Chromatic Characterization in Cielab System for Natural Dyed Materials, Prior Activation in Atmospheric Plasma Type DBD

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*The purpose of this paper is the investigation of the natural dye quantity (carthamin) fixed on the wool fiber and the lay out of the chromatic diagrams in system CIE 1976, also known as CIE L*a*b* space, using mathematical modelling with three independent variables (dyeing duration, dye concentration and dyeing temperature) as experimental tool, using factorial programming inside a 2^k composed revolvable central program. Prior to dyeing, the samples have been activated in atmospheric plasma type dielectric barrier (DBD). For this study we performed tow series of tests: one where the samples, prior to dyeing, have been activated in atmospheric plasma type dielectric barrier (DBD) and a second, where the samples have been dyed without prior fiber activation (witness sample).*

*Keywords: CIE L*a*b* space, natural dyed, plasma DBD, mathematical modelling*

The coloration with vegetal colorants suggests those refined colours where there is used a number of synthesis organic pigments. There is a high number of plants that contain pigments, some in the leaves, the flowers, the stalk, the root, and some in floral buds or in fruits. From these, only a few are those that can get fixed on the wool fiber so that the coloration resistances are good for external factors, such as light and humidity.

One of the most studied textile raw materials, on the background of energy consumption reduction by treatment at temperatures lower than boiling temperature, is the wool fiber, because, besides the economical purposes there are also reached objectives related to the quality of end item. There are obtained superior end characteristics for the influence degree of the textile material. The furs coloration is a chemical process where the keratine functionality decides the affinity of the dye and by default the optical effects generated by the pigments [1-2].

The color, by its characteristics: shading, luminosity and saturation, is defining for the use of pigments for the perfecting of textile materials [3].

From a commercial, technical and scientific point of view, the sensory assessment must be completed with an objective assessment of color, done by experimental measurements that allow the statement of results in numeric terms.

The CIE L*a*b* system is the space of color most frequently used in industry in the whole world, being defined on the base of physical properties of light and the physiological build of human eye [4].

Inside this chromatic system, any color can be specified inside the space by using the rectangural coordinates CIE L^*, a^*,b^*.

This system consists in two axes a* and b* that are perpendicular to each other and that represent the tone of colours. The third axis is the luminosity L* that is perpendicular to the plane made by the axes a* and b* and it refers to the reflected quantity of light by the color or, to the percent of black in the colour. L* takes values from zero (-) for perfect black to 100 (+) for perfect white. In the case that all values are positive, the higher they are, the lower will be the intensity of colouration . The axes of colors are based on the fact that a color can not be at the same time in red or green or in blue and yellow, because these colors oppose each other. For each axis the values are from positive to negative. On the axis +a –a the positive values indicate the sums of red, while the negative values indicate the sums of green. On the axis +b –b the positive values indicate the sums of yellow, and the negative values indicate the sums of blue. For both axes, zero is neutral gray [5-6].

In this paper there are presented the chromatic diagrams in CIELAB system of the colouration of wool fibers yarns with natural pigments, samples that were previously activated in atmospheric plasma type DBD, for the purpose of increasing the pigment quantity fixed to the wool fiber.

Experimental part

For the study there have been used samples of sheep fur, that were previously tanned with chrome basic salts and were treated with the mechanical operations of clipping-shearing with a length of wool fiber of 15 mm, and then they had been part of the activation treatment of wool fiber in instalation type DBD, followed closely by mordanting with bichrome and colouration with carthamin (fig. 1), that is a natural pigment extracted from saffron flowers, according to the mathematical model with three independent variables chosen for this experiment.

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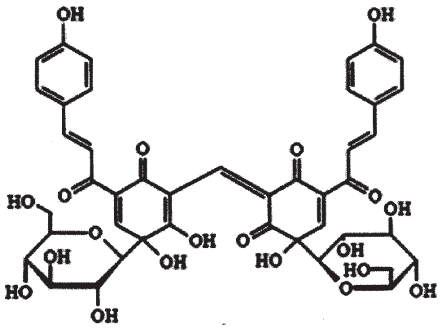

Fig. 1. Carthamin (C.I. Natural Red 26-75140) [7]

Table 1
VALUES OF TECHNOLOGICAL PARAMETERS

Parameter	U.M.	Coded Value				
		-1.682	-1.000	0	+1.000	+1.682
		Real Value				
Dyeing duration, X_1	min	40	50	65	80	90
Dye concentration, X_2	g/L	0.184	0.360	0.600	0.840	1.016
Dyeing temperature, X_3	°C	39.4	46.0	55.0	64.0	70.6

From a structural point of view, the carthamin has in its molecule 5 carbonyl groups (> C = O), that constitute chromophores and 13 hydroxyl groups (- OH) that play the role of auxochromes.

