Electrochemical synthesis and characterization of a polipyrrole/lipase composite film

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Abstract

The advantages of an irreversible immobilized enzyme for heterogeneous catalytic transformations of different substrates are numerous. In particular, since the enzyme macromolecules remains attached to the inert support it may be possible to re-use it. In some cases the immobilized molecules are more stable than the species of the solution. The kinetics of the immobilized species is likely to be influenced by the microenvironment and may be considerably altered from solution kinetics. Slow mass transfer of immobilized enzymes make possible advantageous treatment of substrate dilute solutions (waste waters etc). One of immobilization technique is entrapment in polymer matrices which cover a variety of different polymerization methods and polymer characteristics. The polymer may be an inert support (polystyrene, polyacrylamide etc) or may perform some functions itself. Conducting polymer in particular electrochemically deposited polymers have became of interest as support matrices for enzymes. Polypyrrol (Ppy) films are known to be permeable and appear to offer an ideal matrix for enzymes immobilization. Electro polymerization of pyrrole from an aqueous solution containing an enzyme (glucose oxydase) produced a Polypyrrol film containing the enzyme. The electro polymerization via a radical cation, which reacts with neighbouring pyrrolle to produce a chain that is α, α' coupled. The resulting polymer incorporates anions of supporting electrolyte and has a net positive charge. Some authors[i,ii,iii] have reported that the polypyrrole are degraded at same potential values This finding emphases that slight modifications in polymerization can alter the characteristics of the resultant polymer. Immobilization efficiency depends strongly on the composition and the structure of the entrapping polymer and this depends on the degree of cross linking and concentration of the monomer. So, it is important to manipulate the electropolymerization of pyrrole which would give a film that must be sufficiently porous to assure a maximum entrapping efficiency. The aim of this work is the study of immobilization efficiency in polypyrrole film of an acylhidrolaze (lipase) of molecular mass of 33-65 KDa obtained from Yarrowia lipolitica yeast.

Keywords: polypyrrole, lipase, yarrowia lipolytica, electropolimerisation.

Introduction

Lipases (triacylglycerol acylhydrolases - E.C. 3.1.1.3) are enzymes which catalyses the hydrolysis of esters of glycerol and other alcohols with fatty acids. The hydrolysis of ester bonds takes place at the interface between a lipid substrate phase and the aqueous phase in which the enzyme is dissolved.

Usual industrial lipases act on fats and oils and hydrolyze them gradually into di- and monoacylglycerols and finally into glycerol and fatty acids. In the absence of water, they are

capable of reversing the reaction, leading to esterification [1, 2]. Due to their ability to utilize a wide spectrum of substrates, and also to their chemo-, regio- and enantioselectivity, lipases stand amongst the most important biocatalysts used in organic synthesis for several reactions, such as hydrolysis, esterification and transesterification [3,4]. Based on these reactions, lipases have a great potential for industrial applications in food, chemical, pharmaceutical or detergent industry [5,6]. Promising fields include the biodegradation of plastics [7], such as polyhydroxyalcanoate and polycaprolactone.

Due to their biotechnological interest, many of these enzymes have been identified cloned and characterized [4]. Nevertheless, the demand for the production of highly active preparations of lipolytic enzymes has led to research on lipase producing micro-organisms and culture strategies [9,10]. Among these micro-organisms, *Yarrowia lipolytica* is one of a great interest, being able to naturally secrete several enzymes, including lipase, depending on the growth conditions [10].

Yarrowia lipolytica is the most extensively studied "non-conventional yeast", being currently used as a model for the study of protein secretion, cell dimorphism, degradation of hydrophobic substrate, including triglycerides etc [11 – 13]. Being strictly an aerobic yeast, its growth and lipase secretion are affected by the amount of oxygen available in the culture medium; therefore one of the purpose of our study was to point out the influence of aeration on the biosynthesis of lipase. Extra cellular lipase production by this micro-organism depends also on the composition of the medium, so that another purpose of our study was to establish the optimum concentration of olive oil as an inductor of the enzyme.

Lipase activity was measured by a titrimetric assay with NaOH 0,1 N, using emulsified olive oil as the substrate. 1- 5 mL of enzyme solution, 5 ml 10 mM citrate buffer pH = 7 and 2 mL $CaCl_2$ 0,6% in the above mentioned buffer solution were added to 10 ml emulsion containing 25% (vol./vol.) olive oil and 75% (vol./vol.) Arabic gum. The assay was carried out at 37°C during a 60-minute incubation. After this time interval, the reaction was stopped by adding 20 ml acetone-ethanol 1:1 (vol. /vol.) and the amount of fatty acids was then titrated.

One unit of lipase activity was defined as the amount of enzyme that released 1 μ equivalent of carboxyl groups of fatty acid under analysis conditions (temperature = 37^0C, pH = 7, reaction time = 60 minutes). In our case, the catalytic activity of the biocomposite material was reported to the electrode surface.

Materials and Methods

Chemicals: lipase used in this work was obtained from Yarowia lipolytica Yeast and was used as received. The pyrrole and all substances utilized in this study were purchased from Aldrich Sigma Co. and were used without further purification.

