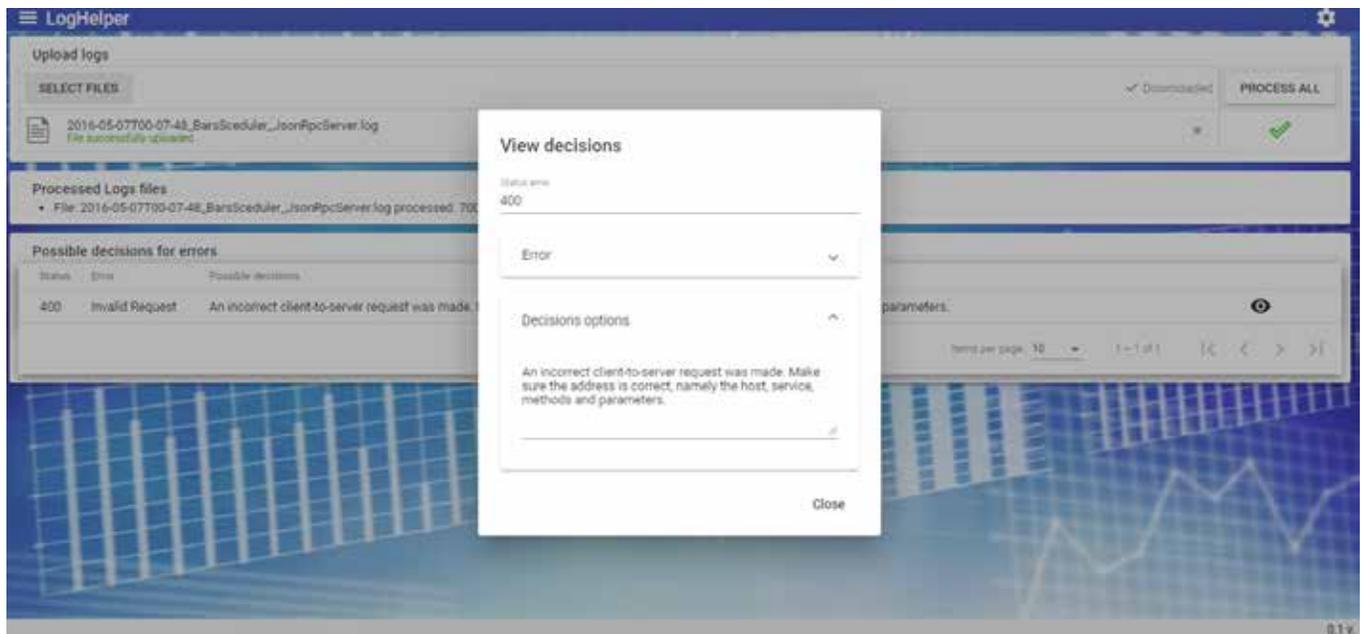


Figure 5. Administrator user interface with solution offer

When the processing of log files is completed, the expert system displays information about the result of processing – this is the number of created objects and errors found, as well as suggestions for their elimination. The user has the opportunity to see the errors which are known to the system and view the solutions offered by the system.

When processing a log file, the LogQuery object is expanded with new properties found during the analysis of the log object. The user has the opportunity to select the desired property and add it to the QueryConfig collection for further quick search for the specified parameters.

A certificate of ownership of the computer program Log Helper was received [5].

#### IV. Efficiency of implementation of expert diagnostic system

One of the tasks of the study was to evaluate the effectiveness of the proposed method and expert system. The effectiveness of the expert system, as proposed in [6] was considered on the example of determining the payback and return (return of lost profits) from investment in the developed project. Profitability of the project – ROI (return on investment) can be calculated by the formula:

$ROI = \text{net return on investment} / \text{amount of expenses (investments)}$

As sources of economic effect (ROI) from the introduction of the expert system, the amount of returned benefit from the successful conduct of transactions in the distributed information system of the bank was considered. The amount of lost profit from the failure of transactions for the settlement period (month) was calculated by the formula (11)

$$V_{(j)} = \sum_j^n P_j x_j, \quad (11)$$

where  $x_j$  – the volume of the bank's provision of the  $j^{\text{th}}$  type of services;

$P_j$  – profit from the provision of the  $j^{\text{th}}$  type of services;

$J$  – transactions which failed as a result of a system error and the benefits of which were lost;

It was assumed that formula (11) corresponded to the lost benefit which can be recovered as a result of the operation of the diagnostic expert system.

The objective function of recovering lost profits through the use of an expert system will be as follows:

$$F_{(j)} = \sum_j^n P_j x_j - (C_a + C_v + C_c) \rightarrow \max, \quad (12)$$

where

$C_a$  – depreciation deductions from the cost of the expert system,

$C_v$  – monthly costs for the operation of the expert system

$C_c$  – monthly expenses for maintenance of the expert system.

As a result, the conclusion was, that it was necessary to assess the return on investment in the developed expert system by making profit from transactions which failed, but were quickly corrected and did not lead to lost profits by either the bank or the client. A few examples of solutions which can be sources of ROI:

1. Monitoring of failures, data on which are already available in the expert system of the bank:

- identification of the cause of failure;
- search for recommendations (solutions) to eliminate the problem;
- transmission of the message to the node of the distributed system.

The solution was providing up-to-date information on the nature of the failure or error and ways to eliminate them. Since the selected DBMS MongoDB has a high speed, the client receives feedback from the system in minutes, in contrast to the manual processing of arrays of log files.

2. Monitoring of failures, data on which are missing in the expert system:

- providing the system administrator with a list of similar errors that have already been described in the knowledge base;
- replenishment of the knowledge base with new knowledge about possible errors, which reduces the entropy of the system.

The solution was replenishment of the knowledge base, which enhances the benefits of implementing an expert system, described in paragraph 1.

3. Monitoring of successful transactions:

- accumulation of data on successful transactions in the knowledge base;
- collection of statistical data based on the calculation of successful transactions;

The solution was use of the accumulated information to analyze the efficiency of the bank's branches.

The result of the implementation of the system will be an increase in the bank's income by reducing losses on individual transactions of the bank by prompt detection of errors.

## V. Conclusions

As a result of the study it was found that log files are very powerful tool for analyzing the performance of remote nodes in a distributed system. Using an expert system, run by LogHelper, allowed to build clear and accurate queries for the analysis of log files, create a classification of errors. The system provides a learning process and has knowledge of known and unknown errors.

With the help of a knowledge base, the expert system has the ability to automatically find and suggest solutions to found errors. All these measures will help to increase the reliability of the distributed system and thus increase the efficiency of the bank.

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## Section 2. Agricultural sciences

<https://doi.org/10.29013/AJT-21-9.10-17-22>

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### **SURVEY AND FIELD MONITORING FOR POTATO PLANT AND POTATO TUBER MOTH (PHTHORIMAEA OPERCULELLA) PEST IN KORCA REGION, ALBANIA YEAR 2020**

**Abstract.** *Phthorimaea operculella* (Zeller 1873) [1] is already considered one of the main pests of potato crop both in the field and in the storehouse. In order to know better and how much this pest affects the potato production in terms of its storage, monitoring and several surveys were conducted in the two municipalities of the Korca region that cultivate significant areas with this crop.

This monitoring was carried out with the farmers of the Municipality of Korca and the Municipality of Maliq who cultivate about 1370 ha with potatoes. Through questionnaires were interviewed in both municipalities by 30 farmers respectively. Econex sexual pheromones were used to monitor moths. Monitoring and surveys showed that potato moth has been a major problem for farmers for three years.

During the monitoring with sexual pheromones in the municipality of Korca were caught, within 10 days, from 112 male butterflies in the first generation, to 218 butterflies in the fourth generation. While in the municipality of Maliq from 120 butterflies caught for 10 days in the first generation to 225 butterflies caught in the fourth generation. During the interview it was found that 98% of farmers in both municipalities had knowledge about this pest. 90% of the farmers of the municipality of Korca and 93% of the farmers of the municipality of Maliq managed this pest through chemical treatments in the field as well as in the storage with the fumigant phostotoxin. Only 3.3% of farmers managed it through irrigation and potato cover.

**Keywords:** monitoring, survey, pheromone, interview, potato tuber moth.

#### **Introduction**

The district of Korca cultivated in 2020 a total of      ity of Korca were cultivated 570 ha by 52 farmers 1370 ha with potatoes. From this in the municipal-

and in the municipality of Maliq were cultivated 800 ha by 42 farmers.

Potato culture occupies an important place in the agricultural economy of the Korca region. In terms of area, it ranks first in the region with 3575 ha. In the municipality of Korca this crop is ranked in the fourth place after the crops of wheat, maize and barley, while in the municipality of Maliq it is ranked in the third place, after the crops of wheat and maize.

Potato is one of the main products in the perspective of agriculture (APP, 1995) [2]. Pests and diseases of potatoes, especially moth and potato blight and also the high prices of agricultural inputs are key factors in increasing the cost of potato production. Especially the production damage in the storage from the potato tuber moth (*Phthorimaea operculella*) (Zeller, 1873) [1] has limited the production and storage of quality potatoes.

However, infested tubers may reduce marketability, and damage can be distinctive in storage, especially in non – refrigerated systems (Arnone, S.; Musmeci, S.; Bacchetta, L.; Cordischi, N.; Pucci, E.; Cristofaro, M.; Sonnino, A. R1998) [3]. Moreover, *P. operculella* is responsible for about 20–30% infestation in the field, and 100% under storage (Gao, Y. L. 2018) [4]. Other authors cite that losses range goes 30–85% in storage (CIP, 1988; Joshi, 1989; Palacios and Cisneros, 1996; Lal, 1998; Douches et al., 1998) [5; 6] Malakar-Kuenen and Tingey 2006, concluded that the thicker periderm thickness of tubers was responsible to slowdown the penetration of larvae inside tubers.

Horgan et al. 2010 [7] and Mansouri et al. 2013 have indicated that the tuber flesh firmness negatively affects larval developmental.

The first damages appeared in the lowland and coastal area of Albania in 1948, with imported potato seed. Korca region did not have big problems with this pest, as the damage from it has been inconsiderable and sporadic. But in 2018 was reported the first serious losses on separate plots. While the years 2019, 2020, 2021 have been dramatic for the farmers

of this region, because almost all the plots planted with this crop were damaged.

During 2019 in the Korca region about 400 ha of potatoes were not harvested due to the damage caused by potato tuber moth and the production in storage was almost totally compromised. Production losses in storage ranged from 40–100%. (CIP, 1988) [5] Other authors conclude about a storehouse loss at levels of 30–70–100% of it Rondon et al. 2010 [8] studied potato lines, some of which show promising results for mining control and number of larvae in potato tubers. She confirmed that the tubers of the transgenic clone Spunta G<sub>2</sub> were resistant to *P. operculella* damage. Spunta G<sub>2</sub> was developed in early 2000 (Joshi, S. L. 2004) [9].

This monitoring and survey were conducted to assess farmers' perception of potato production as well as the knowledge about potato tuber moth (*Phthorimaea operculella*), to control and manage it in both field conditions and potato storage.