The carthamin, because of its low dissolubility (has high molecular mass, $M_{carthamin}$ = 450.38), presents a high substantivity towards the natural protean fibers, forming either chemical ties type ether or ester with wool fibers.

Materials and dyeing methods

For the dyeing operation, we used a bath with the following components:

- the pigment according to the experimental plan presented in table 1;
- surface-active;
- emulsifier to avoid the coloration of skin;
- calcined sodium, Na_2CO_3, 1 g/L;
- formic acid, 85%, 1.1 mL/L;
- emulsifier for lubrication (a combination of synthetic oils with special emulsifiers);
- bichrome.

The hydromodule of fleet is of 20:1 (calculated according to the dry mass of furs), 200 mL.

As independent variables we have chosen the coloration duration, X_1, the concentration of pigment, X_2, and the temperature of coloration bath, X_3, (table 1), and as dependent variable, Y we have chosen the quantity of pigment fixed to the wool fiber.

There were performed two series of tests: one where the samples, prior to coloration, have been activated in atmospheric plasma type dielectric barrier (DBD) and a second where the samples have been dyed without prior activation of the fiber (witness sample).

For the assessment of the coloration intensity there have been performed readings on the three filters red, green and blue of a MINOLTA (CR 300) spectrophotometer, that allowed the establishment of R_x, R_y and R_z ,and with the help of these values there have been calculated the values of trichromatic coordinates of the sample X, Y and Z according to the following formulas [8-9]:

$$X = 0{,}782*R_x + 0{,}198R_z \quad (1)$$

$$Y = R_y \quad (2)$$

$$Z = 1{,}181R_z \quad (3)$$

The trichromatic coordinates X,Y, Z are transformed in rectangular coordinates of the CIELAB space: L*, a*, b*. The equations that define the CIE L*a*b* colour system are:

$$L^* = 116*(y/y_n)^{1/3} - 16 \quad (4)$$

$$a^* = 500*[(x/x_n)^{1/3} - (y/y_n)^{1/3}] \quad (5)$$

$$b^* = 200*[(y/y_n)^{1/3} - (z/z_n)^{1/3}] \quad (6)$$

where:

$x_n = 98.075$
$y_n = 100.00$
$z_n = 118.224$

In agreement with [10-16], for the difference of colour between the two colours there have been used the relation ΔE_{ab}* CIELAB, that represents the geometrical distance (Euclidian) between the corresponding points (of the two samples) in the colour space (the distance from the test sample and the analysis sample), as follow:

$$\Delta E^* = [\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}]^{1/2}$$

where ΔL^* indicates any difference in brightness and is denoted by + if the sample which reproduces is lighter (brighter) than the witness specimen, and by – if it is darker than this.

Results and discussions

There have been established the colouration conditions with carthamin, performing 20 experiments of each array (samples activated in DBD and witness sample), according the chosen experimental plan, using the factorial programming inside a central rotatable composed program 2^k (table 1) [17, 18].

The assessment of the absorbed pigment concentration has been done by the layout of the calibration curve (fig. 2). The readings of extinctions have been done with a spectrophotometer with a glass dish and quartz with a volume of 2 cm^3 (2 mL), at a wave length of 520 nm.

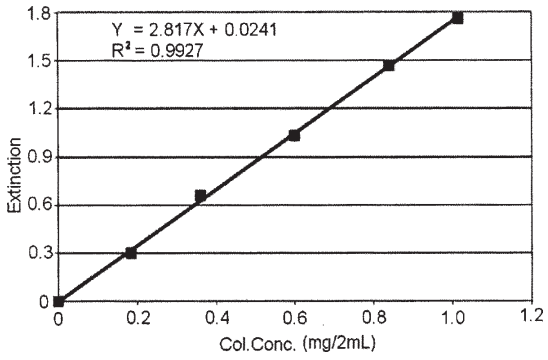

Fig. 2. The calibrator curve obtained at the spectrophotometric dosage in UV of carthamin

With the R_x, R_y and R_z ,values read at the spectrophotometer and with the help of the relations (1) ÷ (6) there have been calculated the trichrome coordinates X, Y, Z and the rectangural coordinates L*, a*, b* of the dyed fur samples without activation into cold plasma type DBD (witness sample) (table 2) and with previous activation in plasma DBD (table 3).