Equipment: A single compartment cell, with glassy carbon and graft working electrodes ($2cm^2$), a platinum gauge auxiliary electrode and a saturated calomel reference electrode were used for all electrochemical experiments. A Gamry potentiostate /galvanostate model and Electrochem analysis software both to electrodeposit films of polypyrrole +lipase and to measure the electrochemical characteristics of the composite. All solution were purged with spectral argon during electrodeposition and were blanketed with Argon during measurement of electrochemical characteristics.

Electrosynthesys of polypyrrole and polypyrrole +lipase films

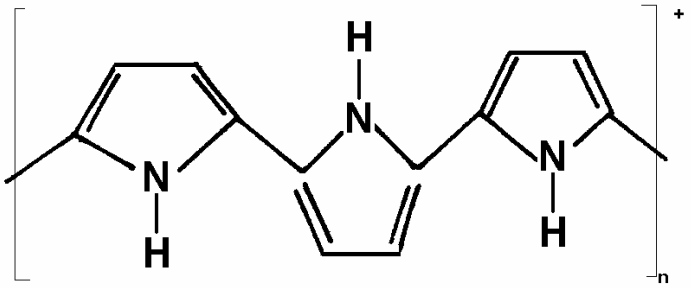
- Constant current method. Films were electrodeposited onto a carbon and glassy carbon electrodes at constant current (0.3 mA cm^{-2}) for 10 minutes prior to measurements of electrochemical characteristics. Films of Ppy and PPy doped with lipase were synthesized from an aqueous solution containing 0,1ML^{-1} pyrrole and 1% Lipase.
- Potential cycling method. Films were electrodeposited onto working electrodes by cycling the potential between 0.00V and 1,00V for 50 cycles with 50m$Vsec^{-1}$, prior to entrapped lipase by adsorption. The lipase was adsorbed from a 10% aqueous solution for 24 hour at 35,5C.

Electrochemical characterization of polypyrrole and polypyrrole +lipase films

- Open Circuit Potential measurement in neutral Na_2SO_4 0,5M solution was conducted for 300sec.
- Electrochemical impedance spectroscopy method was utilized to characterize the films in neutral Na_2SO_4 0,5 M solution at the rest potential and frequencies between 100 KHz and 0.1 Hz. The capacitance - potential dependencies were performed at different frequencies: 1KHz; 100Hz; 10Hz; 1H; 0.1Hz. For experimental data analysis was used the Electrochem Gamry software and equivalent electrical circuit editor.

Results and Discussions

The figures 1-4 present experimental results. Polypyrrolle in its conductive state is cationic with approximately one cation per 3-5 pyrrol subunits [13]:



Electrodeposition of pyrrolle in the presence of lipase results in the entrapment of the enzyme within the polymer matrix, which is electrically conductive. Entrapment of LIP within the polypyrrole matrix involve the entanglement of the two macromolecules (polypyrrole and LIP) to perform ionic interaction between anionic substitutes on LIP and the cationic backbone of conductive polypyrrole.

As results of this interaction, the electrochemical and adsorption characteristics of polymeric matrix are modified as follows:

Open Circuit Potential

The Open Circuit Potential (OCP) of polypyrrole film with and without lipase on glassy carbon and graphite in sulphate solution is presented in fig 1 and 2.

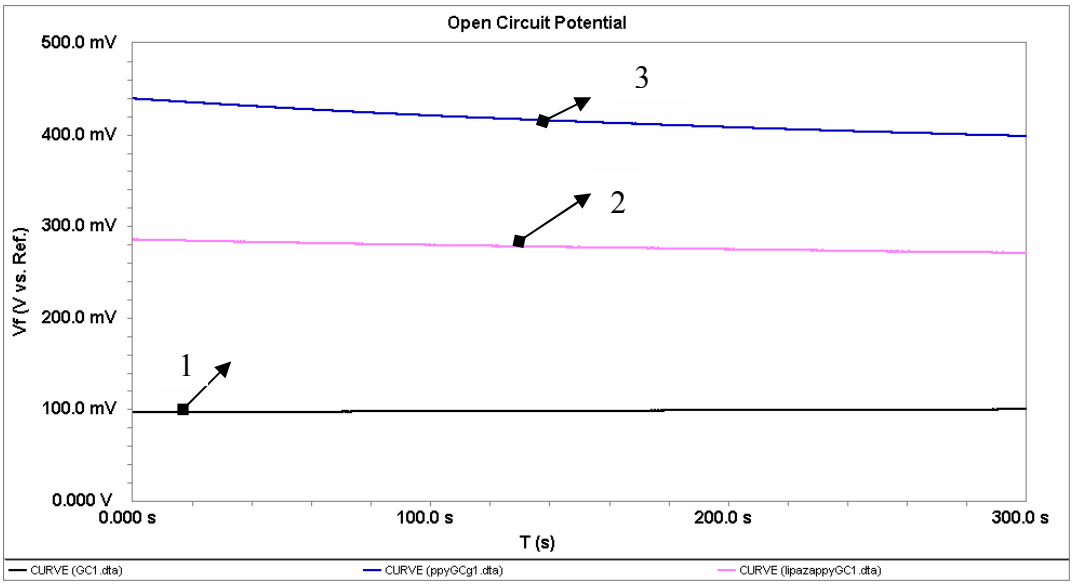


Figure 1. The Open Circuit Potential (OCP) of polypyrrole film with and without lipase on glassy carbon and in sulphate solution. 1-glassy carbon electrode, 2- glassy carbon + Polypyrrole + lipase, 3- glassy carbon + Polypyrrole