### Materials and methods

Interviews with farmers were conducted in the two municipalities of Korca and Maliq, in March-April 2020. Potato tuber moth (*Phthorimaea operculella*) was monitored with sexual pheromones in June, July, August and September of each year. In both municipalities were listed to be interviewed a total of 60 farmers, 30 farmers for each municipality which cultivated larger areas with potatoes, from 5–50 ha. During the interview the farmers were asked about problems related to the factors that have influenced at the control of pests and diseases in the potato crop. Econex sexual pheromone were used to monitor potato tuber moth which can be used for monitoring for about 40 days in a row. In each month three sexual pheromones were used for every three plots in both municipalities. Every two days they were monitored the traps and the number of male moths caught was recorded.

### Results and discussion

#### *Factors affecting the potato production*

Selection of suitable soils, use of high generation seeds, good potato cover during vegetation, irrigation

and measures taken by farmers to treat pest and diseases were some of the factors that led to obtaining high yield. Also, the educational level of farmers is very good, because 80% of them have high school education and 20% have university education, mainly in agriculture.

Negative factors such as pest and disease, high price of chemical fertilizers, pesticides and problems with sales, have led to a reduction in the area planted with this crop. (Tab. 1). The selling price of potato production in the market varies from 30–40 \$.

Table 1. – Factors that have influenced potato production in both municipalities

Swot	Factors	Korce Municipality		Maliq Municipality		Amounts Frequency	Average %
		Frequency	%	Frequency	%		
Positive factors	Suitable soil	21	70	24	80	45	75
	Seed quality	24	80	21	70	45	75
	Mechanization of processes	27	90	30	100	57	95
	Possibility for irrigation	18	60	21	70	39	65
	Plant protection techniques	18	60	18	60	36	55
Negative factors	Diseases and pests	24	80	27	90	51	85
	Small plot areas	21	70	18	60	39	65
	Problems with sales	18	60	15	50	33	55
	High price of inputs	9	30	12	40	21	70
	High price of land rent	18	60	24	80	42	70
	Storage possibility	9	30	9	30	18	30
	Insufficient technical advice	18	60	21	70	39	65
	High prices of works with agricultural mechanics	18	60	24	80	42	70
Opportunities	Subsidies from the state	3	10	3	10	6	10
	Consolidation of agricultural land	6	20	3	10	9	30
	Donations from the EU	–	–	–	–	–	–
	Agrochemical analysis of soil	2	6.6	1	3.3	3	10
	Improving parcel infrastructure	18	60	15	50	33	55
	Increased soil fertility	9	30	6	20	15	50
Threats	Increasing oil prices	27	90	27	90	54	90
	Burning of peat soil	-	-	9	30	9	15
	Increasing air temperatures	18	60	18	60	36	60
	Abandonment of agriculture by young people	18	60	15	50	33	55

Among the main factors that affects the production, 85% of farmers surveyed in both municipalities, singled out mainly pests and diseases, 70% of respondents noted high prices of chemical fertilizers ranging from 40–80 \$/kv and rent of agricultural

land ranging from 70–100 \$/two. Retail price of oil ranging from 16–18 \$/liter, purchase of potato seed ranging from 1.06–1.2 \$/kg. the high price of chemical fertilizers significantly increases the cost of potato production.

Prices of agricultural products such as plowing, discarding, milling, cultivation and irrigation have had high tariffs ranging from 10–15 \$/dynam. Potato fertilization, realized empirically because 90% of farmers have not done agrochemical soil analysis and only three farmers have done them. Only two farmers in both municipalities have typical potato storage, other farmers have adapted different facilities for its storage. From the interview and monitoring in the potato plots it resulted that in both municipalities the main pests were potato tuber moth (90% of farmers) and Colorado potato beetle (63% of farmers), while the main diseases were Late blight, viruses and fusarium wilt, respectively 63%, 23% and 16% of farmers (Table 2).

Four farmers in the municipality of Korca and 2 farmers in the municipality of Maliq did not apply any control measures for pests and diseases. While applying pest and disease control using pesticides, 27 farmers in the municipality of Korca and 28 farmers in the municipality of Maliq (Table 3). The finding is consistent with DADO (2003) [10] and Joshi et al. (2004) [9]. Only 2 farmers in the municipality of Korca and only one farmer in the municipality of Maliq used other control methods such as planting at depths over 10 cm and regular irrigation with reduced water rates, around 250 m<sup>3</sup>/ha, ensuring potato production in wire mesh storage and sulfur combustion in storage using 35 gr/m<sup>3</sup> ambient volume.

Table 2.– Main pests and diseases in potatoes in the Municipalities of Korca and Maliq. 2020 Year

Pests and diseases	Korca Municipal-ity		Korce Municipal-ity		Amounts	Mean%
	Frequency	%	Frequency	%		
<b>PESTS</b>						
Potato tuber moth ( <i>Phthorimaea operculella</i> )	28	93	26	86	54	90
Colorado potato beetle ( <i>Leptinotarsa decemlineata</i> )	24	80	22	73	46	63
Aphids	6	20	4	13	10	16
Wireworms. ( <i>Agriotes lineatus</i> )	4	13	6	20	10	33
Nematodes	3	10	2	6.6	5	8
Turnip moth. ( <i>Agrotis segetum</i> )	2	6.6	4	13	6	10
Field rats. ( <i>Microtus arvalis</i> )	2	6.6	12	40	14	23
<b>DISEASES</b>						
Late blight. ( <i>Phytophthora infestans</i> )	16	53	22	73	38	63
Fusarium wilt. ( <i>Fusarium oxysporum</i> )	4	13	6	20	10	16
Black scurf. ( <i>Rhizoctonia solani</i> )	6	20	2	6.6	8	13
Common scab. ( <i>Streptomyces scabies</i> )	2	6.6	3	10	5	8
Dry scab. ( <i>Spondylocladium atrovirens</i> )	3	10	1	3.3	4	6
Dry rot. ( <i>Fusarium solani</i> )	2	6.6	5	16	7	11
Black leg. ( <i>Pectobacterium carotovorum</i> )	-	-	3	10	3	5
Mosaic. ( <i>Potato virus X. Solanum virus 1</i> )	3	10	4	13	7	23
Bacterial ring rot. ( <i>Corynebacterium sepedonicum</i> )	1	3.3	3	10	7	13
Alternaria blight. ( <i>Alternaria solani</i> )	2	6.6	2	6.6	4	13

Table 3.– Data on the application of control measures against pests and diseases

Municipality	No were applied control measures	% of farmers	Yields Kv/ha	Applied the use of pesticides	% of farmers	Yields Kv/ha	Other control methods were used	% of farmers	Yields Kv/ha
Korca	2	6.6	220	27	90	400	1	3.3	260
Maliq	1	3.3	230	28	93	450	1	3.3	275
Amounts	6			51			3		

For 10 days in the Fabula potato cultivar more butterflies were caught in the municipality of Maliq and from generation to generation their number increased significantly. In the municipality of Korca, from 112 butterflies caught in the first generation, 218 butterflies were caught in the fourth generation in September. While in the municipality of Maliq, in the first generation, were caught 120 butterflies and in the fourth generation were caught 225 butterflies (Table 4).

The capture of more butterflies in the municipality of Maliq is explained by the fact that the vegetative mass of potato culture in this municipality is greater and the lands planted with potatoes are very close to each other.

Pheromone has been suggested as an effective means of monitoring and controlling moths in stored potatoes (Chandla et al. 1994) [11]. This was the first census from the area and given the farmer's response, there is a need for a detailed survey throughout the district.

Table 4.– Number of male butterflies captured by pheromones for 10 days

Date	Korca Municipality	Maliq Municipality
20–30 June	112	120
20–30 July	153	162
21–31 August	192	203
22 september – 1 october	218	225

### Conclusions

- Seed quality and taking chemical control measures for diseases and plant pests are two of the main factors influencing high potato yields;
- Potato pests and diseases negatively affected about 10% of farmers in the municipality of Korca and 7% in the municipality of Maliq, because they did not use any control measures. Their yields were 220 kv/ha and 230 kv/ha, respectively;
- Potato tuber moth, Colorado potato beetle and Late blight are the main threat to potato production for farmers of both municipalities;
- 90% of farmers in the municipality of Korca and 93% of farmers in the municipality of Maliq were relied on the use of pesticides to control potato pests and received good yields, respectively 400 kv/ha and 450 kv/ha while 3.3% of farmers for each municipality used other control measures for potato pests and the realized yield was respectively 260 kv/ha and 275 kv/ha potatoes;
- The number of male moths caught within 10 days, increases from generation to generation, reaching its peak in the fourth generation.

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## Section 3. Technical sciences

<https://doi.org/10.29013/AJT-21-9.10-23-27>

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### VISCOSITY CHARACTERISTICS OF THE BINDING POLYMER COMPOSITION

**Abstract.** Studied changes in the rheological properties of the developed composition depending on the concentration of PVA, AE and OP-10. The dependences of the viscosity of gel-like thickeners on the concentration of components of thickening ingredients and the aging time were established. Defined parameters p Results of silk acetate fabric dyeing with dispersed violet 2 s.

**Keywords:** Fiber, composition, concentration, dye, binders, color intensity, fabric, polymer, PVA, acrylic emulsion.

Currently, mixed fabrics made from chemical and natural fibers so have acquired special significance, and an important place among them is occupied by fabrics made from a mixture of silk and acetate fibers. Fabrics of this group are very promising, since they have high resistance to crumple smearing, strength, and shape stability [1–3].

Considering the specificity of mixed fibers essential value in coloring, the choice of dyes or their mixtures, binding-thickening substances and coloring technologies is of primary importance when coloring such materials substances and technologies of coloring. More often dyeing of silk and acetate composing products, dispersed dyes are used for dyeing silk and acetate components, and when dyeing, the conditions for compatibility of dyes in binding-thickening mixtures in terms of chemical activity and temperature modes of coloring must be observed.

For this the most promising and most reason, dispersed dyes are the most promising and environmentally relevant coloring agents for mixed textile materials dispersed dyes. They are ideally compatible for dyeing fibrous substrates of any composition. Particles of dispersed dyes are “glued” to the surface of substrates using a polymer binder. Sorption and diffusion processes are excluded with this dyeing technology. At the same time, the factors that determine the incompatibility of the components of the dye composition are excluded, which makes it possible to evenly from mixtures of silk and chemical fibers [4–5].

The development of a technology for dyeing fabrics of various fibrous compositions based on polymer binding and thickening preparations of domestic production, which can replace expensive textile compositions, becomes an urgent task for research imported compositions [6].

To solve this problem, at the first stage of the work, a comparison was made in terms of the viscosity properties of binding-thickening compositions used in dyeing silk-acetate fabrics with dispersed dyes when using polymer preparations of foreign and domestic production.

In the presented composition, we used a water-soluble polymer of polyvinyl acetate, an acrylic emulsion, and surfactants OP-10 at different ratios.

Based on the selected components, the compositions of the binder-thickening composition are prepared.

From the obtained data (Table 1) it can be seen that the viscosity of the resulting composition with the same concentration of PVA is relatively high. If at 298 K the viscosity of a 1.0% solution of PVA reaches 17.24 Pa·s, then the viscosity of the same solution with additives AE and OP-10 with concentrations of 1.0 and 0.5%, respectively, relative to the weight.

