THE MODIFICATION OF SOME PHYSICO-CHEMICAL PARAMETERS OF MARGARINE DURING STORAGE*

ROMICĂ CRETU [1], GHEORGHE ZGHEREA[2]

[1] University “Dunărea de Jos” of Galați, Chemistry Faculty, 47 Domneasca Street, RO-800008, Galați, Romania, phone: +40236414871 int. 315, E-mail address: romy_cretu@yahoo.com
[2] University “Dunărea de Jos” of Galați, Chemistry Faculty, 47 Domneasca Street, RO-800008, Galați, Romania, phone: +40236414871 int. 305, E-mail address: romy_cretu@yahoo.com

Received September 26, 2006

Numerous physical and mechanical properties of margarine, as the plasticity, viscosity, color, taste, flavor, melting point, etc. are similar to natural cow butter, which it has to substitute.

In this research paper there was studied the evolution in time of the main physico-chemical parameters of “UNIREA” type margarine (as: unsaturation index, peroxide index and TBA index) and pH; beside these parameters there has been studied the evolution of color. Chromatic characteristics of margarine have been studied using “Tristimulus Colorimetry” method. The main point of the research was to determine the evolution in time of main physical-chemical parameters and the consequences of this variety on consumers.

Beside this we tried to correlate the physico-chemical parameters (IN, IP or TBA) with the ones from the “Tristimulus Colorimetric” method, having in mind that, in general, the color is one of the most important organoleptic characteristics sed to establish the quality and acceptability of food by the consumer.

By systemizing obtained experimental data we result the conclusion that the most underlined chromatic characteristic modification is possible in the first days of light exposure.

Key words: nesaturation index, peroxide index, TBA index, “Tristimulus Colorimetry”.

1. INTRODUCTION

Through derived fat products we understand the fats that have a different composition and structure than their original ones.

The largest part of the derived fat products ken be conditioned through nutritive elements incorporation, colorants, antioxidants, preservatives etc. Such incorporation is not similar to the chemico-structural derivation.

* Paper presented at the National Conference on Applied Physics, June 9–10, 2006, Galați, Romania

Fat derived products are industrially obtained from eatable fats and oils through hydrogenation, interesterification, fragmentation and reformulation. Examples of important food products included in this category are: cow milk butter, cocoa butter, oleine, stearine, oleostearine, salad oil, cooking oil, shortenings, and not least, the margarine.

H. Mege Mauries first described the margarine in 1869, in a patent made for the realization of a tartinable fat starting from the calf fat. The product was destined to replace the cow milk butter who was expensive and in limited quantities. The name "margarine" was proposed on the presumption that in the calf fat a certain margarinic acid predominates. Eventual this supposition was not confirmed, but the name remained in use until today [Leonte, M. and Florea, T., 1998].

The margarine is a typical emulsion of "water in oil" (W/O), who reaches it's stability through the incorporation of emulsifiants (especially monoglicerides), in it's composition with viscosity and uniformity dependent of it's crystallisation system.

Many physical and mechanical properties of the margarines, (like plasticity, viscosity, texture, colour, taste, aroma, liquefying interval etc.) are similar to the butter made from cow-milk (who it has to replace).

The compositional base of the margarines consist either in a single type of hydrogenated oil (especially the soy bean oil, named *single-feed stock*) or in many types of fluid and solid fats (*multi-feed stock*).

Solid and liquid fats are combined with each other so it can give the margarine the following qualities:

– Consistency at +4°C similar to the butter's;

– A pleasant taste and aroma and the presence of the nutritive and specific anti-oxidative factors (vitamins A,D,E, carrotenoids, antioxidants);

– A characteristic microcrystalline structure to give it's plasticity and to stop it from forming rigid masses in fast freezing conditions;

– The obtaining of a dense microcrystalline network which fixes in space the fluid components that enlarges the contact area W/O stabilized with emulsifiants.

This compositional assembly offer the margarine the quality of plastic fat with a minimum 80% fat substance, the rest consisting the liquid phase that includes the fermented milk with the specific leaven, sugars, emulsifiants etc.

The fat phase includes a mixture of liquid and solid fats well homogenized at a temperature higher with 4°C than the melting point. In the mixture are introduced monoglicerines, biglicerines, lecityne, carrotenoid colorants, vitamins etc.