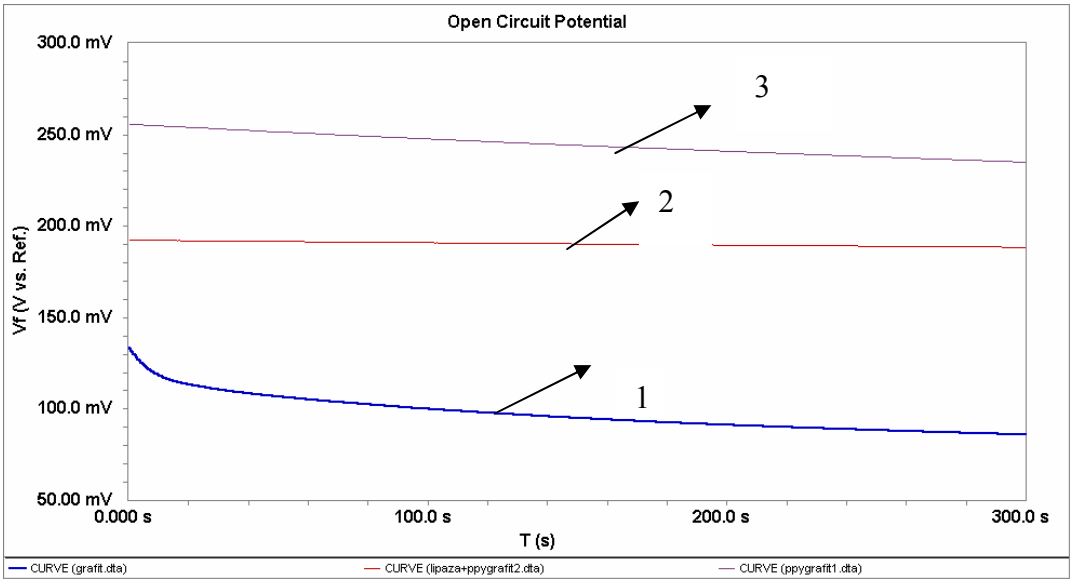


Figure 2 The influence of immobilized lipase in polymeric film on OCP in sulphate solution. 1-graphite 2-graphite + Polypyrrole + lipase, 3- graphite + Polypyrrole

From the **figure 1** can be seen the influence of ionic interaction between PPy and LIP on values of OCP which is changed from 420mV for Ppy conducting film to 290 mV for Ppy + lipase film with ΔV=130 mV. For the same system but on graphite electrode fig.2, ΔV=65 mV. The experiments reported here detect an effect of LIP adsorbed to the polypyrrole matrix. This effect is alteration in the voltage dependence on the surface concentration of the adsorbed YLIP [4]. The magnitude of the effect and the sign of the voltage which induce it both depend on the LIP. When Lipase is added to the aqueous phase, the voltage dependant capacitance changes in a very specific way. The changes depend on both, voltage and enzyme charge sign.

The Ppy membrane surface charge change due to adsorption of Lipaze

$$q_o = zF\Gamma$$

where q_0 is membrane charge cm^{-2}; z is LIP charge; f =Faraday number and Γ is the surface concentration of LIP.

At the given concentration of enzyme in aqueous phase, the change in the capacitance due to changes in adsorbed LIP can be written in the form:

$$\Delta C = \frac{\Delta q_0}{\alpha \Delta V} \quad (2)$$

Where Δq_0 = charge change due to applied potential ΔV and α is a proportionality factor.

Taking in consideration the change in surface charge density with potential, produce an effective capacity given by:

$$C = 2F\Gamma \frac{d\Theta}{dV} \quad (3)$$

Which represents so called pseudo capacitance [8].

Electrically adsorption pseudo capacitance (C) can be represented as a voltage dependent capacitor. The charging rate of this capacitor is proportional to the rate of adsorption of lipase to the polypyrrol matrix.

To demonstrate this behaviour of Polypyrrol +lipase enzyme electrode we studied by electrochemical impedance spectroscopy method and especially Niquist plots and capacitance potential plot the electrochemical characteristics of composite film.

The Niquist plots for Polypyrrole and Polypyrrole lipase films are presented in the **figure 3**.