The PVA will be 23.64 Pa·s. The viscosity of the solution is 22.51 Pa·s if the concentration of PVA is increased to 2.0%. The viscosity of the system increases to 31.27 Pa·s with the introduction of AE and OP-10 (the concentration is 1.0 and 0.5, respectively, of weight PVA), in this case, the viscosity of the system will be 1.5 times greater than the initial one. Based on this, we can say that the functional groups of the initial components interact due to Van der Waals forces. It should also be emphasized that adding air into the system not only increases its viscosity, but also leads to an increase in the degree of thixotropic reduction, which subsequently reduces the yield strength of the thickener. If the concentration of PVA reaches 1.5%, thixotropic reduction – 87.4% and yield strength – 42.10 g/cm<sup>2</sup>, at the same concentration of PVA, with the addition of AE in the range of 1.0% and OP-10 0.5%, then the values will change as follows: 96.6% and 38.57 g/cm<sup>2</sup>, respectively.

Table 1. – Changes in the rheological properties of the developed composition depending on the concentration of PVA, AE and OP-10

Concentration, PVA concentration in binders, %	Concentration of modifiers, % by weight PVA		n, Pa·s (T=298K)	Degree of thixotropic recovery, %	Yield strength, Rm, g/cm <sup>2</sup>
	AE	OP-10			
1	2	3	4	5	6
1.0	–	–	17.24	83.2	44.36
1.5	–	–	of 21.43	87.4	42.10
2.0	–	–	24.51	95.6	28.37
1.0	0.5	–	of 19.63	85.3	43.11
	1.0	–	24.42	87.8	40.70
	1.5	–	33.87	90.1	36.20
	–	0.4	loss of 16.85	82.2	42.25 mln
	–	0.5	15.72	85.3	45.13
	–	0.6	14.17	89.2	46.78
	1.0	0.5	23.64	94.2	of 44.16
1.5	0.5	–	of 21.48	89.6	42.83
	1.0	–	27.35	93.2	of 39.75
	1.5	–	35.08	95.4	36.84
	–	0.4	of 18.43	84.6	41.17
	–	0.5	16.45	88.7	43.28
	–	0.6	15.61	91.3	45.04
	1.0	0.5	of 26.72	96.6	38.57

1	2	3	4	5	6
2.0	0.5	–	was 26.70	92.4	44.15
	1.0	–	32.45	96.7	41.23
	1.5	–	41.07	98.6	of 38.64
	–	0.4	of 20.66	of 86.2	44.72
	–	0.5	20.18	90.4	of 47.17
	–	0.6	of 19.92	93.3	49.54
	1.0	0.5	's 31.27	98.2	40.24

Important factors that determine technological properties binding and its qualities are the chemical nature, structure, complex chemical properties of the ingredients of binding-thickening systems. In addition, the binder must have high elasticity, have sufficient viscosity at a low concentration of binding components and a high wetting capacity of the fibrous material, be stable during storage and use, and have ease of washing.

The porous structures of “alkaline” viscous compositions containing PVA, AE, and OP-10 as binding agents are characterized by good stability. The stability of such compositions prepared from polymer solutions of various concentrations was evaluated by the viscosity of the system immediately after preparation and after holding for a day. The corresponding dependencies are shown in (Fig. a, b).

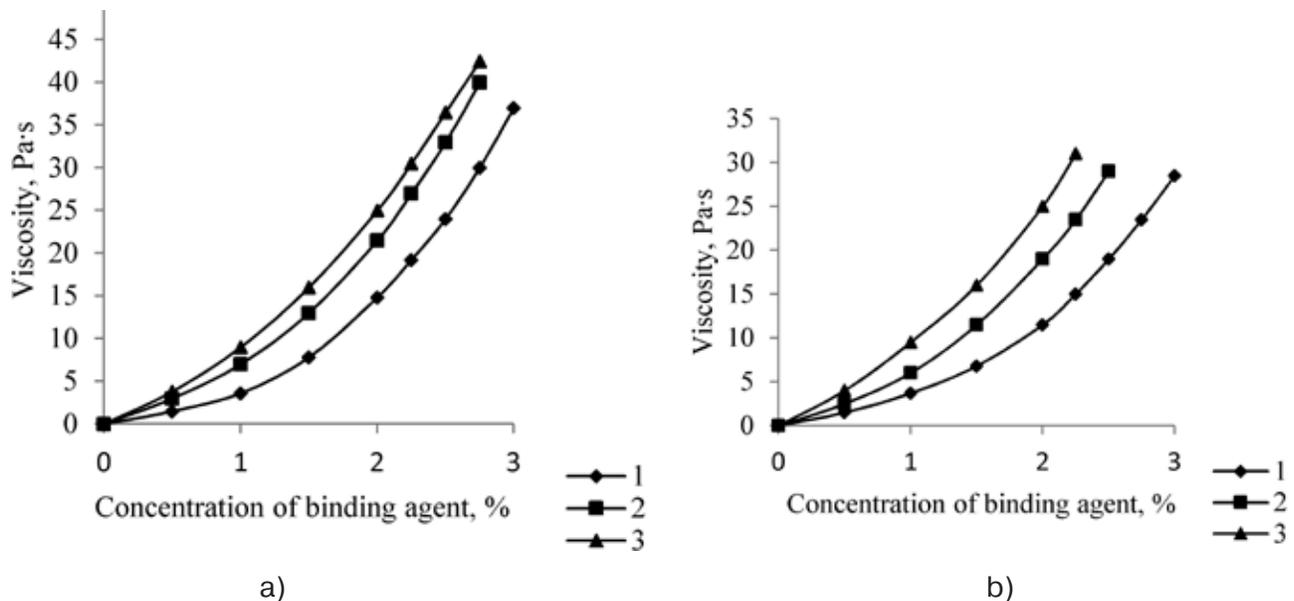


Figure 1. Dependence of the viscosity of gel-like thickeners on the concentration of components of thickening ingredients and the holding time  
 Binding based on: 1. PVA and OP-10; 2. PVA-AE-OP-10; 3. PVA-AE. a) – freshly prepared binder; b) – a viscous system after 24 hours of exposure

It can be seen from the graphs that the most preferred method is to use viscous systems based on PVA, AE and OP-10 preparation (Fig. Curve 3), wherein the compositions of PVA, AE, and OP-10 have the required dynamic viscosity (48 Pa·c) at the concentration of PVA – 2.0%, AE-1.0% and OP-10 0.5%, and after holding the

composition for a day, it decreases to 33 Pa × s. The possibility of preparing binding-thickening three-component compositions from PVA, AE, and OP-10 are not excluded, and the most effective are low-concentration systems based on PVA, AE, and OP-10 and at concentrations of 1.5, 1.0, and 0.5%, respectively.

In order to develop the technology of the process of dyeing with dispersed dyes, the binding-thickening compositions were optimized. The optimization criteria are selected indicators of paint intensity, fabric softness and paint resistance to friction, presented in (Table 2).

The problem of obtaining high resistance of paints to friction when use-dispersed dyes is an actual problem. And when coloring mixed fabrics based on silk and acetate fibers, which are characterized by a 2C violet color C and high chemical inertia, this problem is aggravated.

It is possible to increase the stability of paints when dyeing with dispersed dyes using so-called fillers as additives to polymers, which, due to the presence of functional groups capable of chemical interaction, contribute to the formation of spatial mesh structures in the film-forming polymer and increase its resistance to abrasion. As a filler, we have proposed AE.

Fillers have a positive effect on particle distribution, the effect of dispersed dyes in the painted material on the structure and rheological properties of paints increases the hardness and durability of coatings.

Table 2. – Results of silk acetate fabric dyeing with dispersed dye, purple for 2 seconds C

Component ratio, g/l			Color intensity, K/S	Weaver's softness, deg	Endurance Ok – raskystrength	
PVA	AE	OP-10			to the dry friction	to wash
0.5	–	–	2.3	64	3	2.0
1.0	–	–	2.7	61	3	2.0
1.5	–	–	3.1	60	3	2.5
2.0	–	–	3.3	57	4	2.5
0.5	0.5	–	2.5	60	3.5	2.5
1.0	1.0	–	3.0	56	3.5	3.0
1.5	1.5	–	3.5	52	4.0	3.0
2.0	2.0	–	3.7	47	4.0	3.0
0.5	–	0.3	2.4	62	3.5	3.0
1.0	–	0.4	2.8	56	3.5	3.0
1.5	–	0.5	3.1	53	4.0	4.5
2.0	–	0.6	3.5	48	4.0	4.5
1.5	0.5	–	3.2	58	3.5	4.0
	1.0	–	3.4	55	4.0	4.0
	1.5	–	3.5	52	4.0	4.5
1.5	–	0.4	2.9	55	3.5	3.5
	–	0.5	3.1	53	4.0	4.0
	–	0.6	3.3	46	4.0	4.0
1.5	0.5	0.4	3.5	51	3.5	4.5
	1.0	0.5	3.8	44	4.0	4.5
	1.5	0.6	4.1	38	4.0	4.5
2.0	0.5	0.4	3.8	43	4.0	4.5
	1.0	0.5	4.3	34	4.5	4.5
	1.5	0.6	4.6	27	4.5	4.5

The use of the developed composition for dyeing mixed fabrics as a binding component when dyeing fabrics with dispersed dyes is most effective when the content of PVA, AE and OP-10 is 1.5, 1.0 and 0.5 g/l, respectively.

Thus, analyzing the data obtained, we can conclude, that the introduction of e AE and OP-10 in

the system composition of the binding composition not only leads to an increase in the intensity of coloring, but also increases its strength to dry friction and to washing. The most effective effect of color hardening is observed with the combined content of components included in the binding-thickening compositions.

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## Section 4. Chemistry

<https://doi.org/10.29013/AJT-21-9.10-28-34>

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### REACTIONS OF SODIUM SALICYLATE WITH MONOCHLOROACETIC ACID ESTERS

**Abstract.** It was intended to obtain new ester-bound compounds of salicylic acid. For this purpose, new derivatives of salicylic acid were obtained by reacting the sodium salt of salicylic acid with methyl, ethyl, propyl, butyl, isopentyl, hexyl and benzyl esters of monochloroacetic acid in the presence of aprotic polar solvents. The structure of the obtained compounds was confirmed using physical research methods. The mechanism of reactions, physical, chemical and biological properties of substances were studied.

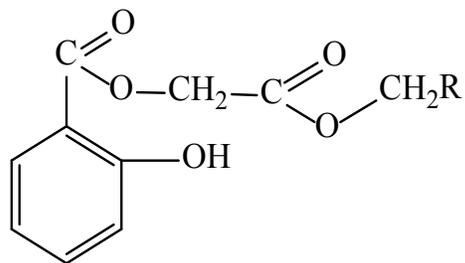
**Keywords:** alkyl halide, nucleophilic substitution, dimethylformamide, esters, sodium salicylate, sodium monochloroacetate, spectroscopy.