In the fat mass the fat crystals are distributed in a 3D network, in which the β' form must dominate; the transformation from β' to β is unwanted because the β form causes a sandy texture with weak plasticity.

The most important operation in the margarine fabrication is the emulsification of the two phases into a continuos colloidal structure at 37°C. From this mass, through moderation at 17–19°C, a micro-crystalline mass is formed, that gives all the plastic qualities when mechanical tensions are applied to the structure.

Some representative types of margarine made from vegetal oils and animal fats, modified through hydrogenation are given in Table 1.

Table 1

The most important types of commercial margarine (after Leonte M. and Traian F., 1998)

Type	Characteristics
1. Cooking margarine	
a) Standard	– *at least 50% vegetal fats*
b) Vegetal margarine	– *minimum 95% vegetal fats*
c) Margarine rich in linnoleyc acid	– *at least 30% linnoleic acid*
2. Half-fat margarine	– *content of fats reduced to half; not recommended for cooking and baking*
3. Melting margarine	– *waterless; weak consistency; recommended for cooking and baking*
4. Special types for:	
a) For panification	– *strong aroma for the baked products*
b) For spinning	– *strong aroma; medium boiling point*
c) For creams	– *pasta like form, plastic texture*

In Romania several types of margarine have been made, codified with M for table margarine and with P for the panification one. The melting point for the M type of margarine is 31–35°C, and for the P type is 32–38°C. The today types of margarine differs after the content of fat, conditioning additives, humidity, milk content and milk derivatives or salts, colorants and aroma substances concentration.

In this research paper there has been studied the evolution in time of the main physical-chemical parameters of "Unirea" type margarine (as: unsaturation index, IN, peroxide index, IP, and TBA index) and pH; beside these parameters there has been studied the evolution of color.

Chromatic characteristics of margarine were also investigated.

The research has been made on a period of almost 3 weeks from the opening of the package.

In this way, the main point of the research has been to determine the evolution in time of main physical-chemical parameters and the consequences of this variety on consumers.

On the other hand, we tried to correlate the physical-chemical parameters (IN, IP or TBA) with the ones from the "Tristimulus Colorimetric" method, having in mind that in general the color is one of the most important organoleptic characteristics sed to establish the quality and acceptability of food by the consumer [Traian F., 2006; Banu C., 2000].

In this study the most important determinations referee to the white degree (W) values and the black degree (B) values, but because $W + B = 1$, only W must be measured.

The white degree represent the percent of light reflected on a surface from all the quantity of light that falls on it. W for a sample is completely exprimated if it is taken in consideration all the trichromatic components (X, Y and Z):

$$W = f(X, Y, Z) \tag{1}$$

On the basis of the trichromatic values, W is calculated with the equations proposed by some authors [Lukas, 1985]:

$$W_{\text{TA-C}} = 3{,}388Z - 3Y \text{ (iluminant C)}; \; W_{\text{TA-C}} = 3{,}676Z - 3Y \text{ (iluminant D65)}; \tag{2}$$

$$W_{\text{HU}} = (17{,}787Z - 11Y)/\sqrt{Y} \tag{3}$$

$$W_{\text{ST}} = (17{,}787Z - 53{,}55X - 64{,}55Y)/\sqrt{Y} \tag{4}$$

were the relations:

(2) defines the white degree after Taube than the two illuminants;

(3) is the Hunter equation (the HU index makes him different; it is the most used equation for the CIE/1931 standard and for the illuminant C made a standard by CIE;

(4) is Stensy equation, with similar applications like Hunter's equation.

Consequently, the white degree differs after the equation used, that depends on the light source used, meaning on the chosen standard.

To compare different samples, the white degree must be calculated using the same formula for the values of the trichromatic components ($X = X_1 + X_2$, Y, Z), which are measured through Tristimulus Colorimetry. The trichromatic components of the white surface of the apparatus for the measurement of W_{HU} where: $X_1 = 64.00$; $X_2 = 16.20$; $Y = 82.60$; $Z = 97.15$ [Traian F., Cretu R., Zgherea Gh., 2004].

2. MATERIALS AND METHODS

The experimental research was realized using "Unirea" type margarine, processed from the market. In order to realize this study several samples of margarine where taken, according to the prelevation methods and instructions of the ISO 707/1997 standards.

The margarine sample prelevation destined to the physico-chemical and sensorial analysis was made with perfectly clean equipments.