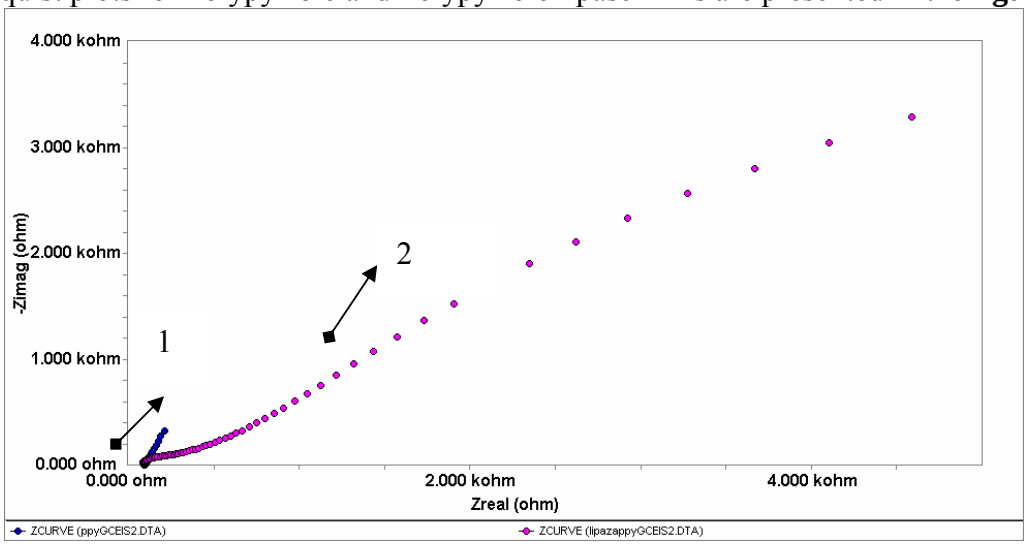


Figure 3 The Niquist curves of Polypyrrole (1) and Polipyrrole with lipase (2) films in 0,5 M Na_2SO_4 solution obtained between 100 KHz and 0,01Hz frequencies

The Niquist plot shows the frequency dependence of impedance implicitly as the imaginary impedance on the real impedance as it results from the known equivalent electric circuit:

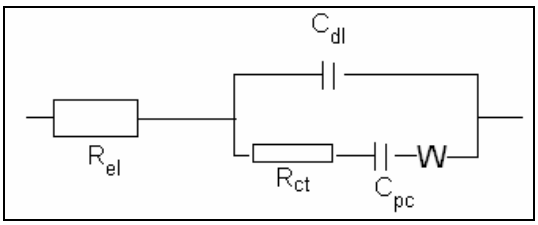


Figure 4 The equivalent electrical circuit for adsorbed charged species on the polymeric film

The dependence on potential of the equivalent circuit parameters and especially the pseudo capacitance is a sensitive indicator of the changes on surface of the composite electrode.

In the **table 1** we present same values of the pseudo capacitance and conductivity both polypyrrole matrix film and of composite polypyrrole +lipase film.
The pseudocapacitance was obtained at open circuit potential values.

Table 1 The influence of entrapped enzyme on the electrical characteristics of Polypyrrole films in Sulphate solution

	PPy	PPy +lipase
Capacity $\mu F/cm^2$	259	274
Conductivity mS/cm^2	50	44

From these data we conclude that entrapment of lipase in the matrix of polypirrole depend on changes in the pseudocapacitance and conductivity of the film.
The catalytic activity of this composite material is expressed in activity units of lipase (about 8 unit cm^{-2}).

Conclusions

- The entrapping efficiency of lipase in polypirrole film was studied by Open Circuit potential and EIS techniquies. It was found that the amount of entrapped enzyme is proportional with the decrease of OCP, increase of pseudocapacitance and decrease of conductivity of film.
- The catalytic activity of the composite biopolymer tested by titration of hydrolysis product of olives oil is 8 unit cm^{-2}.

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Main quality parameters' evolution of the wheat cultivated in Romania during the last years

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Abstract

There have been analyzed 670 wheat samples from the 2002, 2003, 2004 and 2005 crops, in order to establish the quality characteristics' yearly evolution.

Our results show that Romanian wheat crops have been characterized by high values for the variation coefficients, associated with the quality parameters which describe the seed enzymatic activity (gluten deformation and falling number). The most constant quality parameters of Romanian wheat are Hectolitric Weight (Test Weight), Moisture and Protein Content. The most different crops from a qualitative point of view are those obtained in 2002 and 2005, which were years characterized by completely different climatic conditions.

The medium (multiannual) mean coefficient for establishing the relationship between the protein content and the wet gluten was 0.750 for Romanian wheat, value corresponding to a medium correlation coefficient of 0.866.

Keywords: wheat, gluten, falling number, gluten deformation, crops quality

Investigations' purpose

The present study considered the emphasizing of a ground picture of the Romanian wheat bakery qualities, as follows:

- the quality parameters of the wheat produced in our country in the years 2002, 2003, 2004 and 2005;
- the main wheat quality characteristics, envisaging comparatively the crops obtained in our country in the years 2002, 2003, 2004 and 2005;
- the analysis of the subtlety relationships established between the quality parameters of the wheat produced in our country in the years 2002, 2003, 2004 and 2005;

Materials and Methods

We have carried out a complex analysis upon wheat samples taken-off the whole territory of Romania, from the crops of the years 2002, 2003, 2004 and 2005, as shown in table 1.

Table 1. Material, year of the crop and source zone

Origin	Year of the crop	Number of analysed samples
Romania	2002	260
	2003	30
	2004	200
	2005	180

The analysis methods referred to: determination of the Hectolitric Weight [4], determination of the content of Foreign matters [5], determination of Moisture [6], determination of the content of Proteic substances in wheat [7], determination of the content of Wet Gluten in wheat [8], determination of the Gluten Deformation Index in wheat [9], and Falling number [10].

The results have been processed by using the methods and models of statistic analysis, by means of employing the COHORT professional programme.

Results and Discussions

Table 2 shows the variability estimators for the Romanian wheat, from the crops of the years 2002, 2003, 2004 and 2005.