#### Introduction

Salicylic acid and its esters are widely used today in perfumery, national economy, food industry, pharmaceuticals, medicine as drugs [1, 95–105; 2, 95–105; 3, 1179–1206]. For example, acetylsalicylic acid (aspirin) is widely used as a fever-reducing drug,

phenylsalicylate (solol) as an anti-inflammatory and restorative, methyl salicylate, ethyl salicylate as non-narcotic analgesics [4, 622–629; 5, 95–96; 6, 1621; 7, 125–127]. In addition, salicylic acid and its derivatives are also used in agriculture as a means

of accelerating the growth of plants and their fight against various diseases [8, 233–235; 9, 19–39]. Several esters of salicylic and acetylsalicylic acid, including phosphorus-containing esters, and amides, have been synthesized by Russian scientists and their properties have been studied. Some esters of salicylic acid are also found naturally in plants. But using them in the right amount is time consuming and expensive [10, 175176; 11, 325; 12].



Picture 1.

It was scientifically theoretically assumed that the obtained compounds had the same high biological activity and important practical significance as the previously obtained compounds of salicylic acid. The results of experiments confirmed this.

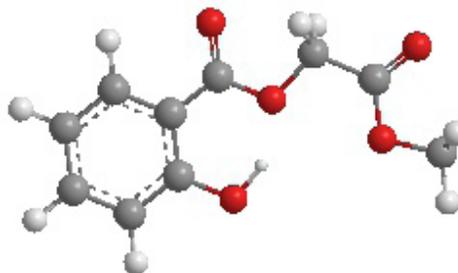
#### Materials and Methods

In the studied scientific studies, we studied the reactions of the sodium salt of salicylic acid with hydrochloric acid with methyl, ethyl, propyl, n-butyl, isopentyl, hexyl and benzyl esters. In the ini-



The results of the experiments showed that the yield of the reactions carried out over 4 hours was high (Table 2). The purity of the reaction products was determined by gas-liquid chromatography at 95–97% (in the instrument “Shimadzu” GS2010 Plus). The obtained ethers are colorless or light yellow oily liquids, insoluble in water, well soluble in organic solvents. In the next step, the reactions of monochloroacetic acid esters with the sodium salicylate salt were performed in a dimethylfor-

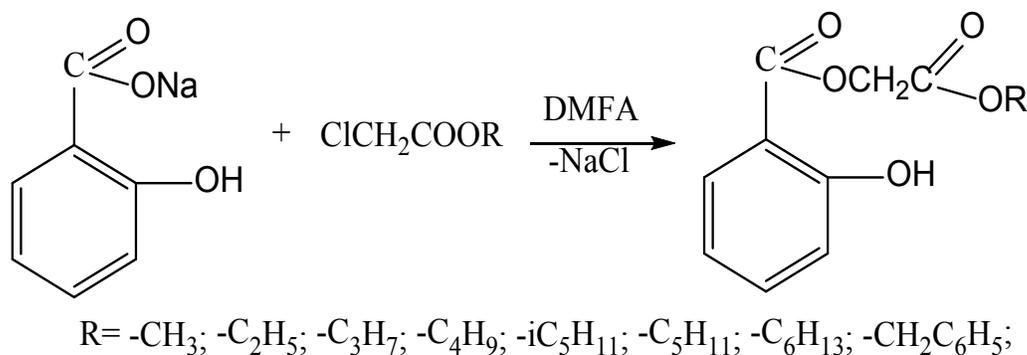
The high demand for them is of great theoretical and practical importance in the study of methods for the synthesis of various new derivatives of salicylic acid, their improvement. In the framework of this research, two complex ether-binding compounds can be obtained when nucleophilic substitution reactions of salicylic acid sodium salt with monochloric acetic acid esters are carried out in the presence of aprotic solvents (Pic. 1–2).



Picture 2.

tial process, nucleophilic substitution reactions of methyl, ethyl, propyl, n-butyl, isopentyl, hexyl and benzyl chlorides with the sodium salt of monochloroacetic acid were carried out in the presence of a dimethylformamide solvent [13, 198–202]. Mole ratios of reagents were obtained in the order 1: 2: 6 in the order of sodium chloroacetate: alkyl halide: DMFA. As a result of the reactions, the corresponding esters of hydrochloric acid were synthesized in high yields.

mamide solvent [14, 43–45]. In the reactions, two new ester-related compounds of salicylic acid, such as carbmethoxymethyl salicylate, carbethoxymethyl salicylate, carbopropoxy methyl salicylate, carbutoxymethyl, carbizopentoxymethyl, carbhexoxymethyl, carbenboxoxymethyl salicylate, were synthesized in high yields. The general equation of the reaction is as follows:



It is known from the literature that reactions involving organic substances can go in different directions depending on the conditions and the influence of external factors. Therefore, the given reactions were studied taking into account the quantitative ratio of initial reagents to the product yield, the duration of the reaction and the influence of other factors (Table 3). The physical properties of the obtained salicylic acid esters were studied and their structure was studied and confirmed using physicochemical research methods (IR,  $H^1$ NMR,  $C^{13}$ NMR).

IR spectral analysis of carbmethoxymethyl-salicylate  $\nu_{Ar-OH}=3205\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2963\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1680-1760$ ,  $\nu_{C-O-C}=1100-1260\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=703-848\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR-[400 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=3.75$  (s, 3H), 4.84 (s, 2H), 6.80 (td,  $J=8.01, 6.32, 7.1\text{ Hz}$ , 1H), 6.90 (dd,  $J=8.44, 8.42\text{ Hz}$ , 1H), 7.40 (td,  $J=8.48, 8.32, 7.29\text{ Hz}$ , 1H), 7.80 (dd,  $J=7.92\text{ Hz}$ , 1H).  $C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=51.6, 60.9, 111.9, 117.2, 119.2, 130, 135.9, 161.4, 168.3, 169.6$ .

IR spectral analysis of carbethoxymethyl-salicylate  $\nu_{Ar-OH}=3216\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2988\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1686-1760$ ,  $\nu_{C-O-C}=1100-1251\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=703-847\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR-[400 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=1.25$  (td,  $J=7.13, 7.14\text{ Hz}$ , 3H), 4.20 (q,  $J=7.16\text{ Hz}$ , 2H), 4.80 (s, 2H), 6.90 (d,  $J=9.03\text{ Hz}$ , 1H), 6.95 (dd,  $J=8.32, 8.21\text{ Hz}$ , 1H), 7.45 (td,  $J=8.45, 7.25, 6.79\text{ Hz}$ , 1H), 7.90 (dd,  $J=8.01, 6.36\text{ Hz}$ , 1H).

$C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=13.1, 61, 61.3, 111.7, 117.2, 119.2, 130, 136, 161.5, 167.8, 169.2$ .

IR spectral analysis of carbpropoxymethyl-salicylate  $\nu_{Ar-OH}=3218\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2968\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1682-1760$ ,  $\nu_{C-O-C}=1100-1250\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=703-847\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR-[400 MHz,  $CD_3OD$ , p.p.m.]  $\delta=0.9$  (t,  $J=7.42$ , 3H), 1.62 (m, 2H), 4.80 (s, 2H), 6.86 (d,  $J=7.23\text{ Hz}$ , 1H), 6.94 (td,  $J=8.31, 8.42, 5.79\text{ Hz}$ , 1H), 7.45 (td,  $J=7.25, 6.83, 8.39\text{ Hz}$ , 1H), 7.88 (dd,  $J=8.00\text{ Hz}$ , 1H).  $C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=9.3, 60.9, 61.3, 66.8, 117.2, 119.2, 128, 130, 136, 161.5, 167.8, 169.2$ .

IR spectral analysis of carbutoxymethyl-salicylate  $\nu_{Ar-OH}=3206\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2963\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1685-1760$ ,  $\nu_{C-O-C}=1100-1250\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=703-848\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR-[400 MHz,  $CD_3OD$ , p.p.m.]  $\delta=0.88$  (t,  $J=7.40$ , 3H), 4.15 (t,  $J=6.46\text{ Hz}$ , 2H), 4.87 (d,  $J=4.45\text{ Hz}$ , 1H), 6.90 (dd,  $J=8.44, 8.42\text{ Hz}$ , 1H), 7.40 (td,  $J=8.48, 8.32, 7.29\text{ Hz}$ , 1H), 7.80 (dd,  $J=7.92\text{ Hz}$ , 1H).  $C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]  $\delta=12.6, 18.7, 30.3, 61, 65, 111.7, 117.2, 119.2, 130, 136, 161.5, 167.8, 169.3$ .

IR spectral analysis of carbpentoxymethyl-salicylate  $\nu_{Ar-OH}=3191\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2959\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1678-1758$ ,  $\nu_{C-O-C}=1100-1248\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=702-849\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR [400 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=0.85$  (m, 3H), 1.3 (m, 4H), 1.6 (m, 2H), 4.90 (t,  $J=9.4\text{ Hz}$ , 1H), 6.90 (dd,  $J=8.44, 8.42\text{ Hz}$ , 1H), 7.40 (td,  $J=8.48, 8.32, 7.29\text{ Hz}$ , 1H), 7.75 (dd,  $J=7.92\text{ Hz}$ , 1H).  $C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=12.9, 22, 27.7, 27.9, 61, 65.9, 113, 117.2, 119.2, 130, 135.6, 161.8, 167.9, 172.4$ .

IR spectral analysis of carbizopentoxymethyl-salicylate  $\nu_{Ar-OH}=3227\text{ cm}^{-1}$ ,  $\nu_{-CH_3}=2959\text{ cm}^{-1}$ ,  $\nu_{-C=O}=1683-1760$ ,  $\nu_{C-O-C}=1100-1250\text{ cm}^{-1}$ ,  $\nu_{C=C}=1615\text{ cm}^{-1}$ ,  $\delta_{CH}=703-847\text{ cm}^{-1}$  (benzene ring).  $H^1$ NMR-[400 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=0.9$  (t,  $J=7.42$ , 3H), 1.62 (m, 2H), 4.80 (s, 2H), 6.86 (d,  $J=7.23\text{ Hz}$ , 1H), 6.94 (td,  $J=8.31, 8.42, 5.79\text{ Hz}$ , 1H), 7.45 (td,  $J=7.25, 6.83, 8.39\text{ Hz}$ , 1H), 7.88 (dd,  $J=8.00\text{ Hz}$ , 1H).  $C^{13}$ NMR-[100 MHz,  $CD_3OD$ , p.p.m.]:  $\delta=9.3, 60.9, 61.3, 66.8, 117.2, 119.2, 128, 130, 136, 161.5, 167.8, 169.2$ .

703–848  $\text{cm}^{-1}$  (benzene ring).  $^1\text{H}$ NMR-[400 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]  $\delta$ = 0.85 (dd,  $J$ =14.4, 16.52 Hz), 1.48 (m, 2H), 1.62 (m, 1H), 4.15 (m, 2H), 4.88 (t,  $J$ = 8.9 Hz, 1H), 6.90 (dd,  $J$ = 8.44, 8.42 Hz, 1H), 7.40 (td,  $J$ = 8.48, 8.32, 7.29 Hz, 1H), 7.80 (dd,  $J$ = 7.92 Hz, 1H).  $^{13}\text{C}$  NMR-[100 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]:  $\delta$ = 21.4, 24.8, 27.6, 36.8, 61.1, 63.8, 111.7, 117.2, 119.2, 130.2, 136, 161.5, 167.8, 169.3.