The lipides peroxidation was studied by the determination of the peroxide index (IP), the unsaturation index (IN) and the thiobarbituric index (TBA).

For the determination of the chemical indicators of the oxidative degradation of the foods rich in fats, experimental research where made after standard methods.

In this way for the determination of the unsaturation index where used Hanus reagent, $Na_2S_2O_3$ N/10 solution, $CHCl_3$, KI 10% and starch 1% solutions.

For the determination of the peroxide index the next reagents where used: a mixture of the CH_3COOH:$CHCl_3$ = 1:2 (v/v), KI saturated solution, $Na_2S_2O_3$ N/500 solution and starch 1% solution, and for the determination of the TBA index where used: CCl_4, acetic acid and thiobarbituric solution [Florea T., 2006].

All reagents were analytical reagent grade or pure.

The trichomatic parameters where determined through tristimulus analysis [Romică C., Mihaela O., Ștefan D., and Gabriela B., 2006] with the trichromatic colorimeter MOMCOLOR D (Hungarian Optical Works, Budapest), which is a bimodular apparatus, that gives the possibility to make measurements on solid and liquid samples (X – for red colour, Y – for green colour, Z – for blue colour).

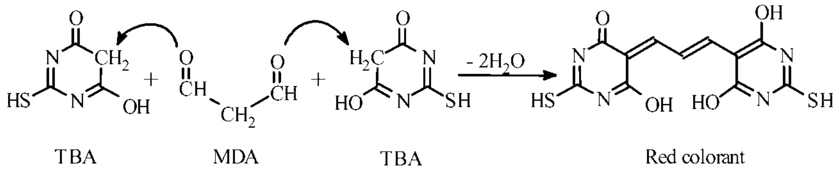
All studies made in this way where effectuated in different conditions, meaning some of the samples where stored at room temperature in dark conditions, while others where stored at light in a cabinet with normal lightening. In this conditions where taken the necessary quantities from each sample, for the determination of the followed indexes for a long period of time.

3. RESULTS AND DISCUSSIONS

The proprieties of fats are correlated with their composition, and these depend on the raw material and the technological processing conditions. The observation of the fat unsaturated acids content variation is important for the appreciation of the self-oxidation kinetics and their degradation while the processes of food fabrication and storage.

Analytically the unsaturated degree of fats is appreciated through the *iodine value* or the *unsaturated value (I.N.)*.

2-thiobarbituric acid (TBA) is a specific reactive for the dialdehyde which is formed in the fats and fat foods through self-oxidation, photo- and thermo-destruction. The method is based on the formation of o red colored composite at the condensation of the malondialdehida (MDA) with 2-thiobarbituric acid (TBA) like in reaction no. 7.



The extinction of the pigment in the solution is proportionate with the concentration according to the Lambert-Beer law, because through photo-measurement we can determine the MDA concentration, on the basis of which quantitative appreciation on the self-oxidation process can be made. [Florea T., 2006].

In Table 2 are represented the results obtained experimentally for the three analyzed values for a period of 3–4 weeks, for both the light and dark storage condition samples.

The determination of the chemical values of the oxidative degradation for the "Unirea" margarine started since day one of the envelope opening.

All the determinations where made at room temperature.

Table 2

The values for the analyzed parameters (minimum, medium and maximum)

Time, day	IN, g I_2/100 g fat			IP, mL $Na_2S_2O_3$ 0,002 N/g fat			TBA, mg malondialdehidă/100 g margarine		
	minim	*medium*	*maxim*	*minim*	*medium*	*maxim*	*minim*	*medium*	*maxim*
1	76.26**	78.38**	80.5**	1.8*	1.97*	2.14*	74.1*	75.86*	77.62*
	83.92*	84.47*	85.02*	1.42**	1.64**	1.86**	53.1**	58.22**	63.3**
3	71.1**	72.4**	73.7**	1.82*	2.32*	2.82*	122.2*	140.79*	159.4*
	77.58*	77.62*	77.66*	–	–	–	–	–	–
5	58.2*	59.6*	61*	3.14*	3.56*	3.98*	141.3*	174.45*	207.6*
	–	–	–	–	–	–	–	–	–
11	–	–	–	3.85*	4.03*	4.21*	228.5*	230.64*	232.8*
	58.12*	58.93*	59.74*	3.58**	3.62**	3.66**	132**	176.62**	221**
18	46.55**	47.92**	49.3**	3.8*	4.12*	4.44*	241.1*	303.03*	364.9*
	56.3*	57.06*	57.82*	3.77**	3.82**	3.87**	232**	234.29**	236**

* at light
** at dark

Table 3 shows the regression equations for each parameter from the first day of the experiment.