Table 2. Variability estimators for the quality parameters of the wheat harvested in our country, between 2002 and 2005

Parameter	Year	$\overline{X} \pm s_{\bar{x}}$	s	CV %	Min.	Max.
Moisture (%)	*2002*	12.887 ± 0.820	0.673	6.364	11.0	16.5
	2003	12.848 ± 0.984	0.968	7657	11.2	15.0
	2004	12.475 ± 1.092	1.193	8.756	9.6	21.3
	2005	13.197 ± 1.197	1.435	9.076	11.1	17.0
Hectolitric Weight (kg/hl)	*2002*	78.209 ± 2.771	7.677	3.542	69.2	84.6
	2003	77.313 ± 1.815	3.296	2.348	73.6	80.3
	2004	79.665 ± 2.788	7.775	3.500	68.3	88.4
	2005	75.466 ± 2.220	4.932	2.942	69.0	82.2
Foreign Matters (%)	*2002*	2.625 ± 1.085	1.178	41.348	1.0	9.8
	2003	2.381 ± 0.731	0.535	30.730	1.0	4.0
	2004	1.383 ± 0.837	0.700	60.520	0.2	6.5
	2005	1.732 ± 0.862	0.744	49.797	0.2	5.1
Protein content (%)	*2002*	11.894 ± 1.532	2.349	12.887	8.7	16.2
	2003	11.788 ± 1.504	2.263	12.760	9.6	14.6
	2004	10.846 ± 1.024	1.049	9.444	8.2	14.2
	2005	10.670 ± 1.215	1.475	11.382	8.5	13.6
Wet gluten content (%)	*2002*	26.121 ± 4.470	19.985	17.115	18.0	40.0
	2003	26.177 ± 4.486	20.127	17.137	20.4	30.8
	2004	23.484 ± 2.739	7.502	11.663	16.8	34.0
	2005	23.705 ± 3.136	9.835	13.230	18.0	33.6
Falling number (sec)	*2002*	371.369 ± 66.753	4389.531	17.840	98	500
	2003	334.315 ± 109.505	11991.257	32.735	62	529
	2004	357.373 ± 64.454	4154.337	17.170	224	575
	2005	199.824 ± 72.664	5280.113	36.364	65	374
	2002	17.238 ±9.251	85.584	53.666	5	35

Gluten deformation (mm)	*2003*	12.740 ± 8.024	64.430	63.000	4	35
	2004	8.894 ± 7.416	83.390	83.391	3	30
	2005	6.446 ± 2.313	5.350	35.879	3	19

As shown in table 2, the **Moisture** parameter had been characterized during the last four years mentioned, by an average variability of 7.96%, the variation coefficients rose constantly from about 6.4% for the wheat samples harvested in 2002, to about 9.1 % for the samples harvested in 2005.

As far as the average value of the moisture is concerned, we have observed a rise from 12.9 % for the wheat samples harvested in 2002, to 13.2 % for the 2005 crop; in this period, the rising tendency is not homogeneous.

Considering the significance of the differences between the 'Moisture' average values in yearly crops, we observed very significant differences between the years 2002-2004 (t = 4.265***), 2002 – 2005 (t = 3.019***) and 2004 – 2005 (t = 6.298***).

The Hectolitric Weight parameter showed a less homogeneous development, characterized by a decrease from 78.2 kg/hl in 2002, to 75.5 kg/hl in 2005, after a maximum in the preceding year of 79.7 kg/hl.

The results obtained at the Student test showed that there are very significant differences between all pairs of years (table 3). This fact proves that the hectolitric weight parameter is considered, as one of the most sensitive evaluation criteria, for the qualitative differences between the annual crops.

Table 3. Differences' significance between the average values of the Hectolitric Weight parameter in the yearly crops

Pairs of years	t	Significance
2002 – 2003	4.561	***
2002 – 2004	3.782	***
2002 – 2005	10.924	***
2003 – 2004	4.475	***
2003 – 2005	4.340	***
2004 – 2005	10.737	***

The content parameter of **foreign matters** showed a decrease from 2.625 % in 2002 to 1.383 % in 2004. The variation coefficients associated to these values were high and extremely high, with an increase tendency in the second part of the interval. The high values of the variation coefficients for this parameter seem to be associated with the structural and technological organization of Romanian agriculture, the normal values for better organized agrarian systems being smaller.

The significance of the differences between the average values of this parameter for the studied years is shown in table 4.

Table 4. The significance of the differences between the average values of the foreign matters' content parameter, for the annual crops

Pairs of years	t	Significance
2002 – 2003	1.402	ns
2002 – 2004	13.420	***
2002 – 2005	9.109	***
2003 – 2004	6.185	***
2003 – 2005	3.913	***
2004 – 2005	4.107	***

In table 4 we notice that for all the pairs of years, excepting the pair 2002-2003, the statistical differences are very significant. The general tendency during the entire period is the decrease in the average value of the parameter of foreign matters.

The parameter **Protein Content** registered during the last four years a homogeneous and relatively constant decrease, from 11.894 % in 2002, to 10.670 % in 2005. The variation coefficients were situated in normal limits, not higher than 14 %.

The significance of the differences for the Protein content parameter, of the wheat crops over the last four years, is shown in table 5.