IR spectral analysis of carbhexoxymethyl-salicylate  $\nu_{\text{Ar-OH}}$ =3210  $\text{cm}^{-1}$ ,  $\nu_{\text{-CH}_3}$ =2958  $\text{cm}^{-1}$ ,  $\nu_{\text{-C=O}}$ =1682–1759,  $\nu_{\text{C-O-C}}$ =1099–1249  $\text{cm}^{-1}$ ,  $\nu_{\text{C=C}}$ =1615  $\text{cm}^{-1}$ ,  $\delta_{\text{CH}}$ = 702–848  $\text{cm}^{-1}$  (benzene ring).  $^1\text{H}$ NMR-[400 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]:  $\delta$ = 0.85 (m, 3H), 1.25 (m, 4H), 1.30 (m, 2H), 1.60 (m, 2H), 4.15 (t,  $J$ =6.52, 2H), 4.88 (t,  $J$ =20.84, 2H), 6.80 (td,  $J$ =8.01, 6.32, 7.1 Hz, 1H), 6.85 (dd,  $J$ = 8.44, 8.42 Hz, 1H), 7.40 (td,  $J$ =8.48, 8.32, 7.29 Hz, 1H), 7.82 (dd,  $J$ = 7.92 Hz, 1H).

$^{13}\text{C}$  NMR-[100 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]:  $\delta$ = 13, 22.2, 25.2, 28.2, 31, 61, 65.3, 112, 117.2, 119.2, 130, 136, 161.5, 167.9, 169.3.

IR spectral analysis of carbbenzoxymethyl-salicylate  $\nu_{\text{Ar-OH}}$ =3205  $\text{cm}^{-1}$ ,  $\nu_{\text{-CH}_3}$ =2957  $\text{cm}^{-1}$ ,  $\nu_{\text{-C=O}}$ =1673–1746,  $\nu_{\text{C-O-C}}$ =1090–1299  $\text{cm}^{-1}$ ,  $\nu_{\text{C=C}}$ =1615  $\text{cm}^{-1}$ ,  $\delta_{\text{CH}}$ = 698–848  $\text{cm}^{-1}$  (benzene ring).  $^1\text{H}$ NMR-[400 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]:  $\delta$ = 4.55 (s, 2H), 5.32 (s, 2H), 6.83 (dd,  $J$ =8.35, 8.09 Hz, 1H), 6.90 (td,  $J$ =8.32, 8.36, 11.81 Hz, 1H), 7.30 (m, 1H), 7.40 (dd,  $J$ =7.31, 7.70 Hz, 1H).  $^{13}\text{C}$  NMR-[100 MHz,  $\text{CD}_3\text{OD}$ , p.p.m]:  $\delta$ = 63.9, 66.7, 112.3, 117.1, 119.1, 128, 128.1, 128.4, 129.1, 129.8, 130.3, 132, 135.6, 161.5, 169.8, 173.2.

The biological activity of several of the synthesized salicylic acid esters against bacteria and fungi was studied in vitro.

Table 1.

Name of substances	Injection zone diameter (mm)		
	Escherichia coli	Pseudomonas aeruginosa	Candida albicans
Carbpropoxymethyl salicylate	7.08 ± 0.12	–	–
Carbethoxymethyl salicylate	7.08 ± 0.12	–	–
Carbmethoxymethyl salicylate	6.08 ± 0.12	–	–

### Results and discussion

In the production of monochloroacetic acid esters, alkyl halides belonging to its sodium salt were affected

in the presence of DMFA solvent. In the reactions, the effect of the reaction time on the product yield was studied and the following results were obtained.

Table 2. – Effect of time on product yield in the reaction of sodium monochloroacetate with alkyl halides in the presence of DMFA

Mole ratios of reagents sodium chloroacetate: alkyl halide: DMFA	Duration of the reaction (Hours)	Yield of chloric acid esters (%)							
		methyl	ethyl	propyl	butyl	pentyl	izopentyl	hexyl	benzyl
1:2:6	3	85	84	82	80	79	78	77	82
1:2:6	4	94	93	92	91	89	87	89	92
1:2:6	5	91	90	89	88	86	87	88	93
Boiling point (°S, 760 mmHg)		129–131	142–144	164	173	197	181–182	213	252–253

In the reactions, the effect of time on product yield was studied and optimal conditions were determined. The following results were obtained when the

effect of time on the product yield was obtained by taking the reagents sodium salicylate: chloric ether: DMFA in the ratio 1: 1.5: 6 mol.

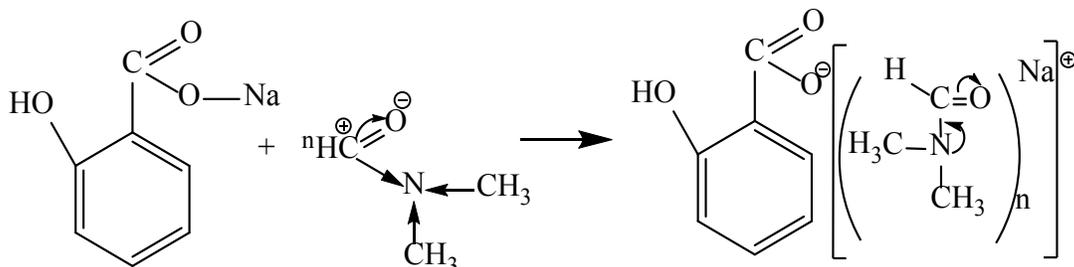
Table 3. – Effect of time on product yield in the reaction of sodium salicylate with monochloroacetic acid esters in the presence of DMFA

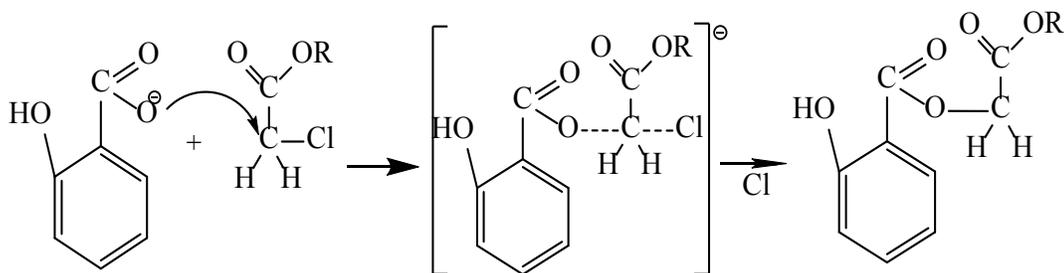
Duration of the reaction (Hours)	Product yield, %							
	Carbomethoxy-methylsalicylate,	Carbethoxy-methylsalicylate,	Carbpropoxy methylsalicylate,	Carbutoxy methylsalicylate,	Carbpentoxy methylsalicylate,	Carbizopentoxy methylsalicylate	Carbhexoxy- methylsalicylate	Carbenzene-methylsalicylate
1	38	37	36	35	34	33	32	30
2	57	55	54	52	50	50	48	47
3	73	72	70	70	69	68	67	65
4	90	89	87	85	84	82	81	77
5	89	88	87	84	83	81	80	79
6	86	85	84	82	81	79	77	78
Rf (silulfol, system methanol: water: ice acetic acid = 7:3:0.2).	0.69	0.72	0.65	0.63	0.61	0.64	0.58	0.67
Boiling point (°S, 760 mmHg)	296–298	305–307	312–315	321–324	332–335	326–328	339–341	347–349

It can be concluded from the results that the optimal conditions for the reactions of obtaining diethers-bonded compounds were 4 hours and it was shown that the product can be obtained with higher yield than others. Experiments have shown that long-term reactions are required to obtain high results from the reaction of hydrochloric acid with benzyl ether with sodium salicylate. This can be explained by the low electrophilic ability of chloric acid in the benzyl ether of the  $S_N2$ - group in the aliphatic esters of chloric acid. It is known that in methylene groups bound to electron receptor groups, they retain specific nucleophilic properties due to the mobility of hydrogen atoms. Therefore, the susceptibil-

ity of this group to nucleophilic attack may be lower than that of other saturated hydrocarbons.

In the experiments performed, dimethylformamide, an aprotic solvent, was used as in our previous work. In these reactions, DMFA was found to act as a solvent and partially catalyst. In other words, the sodium salicylate salt is first dissolved in the solvent, in which DMFA salts the sodium cation formed by the dissociation of the salt and increases the nucleophilic capacity of the carboxylate anion. All the reactions studied proceed in the  $S_N2$  nucleophilic substitution mechanism. The process mechanism can be described as follows:





### Conclusion

In the experiments, nucleophilic substitution reactions of sodium salicylate with monochloroacetic acid esters in the presence of aprotic soluble dimethylformamide were carried out under different conditions, two new ester-bound organic substances were obtained and optimal conditions for obtain-

ing products were determined. The structure of the obtained salicylic acid esters was confirmed by IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR spectroscopy, the physical and chemical properties of the esters were studied. In the indicated methods it is possible to synthesize two ester-bound derivatives of salicylic acid in efficient products.

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<https://doi.org/10.29013/AJT-21-9.10-35-39>

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## SYNTHESIS OF TERTIARY ACETYLENIC ALCOHOLS DIBENZO-18-CROWN-6 FROM 4', 4''-DIAMINODIBENZO-18-CROWN-6

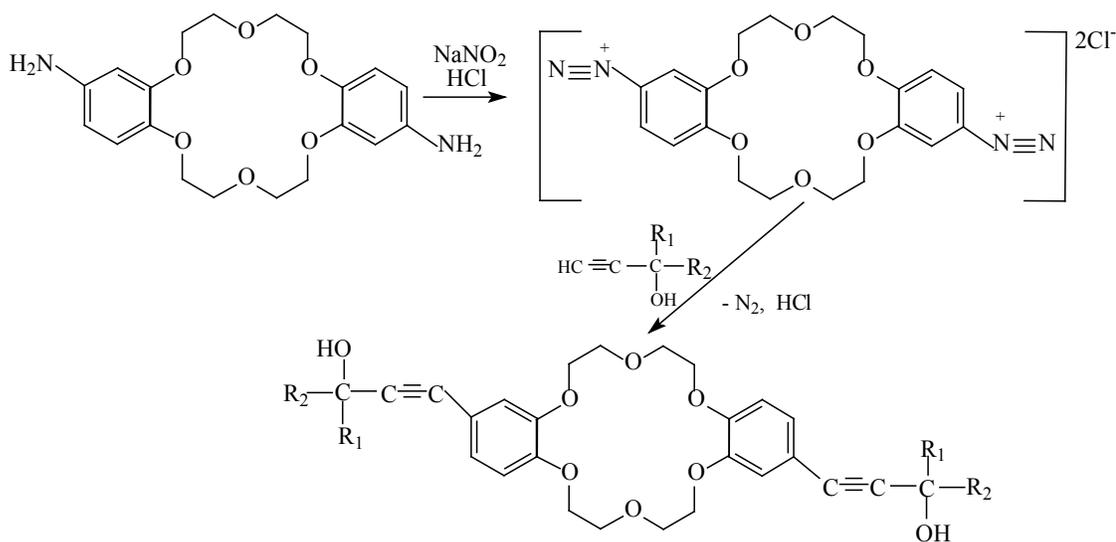
**Abstract.** Tertiary acetylenic alcohols dibenzo-18-crown-6 were synthesized by diazotization of 4', 4''-diaminodibenzo-18-crown-6 followed by nitrogen evolution, the main characteristics of the structures and the data of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra are given.