Several determinations where made on parallel samples, in Table 2 are represented only the high, low and the arithmetical mean between the two.

Table 2 reflects the fact that the unsaturated index decreases with the accession of the peroxide and thiobarbiturical index. Consequently, if at the envelope opening moment the I.N. had the value of 78.38 for the sample kept in the dark, the experimental results shone that for the light exposed sample, after 3–4 weeks, the I.N. reached values of 47.92 and 57.06.

Meanwhile the I.P. and TBA increased from 1.97 and 75.86 to 4.12 and 303.03 for the light exposed samples and from 1.64 and 58.22 to 3.82 and 234.29

Table 3

The regression equations for each studied parameter

Nr.	Parameter	Sample	Equation	r
1	IN, g I_2/100 g fat	(i) (ii)	IN = 75.550 – 1.626·t IN = 84.207 – 1.521·t	–0.9184 –0.9910
2	IP, mL $Na_2S_2O_3$ 0.002 N/g fat	(i) (ii)	IP = 2.2611 + 0.12354·t IP = 1.6965 + 0.13301·t	0.85924 0.94309
3	TBA, mg malondialdehidă/100 g margarine	(i) (ii)	TBA = 92.188 + 12.206·t TBA = 51.790 + 10.459·t	0.97459 0.9955

(i) sample kept in the light; (ii) sample kept in the dark; r: correlation coefficient.

for the dark exposed samples. This fact demonstrates that on the 3–4 weeks period the samples suffered fundamental modifications of the aspect and the nutritional properties, especially for the light exposed margarine. Also significant is the correlation between the variation of these values followed through the experiment, in time. Aspects followed above are confirmed in Figs. 1–3.

Also it is remarked the fact that during the storage, beside the first two values, the TBA index modifies differentially, meaning that the increasing of the TBA value is significant when the sample is stored under sunlight conditions.

The Figs. 1–3 shows the fact that the unsaturated degree decreases while the peroxide and the TBA indexes intensifies. Through the experimental values the white degree (W_{HU}) was calculated.

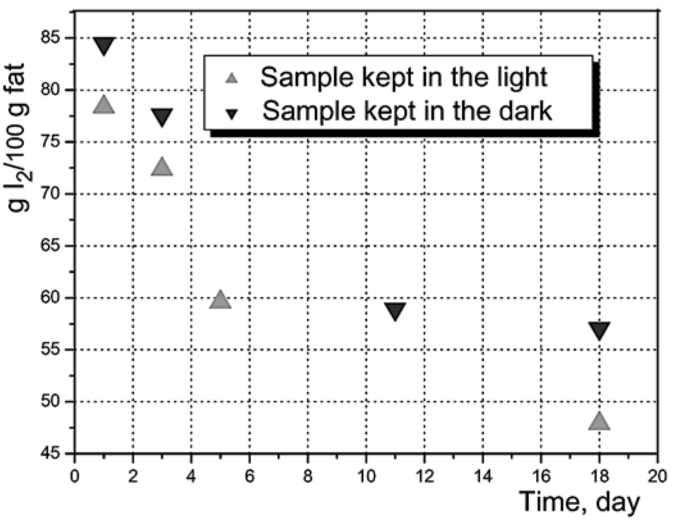


Fig. 1 – The evolution of I.N. in time.