Table 5. The significance of the differences between the average values of the Protein Content parameter, for the annual crops

Pairs of years	t	Significance
2002 – 2003	0.354	ns
2002 – 2004	8.040	***
2002 – 2005	8.851	***
2003 – 2004	3.316	***
2003 – 2005	3.885	***
2004 – 2005	1.566	ns

We can observe that the differences between the parameters are insignificant between the successive pairs of years 2002 – 2003 and 2004 – 2005; but they are very significant between crops proceeded from years separated by at least one production cycle (excepting the pair 2003-2004).

In figure 1 we can notice the general decreasing tendency of protein content, and also the report variation regarding 'protein content/wet gluten content'. In the years 2002 and 2003, respectively 2004 and 2005, this report decreased from 0.455 to 0.450, respectively from 0.462 to 0.450, suggesting that this decrease was due to the aglutenic proteins' decrease, while in the years 2003 and 2004, the increase of the report from 0.450 to 0.762 shows a reducing of the gluten generating proteins.

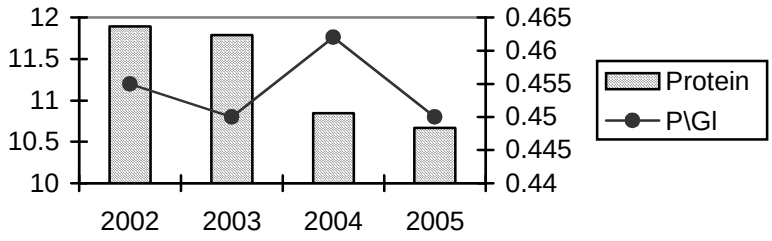

Figure 1. The evolution of the parameter of Protein Content and the report protein/wet gluten for the Romanian wheat proceeded from the 2002, 2003, 2004 and 2005 crops

The Wet gluten content parameter registered a 3 % decrease during the whole period. The strong correlation of this parameter with the protein content determined a similar distribution of the differences' significance between all the pairs of the studied years (table 6, figure 2).

Table 6. The significance of the differences between the average values of the Wet gluten content, for the annual crops

Pairs of years	t	Significance
2002 – 2003	0.063	ns
2002 – 2004	7.113	***
2002 – 2005	6.257	***
2003 – 2004	3.199	***
2003 – 2005	2.913	**
2004 – 2005	0.750	ns

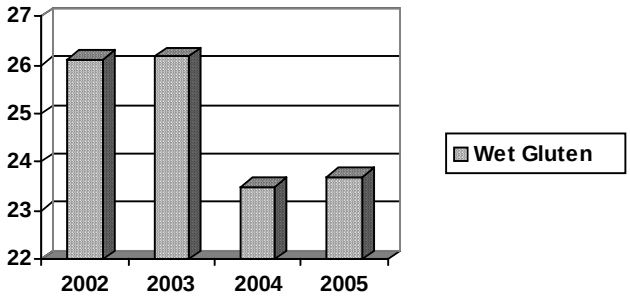

Figure 2. The evolution of the Wet Gluten Content parameter for the Romanian wheat, proceeded from the 2002, 2003, 2004 and 2005 crops

The gluten quality, analyzed by the **Gluten deformation index**, improved significantly from one year to another, decreasing from about 17 mm in 2002, to almost 6.5 mm in 2005.

We observed significant differences between all the studied pairs of years; these differences make us consider the Gluten deformation, as one of the most sensible parameters regarding the quality differences between crops.

The differences' significance, respectively the multiannual evolution of Gluten deformation index's average values are shown in table 7, figure 3.

Table 7. The significance of the differences between the average values of the Gluten deformation Index, for the investigated crops

Pairs of years	t	Significance
2002 – 2003	2.523	*
2002 – 2004	9.951	***
2002 – 2005	15.975	***
2003 – 2004	2.620	**
2003 – 2005	4.254	***
2004 – 2005	4.456	***

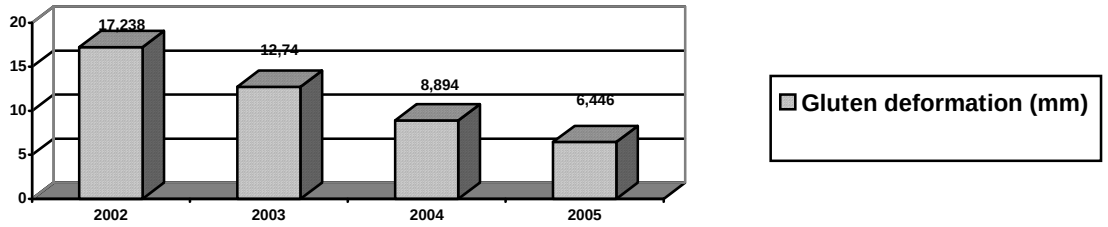

Figure 3. The evolution of the Gluten deformation parameter for the Romanian wheat proceeded from the 2002, 2003, 2004 and 2005 crops

The **Falling Number** parameter registered a decreasing tendency during the whole period (accordingly, an increase of the α-amylase activity), which is heterogeneous (table 8, figure 4).

As a matter of fact, the significance test showed that the only year which differs very significantly from all the previous years is 2005, characterized as the year with the highest activity of α-amylase. This phenomenon is due to the unfavourable weather conditions during the harvesting period; which caused the acceleration of the physiologic processes which occur during seed germination.