**Keywords:** acetylenic alcohols, dibenzo-18-crown-6, diazotization.

Acetylenic alcohols are of considerable interest due to a wide range of their useful properties; in addition, these compounds serve as objects for the study of many fundamental problems of organic chemistry.

Acetylene compounds play an important role as unique synthons with high synthetic potential, since the triple bond is prone to electrophilic, radical, and bipolar addition reactions, as well as transformation involving the methine hydrogen atom with abnormally high acidity.

Acetylene alcohols are widespread in various natural resources: in plants, fungi, bacteria, algae, and in sponges [1, 399–402]; possess several reaction centers [2, 1924–1928], have an OH- and acetylene group, are potential donors of hydrogen bonds, as well as acceptors [3, 54318–54325], exhibit anticorrosive properties [4, 496–508]. Acetylene lipids have been created to determine the configurations of aminoalkanes [5, 2291–2298] and many others [6, 101–112].



I:  $\text{R}_1=\text{R}_2 = -\text{C H}_3$ ; II:  $\text{R}_1 = -\text{C H}_3$ ,  $\text{R}_2 = -\text{C}_2\text{H}_5$ ; III:  $\text{R}_1 = -\text{H}$ ,  $\text{R}_2 = -\text{C}_2\text{H}_5$

There are many ways to introduce the  $C\equiv C$  fragment into an organic molecule [7, 23–25]. Many works on the synthesis of acetylene compounds of benzocrown ethers are based on the Heck-Sonogashira reaction [8, 27–39], cross-coupling of terminal alkynes with aryl halides. Earlier [9, 18–21], we obtained tertiary acetylenic alcohols dibenzo-18-crown-6 by the Favorsky method, but the ethynyl group –  $C\equiv C$  – is linked to the aromatic system through 1 carbon atom.

The main goal of this study is the synthesis of tertiary acetylene alcohol by diazotization of 4', 4''-diaminodibenzo-18-crown-6 and subsequent reaction with acetylenic alcohols with the evolution of nitrogen. A feature of this synthesis is the forma-

tion of a product with a  $C\equiv C$  triple bond directly linked to the benzene ring of dibenzo-18-crown-6.

Acetylenic alcohols dibenzo-18-crown-6 were synthesized by the diazotization method 4', 4''-diaminodibenzo-18-crown-6. The resulting salt of the diazo compound dibenzo-18-crown-6 is formed by the interaction of the diamino derivative of dibenzo-18-crown-6 with sodium nitrite in dilute hydrochloric acid in the presence of copper (I) salts. Diazonium salt based on 4', 4''-diaminodibenzo-18-crown-6 is stable during the day, when interacting with acetylenic alcohols with a terminal triple bond, acetylenic alcohols dibenzo-18-crown-6 are formed, in the molecule of which there is a triple bond directly at the benzene nucleus of the macrocycle.

Table 1. – Some characteristics of a series of 4', 4''-diacetylenic alcohols based on 4', 4''-diaminodibenzo-18-crown-6

№	Compounds	m.p. °C	Yeild,%	Found,%		Gross formula	Calculated,%		
				C	H		C	H	O
I	4',4''-di-(3-methyl-3-ol-butynyl) –DB18C6	178–182	28	68.38	6.82	$C_{30}H_{36}O_8$	68.70	6.87	24.43
II	4',4''-di-(3-methyl-3-ol-pentynyl) –DB18C6	194–198	26	70.04	7.37	$C_{32}H_{40}O_8$	69.57	7.24	23.19
III	4',4''-di-(3-ol-pentynyl) –DB18C6	206–211	32	68.97	6.94	$C_{30}H_{36}O_8$	68.70	6.87	24.43

The obtained elemental analysis data are in agreement with the calculated data. The increase in the melting point of the homologous series of acetylenic alcohols, dibenzo-18-crown-6, is similar to the homologous series of alkynes.

$^{13}C$  spectra show new signals characteristic of the C–C bond of quaternary substituted carbon, acetylenic carbons and individual signals of radicals.

The diazotization process was carried out at a temperature of 0–5°C, the rationale for this is that with increasing temperature, the formation of by-products increases. The process was carried out for 2 hours while stirring the reaction mixture. The structures of the obtained compounds were proved by modern physicochemical methods (table 1,2,3).

### Experimental part

$^1H$ - and  $^{13}C$ -NMR spectra were obtained in a  $CDCl_3$  solution on a Bruker VXR-400 spectrometer at an operating frequency of 400 MHz, using a TMS solvent as an internal standard (7.27 ppm by TMS)

Melting points were determined in the usual way in a metal block.

**4', 4''-diaminodibenzo-18-crown-6** was obtained according to [10, 878–884]. Yield 5.0g (72%) mp. 176–178 °C. Lit. data. [10, 878–884] m.p. 177–178 °C.

**4', 4''-dibenzo-18-crown-6-yl-diazonium chloride** was obtained from 2.5 g (6.41 mmol) of 4', 4''-diaminodibenzo-18-crown-6, 83 ml of water with 3 ml (32.96 mmol) of 34% HCl. Then the so-

Table 2. – Data of <sup>1</sup>H-NMR spectra of 4', 4''-diacetylenic alcohols based on 4', 4''-diaminodibenzo-18-crown-6 (δ, ppm)

No	Compounds	Individual	α-CH <sub>3</sub>	-OH	β-O-CH <sub>2</sub>	α-O-CH <sub>2</sub>	Ar-CH 6', 6''	Ar-CH 3', 3''	Ar-CH 5', 5''
<b>I</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>I</b>	4', 4''-di-(3-methyl-3-ol-butynyl)–DB18C6		1.48 (12H, s)	2.96 (2H, s)	3.89–4.02 (8H, m)	4.24–4.26 (8H, m)	6.69 (2H, s)	6.81 (2H, m)	6.83 (2H, m)
<b>II</b>	4', 4''-di-(3-methyl-3-ol-pentynyl)–DB18C6	1.16 (6H, s, R-CH <sub>3</sub> ) 1.65–1.67 (4H, s, CH <sub>2</sub> )	1.36 (6H, s)	2.86 (2H, s)	3.87–3.94 (8H, m)	4.12–4.22 (8H, m)	6.67 (2H, s)	6.73 (2H, d)	6.78–6.80 (2H, d)
<b>III</b>	4', 4''-di-(3-ol-pentynyl)–DB18C6	1.94 (4H, d) R-CH <sub>2</sub> 4.60–4.62 (2H, s, CH-OH)	1.10 (6H, s)	2.75 (2H, s)	3.81–3.92 (8H, m)	4.07–4.18 (8H, m)	6.68 (2H, s)	6.72 (2H, d)	6.76–6.80 (2H, d)

Table 3. – Data of <sup>13</sup>C-NMR spectra of 4', 4''-diacetylenic alcohols based on 4', 4''-diaminodibenzo-18-crown-6 (δ, ppm)

Compounds	Individual	-CH <sub>3</sub> (2C)	β-O-CH <sub>2</sub> α-O-CH <sub>2</sub> (8C)	-C≡CR(2C)	-C≡CR(2C)	Ar-CH 3', 3'' (2C)	Ar-CH 6', 6'' (2C)	Ar-CH 5', 5'' (2C)	Ar-C 4', 4'' (2C)	Ar-C 2', 2'' (2C)	Ar-C 1', 1'' (4C)
<b>I</b>	4', 4''-di-(3-methyl-3-ol-butynyl)–DB18C6	31.35 (4C)	65.83 69.64 70.49– 71.08	81.19	93.10	117.38	114.16	124.36	116.52	149.54	150.49
<b>II</b>	4', 4''-di-(3-methyl-3-ol-pentynyl)–DB18C6	28.29	68.75 69.58 70.32– 71.04	80.82	93.19	117.19	113.25	124.17	116.42	149.52	150.41
<b>III</b>	4', 4''-di-(3-ol-pentynyl)–DB18C6		64.40 CH- OH	86.25	96.43	117.53	112.97	124.51	116.54	149.54	150.57

lution was cooled in an ice bath to 0°C and 0.92 g (13.33 mmol) NaNO<sub>2</sub> was added. The resulting diazonium salt was not isolated. For each reaction, the diazonium salt of dibenzo-18-crown-6 was prepared separately according to equimolecular ratios.

**4',4''-di-(3-methyl-3-ol-butynyl)-dibenzo-18-crown-6 (I).** To a freshly prepared equimolar ratio of 4', 4''-dibenzo-18-crown-6-yl diazonium chloride 2.5 g (6.41 mmol) with mechanical stirring in an ice bath was added 3-methylbutin-1-ol-3 6.84 ml (7.692 mmol,  $d = 1.0595 \text{ g/cm}^3$ ), gas evolution was observed. The progress of the reaction was monitored by TLC on silufol, in the system acetone: hexane 2:1. The reaction time was 2 hours. It was purified by column chromatography, eluent hexane. Light yellow powder, m.p. 178–182 °C. Yield 0.94g, (28%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta_{\text{H}}$ , m.p.: 1.48 (12H, s, -CH<sub>3</sub>), 2.96 (2H, s, -OH), 3.89–4.26 (16H, d. m,  $\alpha$ -,  $\beta$ -O-CH<sub>2</sub>), 6.69 (2H, d, Ar-H 3'), 6.81 (2H, d, Ar-H 6'), 6.83 (2H, d, Ar-H 5'). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ , m.p.: 31.35 (4C, -CH<sub>3</sub>), 65.83 (2C, -C-), 69.64–71.08 (8C,  $\beta$ - $\alpha$ -O-CH<sub>2</sub>), 81.19 (2C, ArC $\equiv$ ), 93.10 (2C, ArC $\equiv$ C-), 114.16 (2C, Ar-C 6'), 117.38–124.36 (6C, Ar-C 3', 5', 6'), 150.49 (4C, Ar C4'). Elemental analysis: Found, %: C 68.38, H 6.82. Calculated, %: C 68.70, H 6.87, O 24.43, Gross formula: C<sub>30</sub>H<sub>36</sub>O<sub>8</sub>.