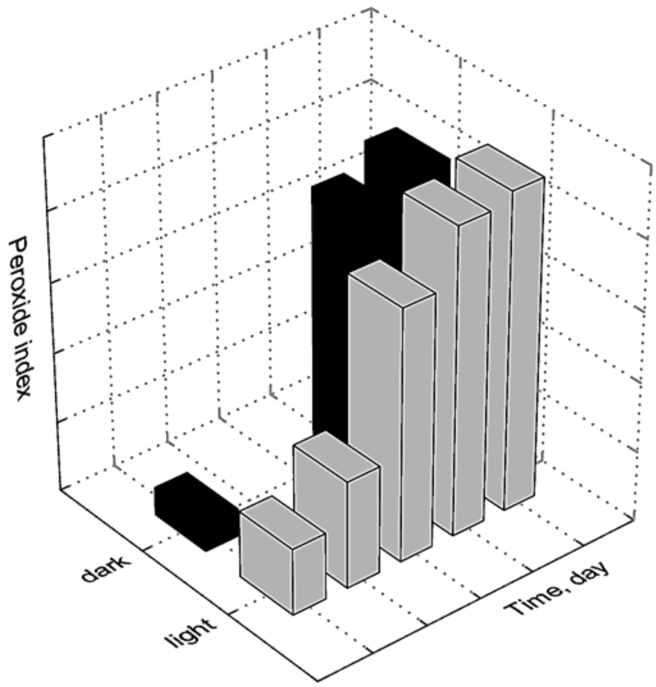


Fig. 2 – The variation of I.P. with the time during storage at room temperature.

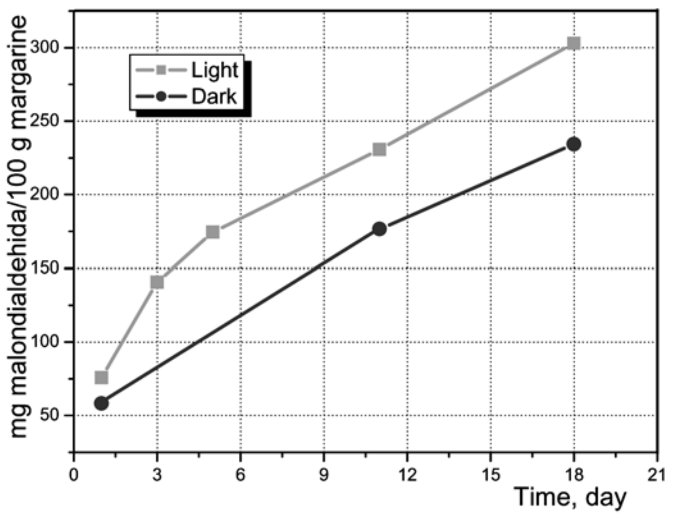


Fig. 3 – The variation of TBA (mg malondialdehidă/100 g margarine) with the time for the samples subject to light and dark during storage at room temperature.

The experimental values are shone in Tables 4 and 5 and in Fig. 5.

The experimental determinations where followed by the sequence of calibration and the detector's and circuit measurement answer towards the trichromatic components of the white reference standard.

MOMCOLOR D operates only with the basic colours (red, green and blue); the red component (X) is obtained through the linear adding of other two components ($X = X_1 + X_2$) to who presents different optic filters.

Table 4

The trichromatic components values and white degree for all samples during storage at room temperature after 14 days

The white reference standard	**Sample**	**Value**	**Trichromatic components**					W_{HU}
			X_1	X_2	X	Y	Z	
The white surface standard	(i)	Minim		10.75	81.20	83.9	64.45	1.3397
		Mediu	70.45	10.8167	81.527	84.15	64.717	
		Maxim	71.23	11.05	82.28	84.7	65.8	
	(ii)	Minim	38.75	4.65	43.40	76.45	27.85	–2.2521
		Mediu	59	4.667	63.667	76.717	28.017	
		Maxim	69.35	4.70	74.05	77.10	28.35	
	(iii)	Minim	70.45	5.45	75.90	79.45	32.75	–1.8334
		Mediu	70.75	5.467	76.217	79.8	32.9	
		Maxim	71.05	5.5	76.55	80.20	33.25	

(i) inițial sample (storage at 4–6°C); (ii) the sample storage at light; (iii) the sample storage at dark.

Table 5

The trichromatic components values and white degree for all samples during storage at room temperature after 28 days

The white reference standard	**Sample**	**Value**	**Trichromatic components**					W_{HU}
			X_1	X_2	X	Y	Z	
The white surface standard	(ii)	Minim	69.55	5.02	74.57	78.40	27.6	–2.0222
		Mediu	69.60	5.04	74.63	78.43	27.66	
		Maxim	69.65	5.05	74.70	78.50	27.75	
	(iii)	Minim	70.95	5.20	76.15	79.70	31.50	–1.9785
		Mediu	70.98	5.27	76.25	79.73	31.57	
		Maxim	71.05	5.4	76.45	79.80	31.65	

(i) inițial sample (storage at 4 –6°C); (ii) the sample storage at light; (iii) the sample storage at dark.