Table 8. The significance of the differences between the average values of the Falling Number parameter, for the annual crops

Pairs of years	t	Significance
2002 – 2003	1.794	ns
2002 – 2004	0.613	ns
2002 – 2005	24.748	***
2003 – 2004	1.992	ns
2003 – 2005	6.551	***
2004 – 2005	25.556	***

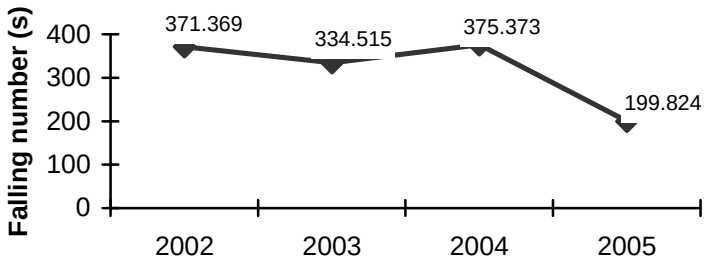

Figure 4. The evolution of the Falling Number parameter for the Romanian wheat proceeded from the 2002, 2003, 2004 and 2005 crops

In order to analyze the general evolution of the parameters for wheat quality and taking into consideration the main statistical characteristics established during the four year research period, we applied some test methods based on calculating the arithmetic mean for some statistic indicators (variation coefficient, t, etc).

Figure 5 shows the graphic for the variation of the average values of coefficients, associated with the quality parameters, studied yearly during four years.

We can observe that the highest variation coefficients generally attend the quality parameters which reflect the enzymatic activity of the wheat (the proteolitic activity has the highest variation coefficient, while the variation coefficient of diastazic activity is ranked third). Another parameter affected by excessive variations was the content of foreign bodies.

The most stable parameters of Romanian wheat were: Hectolitric Weight, Moisture and Protein Content, all of them being characterized by average variation coefficients under 14 %.

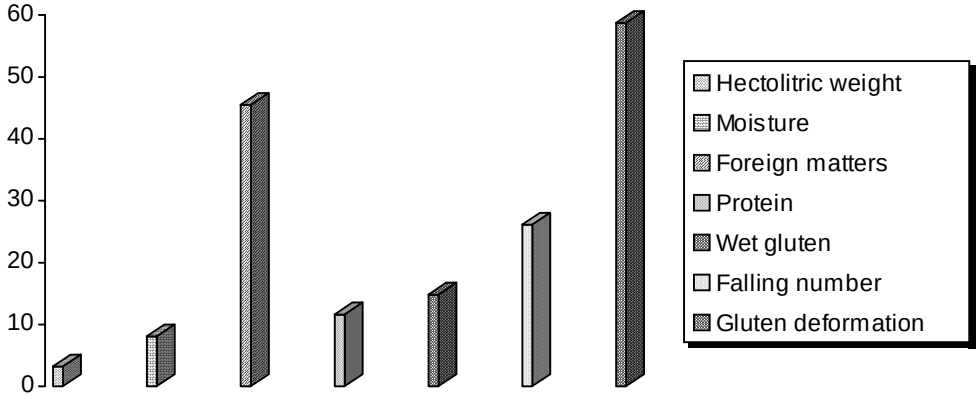

Figure 5. Average values of variation coefficients for Romanian wheat quality parameters, for 2002 – 2005 period

The years with the highest variation coefficients were 2003 and 2004. The year with the smallest variation coefficient was 2002, as figure 6 shows.

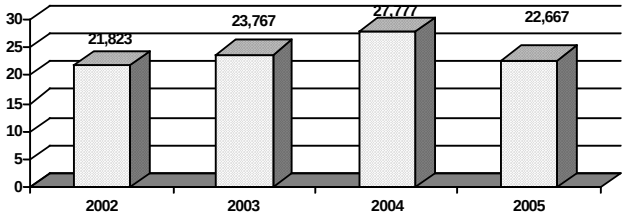

Figure 6. Average values of variation coefficients for Romanian wheat quality parameters, for 2002 – 2005 period

For evaluating the wheat quality parameters' sensibility, we used the following algorithm for the differences between crops:

- we calculated the arithmetic mean between 't' coefficients, associated to each quality parameter that has been investigated, as an arithmetic mean of the characteristic values for each year ('t_m');
- we established the number of years when the parameter has been significant;
- we calculated the mean power of significances in differences (p), for each parameter separately, as a sum of the level significance for all the investigated years, divided by the number of years.
- the sensibility was calculated as $\mathbf{t_m * n * p}$. Figure 7 shows the obtained results.