**4',4''-di-(3-methyl-3-ol-pentynyl)-dibenzo-18-crown-6 (II).** By analogy with (I) 2.5 g (6.41 mmol) 4',4''-dibenzo-18-crown-6-yl diazonium chloride, 3-methylpentin-1-ol-3 6.23 ml (7.692

mmol,  $d = 1.061 \text{ g/cm}^3$ ). m.p. 194–198°C, yield 0.92 g (26%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta_{\text{H}}$ , m.p.: 1.16 (6H, s, R-CH<sub>3</sub>) 1.36 (6H, s, -CH<sub>3</sub>), 1.65–1.67 (4H, s, -CH<sub>2</sub>), 2.86 (2H, s, -OH), 3.87–4.22 (16H, d. m,  $\alpha$ -,  $\beta$ -O-CH<sub>2</sub>), 6.67 (2H, d, Ar-H 3'), 6.73 (2H, d, Ar-H 6'), 6.78–6.80 (2H, d, Ar-H 5'). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ , m.p.: 9.00 (2C, R-CH<sub>3</sub>), 28.29 (2C, -CH<sub>3</sub>), 36.26 (2C, -CH<sub>2</sub>-), 68.75 (2C, -C-), 69.58–71.04 (8C,  $\beta$ - $\alpha$ -O-CH<sub>2</sub>), 80.82 (2C, ArC $\equiv$ ), 93.19 (2C, ArC $\equiv$ C-), 113.25 (2C, Ar-C 4'), 116.42–124.17 (6C, Ar-C 3', 5', 6'), 150.41 (4C, ArC4'). Elemental analysis: Found, %: C 70.04, H 7.37. Calculated, %: C 69.57, H 7.24, O 23.19, Gross formula: C<sub>32</sub>H<sub>40</sub>O<sub>8</sub>.

**4', 4''-di-(3-ol-pentynyl)-dibenzo-18-crown-6 (III).** By analogy with (I) 2.5 g (6.41 mmol) 4',4''-dibenzo-18-crown-6-yl diazonium chloride, pentin-1-ol-3 6.21 ml (7.692 mmol,  $d = 1.0598 \text{ g/cm}^3$ ). m.p. 206–211°C, yield 1.075 g (32%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta_{\text{H}}$ , m.p.: 1.10 (6H, s, -CH<sub>3</sub>), 1.94 (4H, d, -R-CH<sub>2</sub>), 2.75 (2H, s, -OH), 3.81–4.18 (16H, d. m,  $\alpha$ -,  $\beta$ -O-CH<sub>2</sub>), 4.60–4.62 (2H, s, -CH-OH), 6.68 (2H, d, Ar-H 3'), 6.72 (2H, d, Ar-H 6'), 6.76–6.80 (2H, d, Ar-H 5'). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ , m.p.: 9.90 (2C, -CH<sub>3</sub>), 30.80 (2C, -CH<sub>2</sub>), 64.40 (2C, -CH-OH), 68.97–70.94 (8C,  $\beta$ - $\alpha$ -O-CH<sub>2</sub>), 86.25 (2C, ArC $\equiv$ ), 96.43 (2C, ArC $\equiv$ C-), 112.97 (2C, Ar-C 4'), 116.54–124.51 (6C, Ar-C 3', 5', 6'), 150.57 (4C, ArC4'). Elemental analysis: Found, %: C 68.97, H 6.94. Calculated, %: C 68.70, H 6.87, O 24.43, Gross formula: C<sub>30</sub>H<sub>36</sub>O<sub>8</sub>.

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<https://doi.org/10.29013/AJT-21-9.10-40-46>

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## **SOLID PHASE IMMUNOENZYME METHOD FOR DETERMINATION OF HUMAN CHORIOGONADOTROPIN WITH PHOTOGRAPHIC REGISTRATION OF ANALYSIS RESULTS**

**Abstract.** Using the example of the determination of the  $\beta$ -subunit of human choriogonadotropin in biological fluids using commercial ELISA test kits for enzyme-linked immunosorbent assay, the analytical possibilities of using photographic materials as a “dry reagent” for recording the results of the analysis are shown. The proposed method allows you to determine up to 0.6 ng / ml peroxidase – an enzyme label, for variants of the test kits “beta-hCG-Express ELISA” and “beta – hCG-ELISA” for the determination of choriogonadotropin in urine and serum, respectively. We examined 23 apparently healthy pregnant women with various stages of pregnancy. The concentration of  $\beta$  – HCG in the blood serum, depending on the duration of pregnancy, with its normal course, is in a wide range. However, the highest values of  $\beta$ -HCG concentration are observed at 10–14 weeks of pregnancy, followed by a decrease in its level in the second and third trimesters of the normal course of pregnancy.

The obtained data correlate well with the results of other immunological studies and reflect the physiology of intrauterine development of the fetus. Comparative analysis of  $\beta$ -HCG determination in blood serum by enzyme immunoassay using spectrophotometric and photographic registration shows a satisfactory correlation:  $R^2 = 0.9363$ . The use of this method for registering the results of express diagnostics of pregnancy based on urine samples showed a high contrast of samples of pregnant and non-pregnant women, which makes it possible to recommend the method for non-invasive diagnostics. Thus, the studies show that the method developed enzyme immunoassay determination of  $\beta$  – hCG in body fluids using photographic registration ELISA results has sufficient sensitivity, ease of formulation can be used for early detection of pregnancy, as well as to predict its outcome, and the ELISA system with photographic detection expands the analytical capabilities of test methods in clinical diagnostics.

**Keywords:** human choriogonadotropin, ELISA, biological fluids, photographic registration, non-invasive methods of pregnancy diagnosis.

## 1. Introduction

The need to determine human chorionic gonadotropin (HCG) in biological fluids is due to the high information content of the biochemical test in the diagnosis of early pregnancy, predicting its outcome in threatening miscarriages, trophoblastic and other malignant neoplasms [12; 18]. HCG is a glycoprotein with a molecular weight of ~ 40.000 daltons, consists of two subunits: an  $\alpha$ -chain and a  $\beta$ -chain. It is formed in the chorion tissue, namely in the syncytial cells of the placenta, and its synthesis rapidly increases after embryo implantation [10]. Normally, HCG is found in the blood serum and urine of pregnant women within 6–10 days after fertilization, its content increases until the end of the first trimester of pregnancy, and then falls. Therefore, its change in biological fluids – blood serum, plasma, urine of women, serves as a reliable pregnancy detector. A reduced level of HCG is observed with a delay or cessation of fetal development. Also, a decrease in the average values of the concentration of HCG can be with an ectopic pregnancy, with chromosomal abnormalities in the fetus [13]. Hypersecretion of HCG is observed in multiple pregnancies, with intrauterine infection, with cystic drift, and with some fetal malformations. It was found that an increase in the level of  $\beta$ -HCG in men and non-pregnant women is a sign of the development of malignant neoplasms. Such an increase is observed in tumors of trophoblastic or germinal origin (testicular and ovarian cancer, choriocarcinoma, chorioadenoma), as well as in breast cancer. The highest concentration is observed in choriocarcinoma [9]. In this regard, the quantitative determination of  $\beta$ -HCG is necessary both for early diagnosis of pregnancy and monitoring pregnant women at high risk, detection and monitoring of malignant tumors secreting  $\beta$ -HCG: trophoblast, ovarian or placental choriocarcinomas, chorioadenomas and some types of breast cancer. For the quantitative determination of HCG, various variants of immunochemical binding methods have been developed [1; 8; 11; 15]. However, the most promising

of them is the enzyme immunoassay based on the use of antibodies and antigens labeled with an enzyme [1; 2]. The enzyme immunoassay method has found its application in various fields of medicine, however, as a rule, the enzyme immunoassay is based on spectrophotometric systems for recording the enzymatic activity of the conjugate, bound to the solid phase of the immunosorbent [4]. These systems are expensive, complex and not always economically viable in small clinical diagnostic laboratories. The aim of this work is to test a photographic detection system in a solid-phase enzyme-linked immunosorbent assay (ELISA) of the  $\beta$ -subunit of HCG using commercial kits of the JSC “Rosh-Moscow”.

## 2. Experimental

**Reagents and chemicals.** In this work, enzyme immunoassays were used to determine the  $\beta$  – subunit of human chorionic gonadotropin in the “express” variants for the qualitative detection of  $\beta$  – HCG in urine and for the quantitative determination of  $\beta$ -HCG in plasma and serum: “Beta-hCG-ExpressIFA” and “beta-hCG-IFA”, respectively. The enzyme-linked immunosorbent assay for the determination of  $\beta$ -HCG is based on the “sandwich” principle [6]. The immunosorbent beads coated with antibodies to  $\beta$ -HCG were incubated together with the analyzed sample and a solution of the conjugate of peroxidase and antibodies to  $\beta$ -HCG [4]. Residual peroxidase activity was determined photographically using photographic material as a ‘dry’ reagent [2; 3; 14]. For this, we used positive photographic plates of domestic and foreign production and black-and-white positive film MZ-3L (“Tasma”). The substrate mixture contained a standard solution of phenidone-hydroquinone developer and 0.01 M hydrogen peroxide solution. The intensity of blackening of spots on the photographic material was determined using an MF-2 microphotometer. Spectrophotometric registration of ELISA results was carried out using an SF-46 (LOMO) spectrophotometer with a quartz cuvette  $l = 10.0$  mm at  $\lambda = 492$ . The substrate was a mixture of 3.3 ‘, 5.5’ – tetrameth-

ylbenzidine in dimethyl sulfoxide and hydrogen peroxide in 0.1 M citrate buffer, pH 5.5.

### 3. Results and Discussion

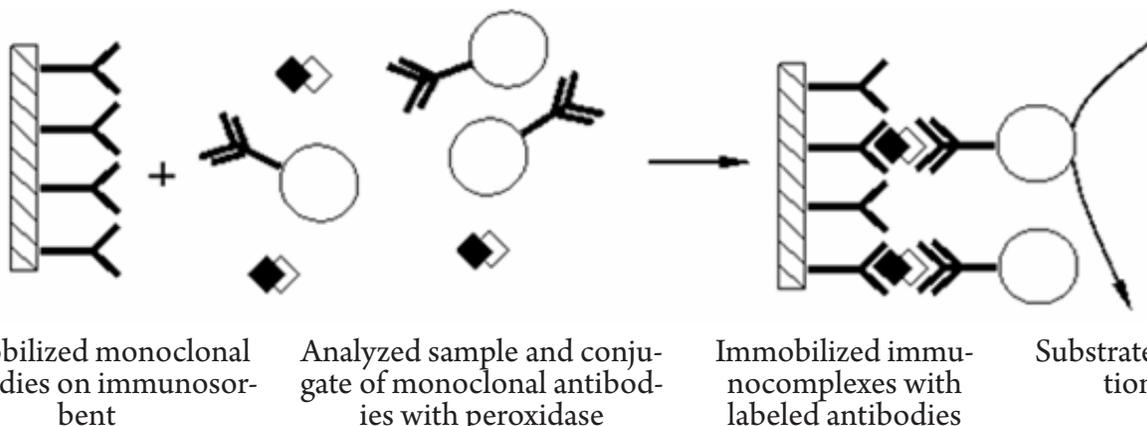


Figure 1. Scheme of the one-stage "sandwich" ELISA method

Thus, the indirect determination of HCG in the analyzed sample is based on the determination of the peroxidase activity of the immobilized conjugate of monoclonal antibodies with peroxidase.