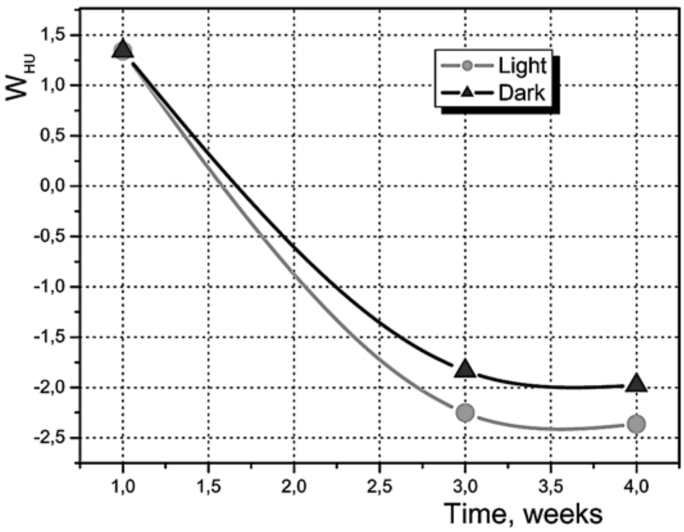


Fig. 4 – The white degree, W_{HU} dynamics during storage at room temperature.

The Tables 4 and 5 and Fig. 5 shows that during the 4–5 weeks the white degree has a significant and differentiated decrease, especially for the first three weeks. The descent of the white degree (W_{HU}) can be explained through the formation of the peroxides during the self-oxidation process of the stored margarine.

On the other hand, it can be remarked a higher descend of the white degree for the sample stored in sunlight and room-temperature conditions, in comparison with the sample exposed to dark.

4. CONCLUSIONS

During the oxidation of the “Unirea” margarine it takes place an important descent of the unsaturated index (IN) and, in the same time an ascend of the peroxide index (IP) and TBA. In all the analyzed situations it was discovered the fact that the variation of the followed values is less visible in case of the margarine sample kept in dark condition.

For both cases the major fluctuation of the colour parameter variation is produced in the first three weeks of light and dark storage conditions. The white degree is more pronounced for the sample kept in the dark, to who was assured this way a colour accepted by the consumer.

As a final conclusion, we believe that for the studied product, the “Unirea” margarine respectively, a dark or a low-light storage condition is the most appropriate one in order to reduce the photo-oxidation process.

REFERENCES

1. C. Banu, N. Butu, C. Lungu, P. Alexe, D. Rasmerita, C. Vizireanu, *Aditivi și ingrediente pentru industria alimentara*, Editura Tehnică, Bucuresti, 467–489, 2000.
2. C. Banu, M. Leonte, *Tratat de chimia alimentelor*, Editura Agir, București, 115, 2002.
3. M. Leonte, T. Florea, *Chimia Alimentelor*, *vol. I*, Editura Pax-Aura Mundi, Galați, 267, 1998.
4. Gy. Lukacs, *Whiteness the feasible method for evaluation*, Hungarian Scientific Instruments, 60, 1–5, 1985.
5. D. J. McClements, *Food Emulsions: Principles, Practice, and Techniques,* CRC Press: Boca Raton, 1999.
6. C. Romica, O. Mihaela, D. Stefan, B. Gabriela, *Food Colorants Immobilization by Emulsification/External Gelation Method*, CIGR International Symposium, Future of Food Engineering, Warsaw, Poland, 2006.
7. I. Sas, *Analize Fizico – Chimice și Controlul Calității Produselor*, Editura Fundatiei Universitare, Galați, 1989.
8. D. Stefan, *Chimie fizică și coloidală. Aplicații în Știința și Ingineria Alimentelor*, Editura Didactică și Pedagogică, București: 370–374, 2005.
9. D. Stefan, S. Aurel, *Chimie fizică și coloidală*, Editura Fundației Universitare "Dunărea de Jos" Galați, 219, 2001.
10. F. Traian, *Chimia Alimentelor – Teorie și practică analitică*, Editura Academica, Galați: 122–126, 2006.
11. F. Traian, C. Romica, Z. Gheorghe, *Studiul afinității unor coloranți alimentari față de fracțiile majore ale laptelui*, Buletin de Informare pentru Industria Laptelui, 19 (2): 86–102, 2004.
12. Gh. Zgherea, *Aparate și lucrări practice de analize instrumentale*, Editura Fundației Universitare "Dunărea de Jos", Galați, 2002.