The reference sample found in the memory of the spectrophotometer software has the following characteristics: L^* = 8.992; a^* = 0.791; b^* = 2.333

Table 2
VALUES OF TRICHROME AND RECTANGULAR COORDINATES OF THE WITNESS SAMPLES

No. Exp.	R_x	R_y	R_z	X	Y	Z	L^*	a^*	b^*
1	63.2973	37.5603	27.4572	54.9350	37.5603	32.4270	67.722	51.367	14.347
2	63.7839	39.5619	23.4562	54.5233	39.5619	27.7018	69.182	26.719	23.506
3	63.6741	39.2810	23.5601	54.4580	39.2810	27.8245	68.980	27.076	22.976
4	64.4276	40.2538	24.5520	55.2437	40.2538	28.9959	69.675	26.790	22.467
5	63.7809	38.5629	23.7838	54.5859	38.5629	28.0887	68.460	28.490	21.690
6	64.0016	39.4539	22.1992	54.4447	39.4539	26.2173	69.105	26.765	25.615
7	63.4725	39.3562	25.4529	54.6752	39.3562	30.0599	69.034	27.320	19.850
8	62.8624	38.0510	16.7257	52.4701	38.0510	19.7531	68.085	25.748	34.753
9	50.0902	26.4502	14.9713	42.1349	26.4502	17.6811	58.494	27.519	22.211
10	72.0043	38.8375	26.7257	61.5991	38.8375	31.5631	68.660	39.951	17.127
11	50.0332	28.3860	10.2916	41.1637	28.3860	12.1544	60.267	22.642	37.732
12	72.5620	41.0076	29.5438	62.5932	41.0076	34.8912	70.206	38.023	15.420
13	52.5672	28.0566	13.7603	43.8321	28.0566	16.2509	59.972	27.726	27.700
14	69.2674	38.4904	30.5732	60.2206	38.4904	36.1069	68.407	38.187	10.789
15	63.1269	35.0583	17.7530	52.8803	35.0583	20.9664	65.822	31.433	28.642
16	62.7839	35.2232	17.9456	52.6502	35.2232	21.1938	65.950	30.767	28.458
17	62.4503	35.5907	17.4085	52.2830	35.5907	20.5594	66.234	29.530	30.083
18	62.7279	35.6230	18.2201	52.6608	35.6230	21.5179	66.259	30.119	28.418
19	62.7753	35.7504	17.6979	52.5945	35.7504	20.9012	66.357	29.794	29.680
20	63.0681	35.1736	18.1064	52.9043	35.1736	21.3837	65.912	31.281	28.056

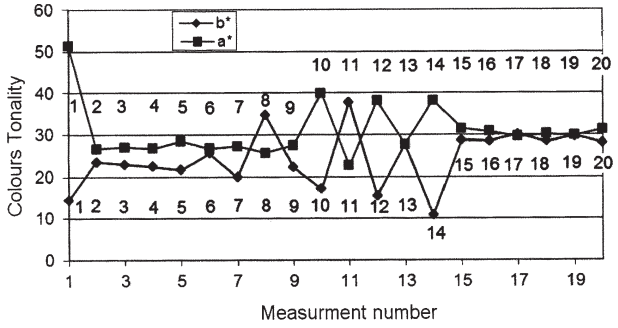

Fig. 3. The dynamics of red for witness samples

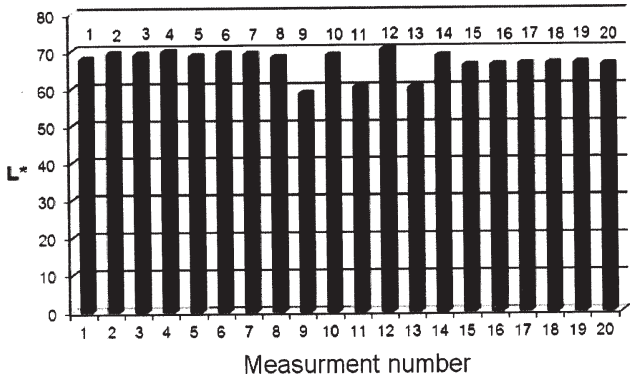

Fig. 4. The position of luminosity for witness samples

It is noticed that along with the increasing of temperature and of pigment concentration, the colour becomes more saturated, positioning in the positive zone of color coordinates a* and b*, and the difference of colour towards the reference is diminished, positioning the colour in the red – yellow quadrant, with a slight increasing tendency of the red component (fig. 3).

The luminosity decreases along with the increase of the pigment concentration, related to its calibration curve. The maximum absorbtion has been registered for experiment 12, when the absorbed pigment quantity is the lowest, also confirmed by the maximum luminosity registered in the case of the same variant (fig. 4).