The lower limit of the determined amount of the marker enzyme (peroxidase), which determines the detection sensitivity in the enzyme immunoassay method, depends on a number of factors: the parameters of the catalytic constant of the enzymatic reaction, the incubation time, the state of the surface of the photographic material. So, the lower limit determined by the concentration of peroxidase can be calculated to the formula [5]:

$$C_{\text{lim}} = \frac{N}{k_{\text{cat}}} \cdot \gamma.$$

where  $N$  – is the minimum detectable level of the reaction product per unit volume per unit time;  $k_{\text{cat}}$  – is the catalytic constant of the enzyme;  $\gamma$  – is a coefficient reflecting the stoichiometry of the reaction.

The figure 1 shows a schematic diagram of a one-stage "sandwich" method of solid-phase enzyme-linked immunosorbent assay.

The minimum concentration of hydroquinone in the developing solution, which can cause changes on the surface of the photoemulsion layer sensitized by photons of light of the silver halide layer of photographic material, is  $10^{-4}$ – $10^{-3}$  M.

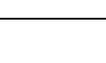
With a value of  $k_{\text{cat}} = 800 \cdot 10^4 \text{ s}^{-1}$  [17]  $C_{\text{lim}} = 1.25 \times 10^{-11}$ – $1.25 \times 10^{-10}$  M.

Table 1 shows a photogram of a calibration scale for peroxidase with an indication of the concentration of peroxidase in ng / ml and the corresponding intensities of blackening on the photographic material  $S$  in units of the MF-2 microphotometer scale.

Figure 2 shows the calibration curve in semi-log coordinates for determining the concentration of peroxidase. The enzymatic reaction time was 20 minutes, and the contact time of the enzyme-substrate mixture with the surface of the sensitized photoemulsion layer was 2 minutes.

Table 1. – Results of measuring the intensity of blackening on a photographic material at various concentrations of peroxidase (HRP)

HRP peroxidase concentration, ng/ml	Photogram	Blackening intensity, S unit
1	2	3
280.0		$36 \pm 4$

<b>1</b>	<b>2</b>	<b>3</b>
140.0		$55 \pm 3$
70.0		$71 \pm 2$
35.0		$93 \pm 3$
17.5		$103 \pm 4$
9.0		$118 \pm 6$
4.5		$128 \pm 6$
2.2		$131 \pm 6$
1.1		$134 \pm 8$
0.6		$138 \pm 8$
$\Phi_{OH}$		$141 \pm 8$
Veil density		$23 \pm 3$

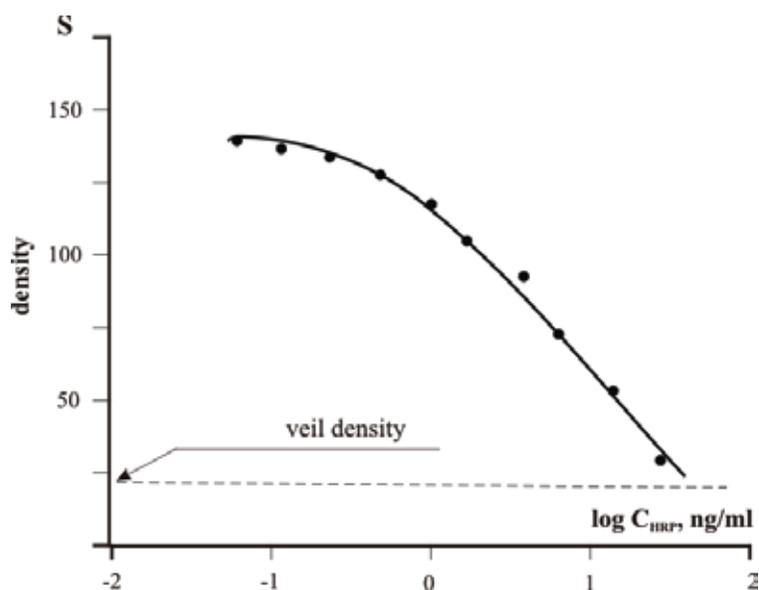


Figure 2. Calibration plot for the determination of peroxidase in semi-logarithmic coordinates

To determine  $\beta$ -HCG in blood serum, the following technique was developed: up to 0.02 ml of standard solutions of HCG (0; 10; 25; 50; 100;

200 mIU/ml) were poured into test tubes, 0.25 ml of the conjugate was added (anti- $\beta$ -HCG-peroxidase), one bead coated with anti-HCG antibodies was

placed in each tube, shaken and incubated at 37 °C for one hour. After incubation, the solution was removed from the tubes, the beads were washed with distilled water three times, and the water was thoroughly removed. Then, 0.25 ml of a solution of phenidone-hydroquinone developer, previously diluted with distilled water in a ratio of 1: 2 and 0.25 ml of  $3 \times 10^{-2}$  M hydrogen peroxide, was added to each test tube; kept at room temperature for 30 minutes and dug out with a pipette microdispenser onto the surface of the photographic material. After 1.5–

– 2 minutes, the photographic material was rinsed with water and the image was fixed in the usual way. During the analysis, the analyzed sample was introduced instead of the standard solution of  $\beta$ -HCG.

In the course of the work, 23 apparently healthy pregnant women with various stages of pregnancy were examined. Of these, under the age of 20– 6 people, up to 30–14 people and over 30 years – 3 people. Including first-born – 7 people, re-giving birth – 13 people and multiparous (more than 5 times)-3 people (Table 2).

Table 2. – Results of  $\beta$ -HCG determination in blood serum of healthy pregnant women

No.	Age	Number of pregnancies	Pregnancy period, weeks	HCG level, mIU/ml	
				Spectrophotometric registration	Photographic registration
1.	20	1	13–14	34	50
2.	27	3	12–13	34.6	46
3.	26	2	13–14	30.5	40
4.	18	1	13–14	32.5	37
5.	21	1	9–10	22.5	32
6.	19	1	10–11	42.5	58
7.	34	7	18–19	33.4	45
8.	19	1	12–13	21.5	30
9.	22	2	7–8	18.5	20
10.	24	3	9–10	24.5	26
11.	36	7	32	3.0	5
12.	26	2	12–13	32.5	35
13.	18	1	17–18	25.0	30
14.	20	1	33–34	3.8	6
15.	25	3	8–9	20	25
16.	24	3	17–18	29	30
17.	26	2	23–24	13.5	20
18.	21	2	23–24	12.5	20
19.	23	2	35–36	18.5	22
20.	38	9	17–18	28.5	38
21.	29	3	35–36	16.8	20
22.	26	3	19–20	10	10
23.	28	3	36	6	8

Correlation analysis of two methods for determining  $\beta$ -HCG in the blood serum of pregnant

women shows satisfactory convergence of the analy-

sis results. Correlation coefficient  $R^2 = 0.9363$ . The linear regression equation has the form

$$y = -0.0539 + 1.2738 x \text{ (Fig. 3).}$$

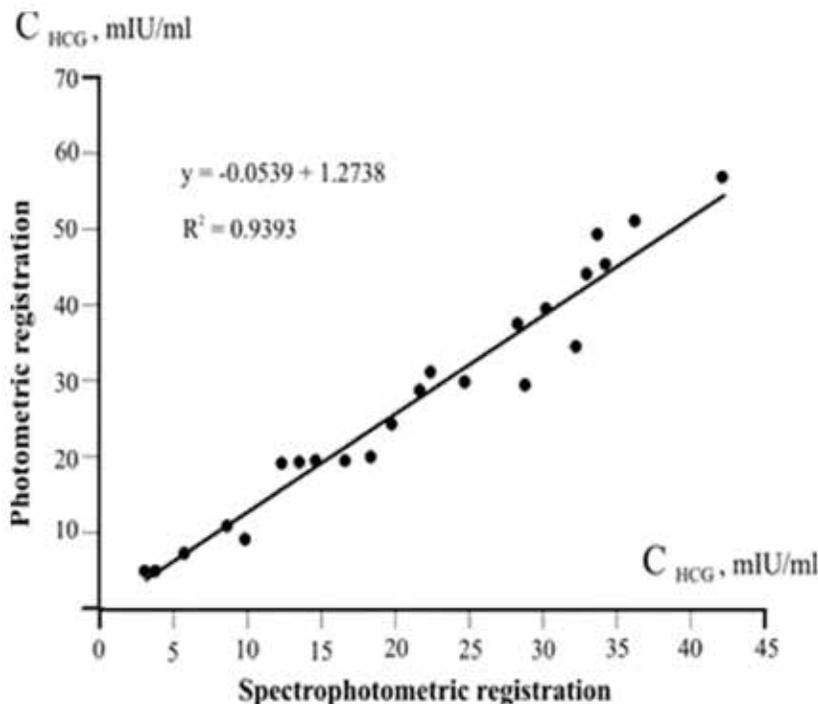


Figure 3. Correlation dependence of the enzyme-linked immunosorbent assay for HCG with spectrophotometric and photographic detection

As can be seen from the diagram, the values of  $\beta$ -HCG concentrations are in a wide range. However, the highest concentration values of  $\beta$ -HCG are observed at 10–14 weeks of pregnancy, followed by a decrease in its level in the second and third trimesters of the normal course of pregnancy. The data obtained are in good agreement with the results of radioimmunological studies and reflect the physiology of intrauterine development of the fetus [15; 16].

The developed method was tested in ELISA for qualitative express determination of  $\beta$ -HCG in the urine of pregnant women. This method can be attributed to non-invasive methods for diagnosing early pregnancy. For its implementation, we acted in the same way as described above, using urine samples as an analyzed sample.

Based on the studies carried out, a diagram of the dependence of the  $\beta$ -HCG concentration in the blood serum on the duration of pregnancy in its normal course was built (Fig. 4).

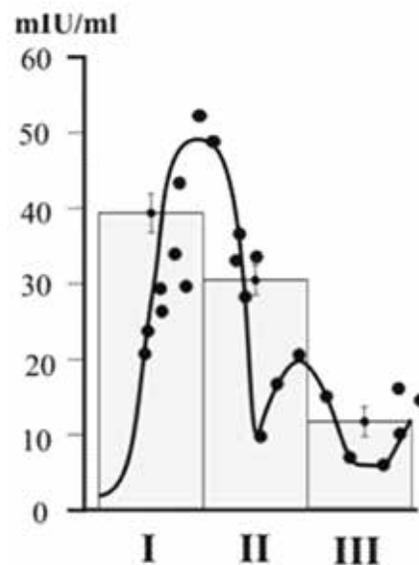


Figure 4. Diagram of the dependence of the concentration of  $\beta$ -HCG in the blood serum of the period of pregnancy

In Figure 5 shows a photograph of the results of pregnancy diagnostics based on urine samples of pregnant and non-pregnant women.



Figure 5. Photographs of a qualitative express determination of  $\beta$ -HCG in the urine of a pregnant (1) and non-pregnant (2) woman

Unlike urine samples that do not contain chorio gonadotropin, when analyzing the urine of pregnant women, the photographs have a significantly lower intensity of blackening, which makes it possible to test pregnancy reliably and with documentary accuracy.

### Conclusions

This studies show that the developed method for the enzyme-linked immunosorbent determination of  $\beta$ -HCG in biological fluids using photographic registration of ELISA results has sufficient

sensitivity, ease of installation, can be used for early detection of pregnancy, as well as for predicting its outcome, and the ELISA system with photographic detection expands the analytical capabilities of test methods in clinical diagnostics.

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