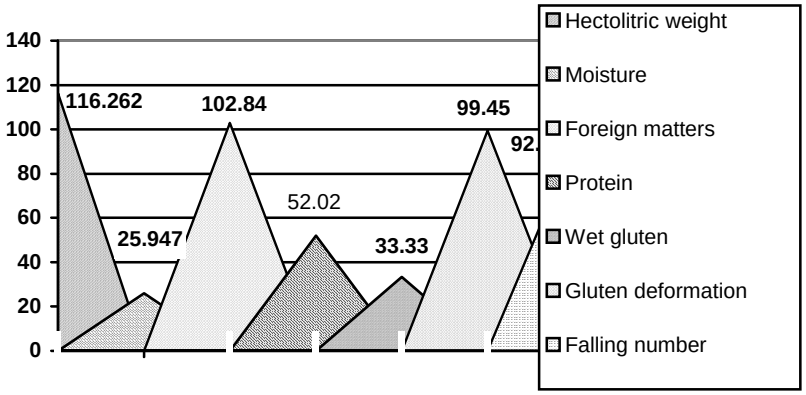

Figure 7. Sensitivity of Romanian wheat quality parameters, Regarding the differentiation of crops

Figure 7 shows that the most sensible parameter was the Hectolitric Weight, followed by the Content of Foreign matters, the Gluten deformation Index and the Falling Number. Unlike the other parameters, the Hectolitric Weight had, as seen previously, extremely small variation coefficients. Accordingly, we may consider that intervened modifications in the value of this parameter from one crop to another, synchronize with the annual climatic changes.

For evaluating the pairs of years with the highest differences, we applied a similar algorithm, multiplying the average value associated to 't' from one pair, by the number of the parameter which showed significant differences and by the mean power of significances (sum of the significance level of the parameters, divided by the number of investigated parameters). Figure 8 shows the obtained results.

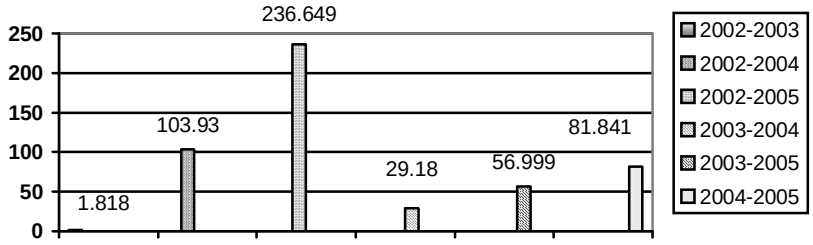

Figure 8. Mean of Romanian wheat crops' differences, analyzed during four years

Figure 8 shows that years 2002 and 2005 presented the highest differences as regards the crops from qualitative point of view. 2002 was a drought-afflicted year from climatic point of view, while 2005 was a very rainy year. The 2005 crop presented high differences against all previous crops, as a result of the special climatic conditions that characterized the year. The smallest difference can be observed in the crops of the 2002-2003 pair, years with similar climatic evolution.

Table 9 shows the correlation of the values of the coefficients and their significance for every wheat quality parameter, for each annual crop separately.

Table 9. Main correlations between the investigated quality parameters, in studied crops

Pairs of parameters		**Crop**			
		2002	**2003**	**2004**	**2005**
Hectolitric Weight	Foreign matters	-0.402***	-	-0.428***	-0.223**
	Gluten deformation	-0.351***	-0.612**	-	-
	Falling number	0.366***	0.524*	0.383***	0.161*
	Protein Content	-	-0.438*	0.144*	0.244**
	Moisture	-	-	-0.150*	-
	Wet gluten	-	-	-	0.234**
Protein	Wet gluten	0.881***	0.902***	0.846***	0.830***
	Gluten deformation	0.206***	-	-	0.320***
	Falling number	-	-	0.195**	-
Wet Gluten	Gluten deformation	0.339***	0.488*	0.168*	0.392***

In table 9 we notice that Hectolitric Weight correlates with all the other wheat quality parameters, but the only correlation which maintained during the four years was the correlation with the Falling Number.

The Protein Content correlates normally with the Wet Gluten Content, for this relation the average determination coefficient being about 0.75. In other words, the protein content in Romanian wheat determined the quantity of wet gluten in proportion of 75%.

We consider that results obtained in this research are useful for the characterizing the actual state of the Romanian agriculture, from the point of view of the climatic variations and the annual technologies.

Our results confirm the importance of the qualitative analysis of the crop for a correct evaluation of the yearly crop.

We are used to quantitative reports, regarding the momentary status of the wheat crop, however, in principle it is not the quantity which determines a relevant profit for the producer, but the quality of the wheat.

Conclusions

♦ Romanian wheat crops are characterized by high variation coefficient values for quality parameters which describe the enzymatic activity of the seed (Gluten deformation index and Falling number).

♦ The most stable quality parameters for Romanian wheat are the Hectolitric Weight, Moisture and Protein content.

♦ Very distinctive significant crops from qualitative point of view are those obtained in 2002 and 2005, years characterized by extremely different climatic conditions.

♦ The average determination coefficient (multiannual) between Protein content and Wet Gluten content, was 0.750 for the Romanian wheat, according to an average correlation coefficient of 0.866.

♦ In the years 2002 and 2003, respectively 2004 and 2005, the report between the Protein content and the Wet Gluten content decreased from 0.455 to 0.450, respectively from 0.462 to 0.450, suggesting that the decrease is due to reducing the aglutenic proteins; in the years 2003 and 2004, the report increase from 0.450 to 0.462 shows a higher decreasing of the gluten generating proteins.

♦ The Falling number parameter registered, during the four years, a heterogeneously decrease tendency (that means an α-amylase activity increase). 2005 is the only year that differs significantly of the others, by the α - amylase activity highest values.

♦ The parameters, most sensitive to the differences between crops, were the Hectolitric Weight, followed by the Foreign matters, the Gluten deformation index and the Falling number.

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