For the witness samples (Table 2) the chromatic parameter a* situated on the coordinate of red – green colours has values between 51.367 and 22.642 with an average of 30.862. For the activated samples, prior to coloration, in atmospheric plasma type DBD (table 3) has values between 60.655 and 35.975 with an average of 44.053. The fact that the parameter a* has high positive values reflects the predominance of red shades over green ones.

The chromatic parameter b* situated on the coordinate of yellow – blue colors has values between 37.732 and 10.789 with an average of 24.476 for the witness samples and for the activated samples has values between 23.388 and 10.471 with an average of 19.496. Because all the values of the chromatic parameter b* are positive it can be concluded that in the case of examined samples the yellow shades are predominant over the blue ones with a plus for the witness samples (fig. 5).

The same as for the witness samples case, the tonality is situated in the positive area of the coordinates a* and b*, and the color is situated in the red – yellow quadrant, with

No. Exp.	R_x	R_y	R_z	X	Y	Z	L^*	a^*	b^*
1	68.1933	41.2820	28.3495	58.9403	41.2820	33.4807	70.3755	49.6424	17.5791
2	67.1819	40.5932	27.9302	58.0664	40.5932	32.9855	69.8925	49.6289	17.3970
3	67.1711	44.4235	28.9305	58.2560	44.4235	34.1669	72.5130	38.7900	20.3732
4	65.9006	43.5105	31.2941	57.7305	43.5105	36.9583	71.9025	40.1541	15.8136
5	66.7719	43.2800	27.5623	57.6729	43.2800	32.5510	71.7470	40.6849	21.1707
6	67.3014	45.3452	28.0073	58.1751	45.3452	33.0766	73.1209	35.9751	22.8430
7	67.6222	43.2317	30.4518	58.9100	43.2317	35.9635	71.7144	43.7994	16.7181
8	65.1227	39.0283	25.3924	55.9536	39.0283	29.9884	68.7744	49.2936	19.5534
9	64.2415	40.4285	25.2201	55.2304	40.4285	29.7849	69.7762	43.1812	21.5677
10	74.2012	44.5326	31.7261	64.3071	44.5326	37.4685	72.5854	52.5526	16.3693
11	66.3682	37.4563	23.1192	56.4775	37.4563	27.3037	67.6207	55.5567	21.4608
12	71.5229	46.3420	33.1401	62.4926	46.3420	39.1384	73.7692	43.3260	16.4140
13	62.4967	39.0902	27.5133	54.3200	39.0902	32.4932	68.8192	45.0252	16.1998
14	72.2116	40.7342	32.7325	62.9505	40.7342	38.6570	69.9918	60.6559	10.4710
15	66.1242	43.3418	27.4412	57.1424	43.3418	32.4080	71.7887	39.2167	21.4335
16	66.8732	43.4902	26.7219	57.5857	43.4902	31.5585	71.8888	39.8624	22.7512
17	66.5583	43.5804	27.1932	57.4328	43.5804	32.1151	71.9495	39.2299	22.1033
18	66.3217	43.8307	26.5034	57.1112	43.8307	31.3005	72.1176	37.7234	23.4975
19	66.5652	43.4328	26.6393	57.3285	43.4328	31.4610	71.8501	39.4049	22.8173
20	66.9055	44.4211	26.9942	57.6649	44.4211	31.8801	72.5114	37.3706	23.3887

Table 3
VALUES OF TRICHROME AND RECTANGULAR COORDINATES OF THE ACTIVATED SAMPLES

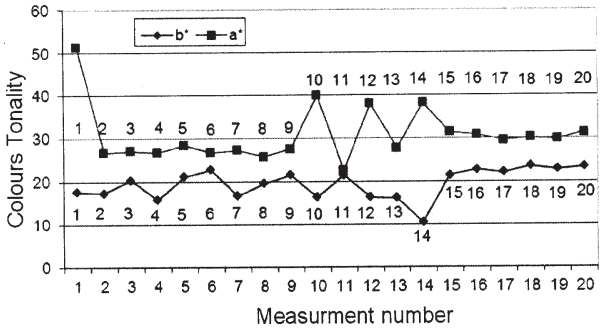

Fig. 5. The red degree dynamic for activated samples

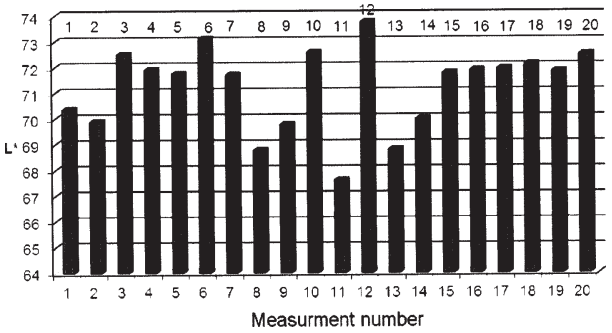

Fig. 6 - The positioning of luminosity for activated samples

an increased tendency of higher red component (experiments 6, 15, 16, 17, 18, 19 and 20).

A diminishment of luminosity L* causes a decrease of the chromatic parameter a* and an increase of b*. On the other side, the increase of pigment concentration from the coloration fleet leads to an increase of the the parameters a* and b*, at the same time with a decrease of L*. Through the increase of the pigment quantity in the solution, paralleled with the increase of temperature, there has been obtained the increase of the red degree. This increase is direct proportional with the difused pigment quantity in the wool fiber at the same time with the decrease of sample luminosity (fig. 6, experiments 8, 11 and 13). From a sensory point of view that means that the colour becomes less intense the more the quantity of pigment per volume unit increases and becomes less significant according to the concentration of the pigment.

Conclusions

The method of chromatic characteristics assessment proposed by the „Commission Internationale pour l2 Eclairage" in CIE L*a*b* - 76 is the most complete color model used for the description of colours in the visible spectre, because it provides the possibility of assessing the difference between two close colours, from all parameters (shade, saturation and luminosity). For the pigment solutions, the parameters L*, a* and b* lead to more exact results and to a more precise assessment of the accuracy of perceived colour by positive tristimulus values.

There have been determined the values R_x, R_y R_z and there have been calculated the trichrome coordinates X, Y, Z and the rectangural coordinates L*, a*, b* in system CIELAB, of the dyed samples in both cases.

There have been assigned the chromatic diagrams in CIE L*a*b* space of both coloration variants and the calibration curve of carthamin.

The CIE L*a*b* - 76 method makes it easier to understand the relation between the visual appearance of the colour and the numeric articulation of the chromatic parameters of dyed textile materials.

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References

1.BUTNARU, R., DONCEAN, GH., Procese neconvenţionale pentru finisarea materialelor textile, vol. II, Ed. Performantica, Iaşi, 2006.
2.BUTNARU, R., DONCEAN, GH., Procese neconvenţionale pentru finisarea materialelor textile, vol. I, Ed. Performantica, Iaşi, 2005.
3.BUTNARU, R., BERTEA, A., Finisarea produselor textile, Ed. Rotaprint, Iaşi, 2001.
4.BERCU E., DIACONESCU R-M., RADU C-D., POPESCU V., European Journal of Science and Theology, **8, (4),** 2012, p. 247.
5.PUSCAS E.L., Teoria şi măsurarea culorii, Ed.Rotaprint, Iaşi, 1983, p.167.
6.WARDMAN R. H., Rev. Prog. Coloration, **24,** 1994, p. 55.
7.*** Colour Index, 1982, The Society of Dyers and Colorists – The American Association of Textile Chemists and Colourists, Third Edition,Vol. 3

8.RADU C. D., Măsurarea culorii, Ed. Rotaprint, Iaşi, 2004, p.61.
9.PUSCAS E. L., RADU C-D., Introducere in cunoasterea si masurarea culorii, Ed. Dosoftei, Iasi, 1997, p. 58.
10.SANDU I. , SANDU I.C.A., SANDU I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.
11.SANDU I.C.A., LUCA C., SANDU I.. Rev. Chim, (Bucharest), **51**, 2000, p. 532
12.SANDU I., LUCA C., SANDU I.C.A., A. CIOCAN, N. SULITANU. Rev Chim. (Bucharest), **52**, 2001, p. 485
13.SAVIUC-PAVAL A.-M., SANDU I., POPA I.M., SANDU I.C.A., VASILACHE V., SANDU I.G., Rev. Chim. (Bucharest), **63,** no. 2, 2012, p.170.
14.BERCU E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., ALDEA, H.A., Mat. Plast., **49**, no. 4, 2012, p. 270.
15.WYSZECKI G, STILES W., Color Science concepts and methods, quantitative data and formulae, 2nd edn, New York, 2000.
16.SANDU I., Aspecte moderne privind conservarea bunurilor culturale, vol.V, Ed. Performantica, Iasi, 2007.
17.CIOCOIU, M., Bazele statistico-matematice ale analizei şi controlului calităţii în industria textilă, Ed. Performantica, Iaşi, 2002.
18.CIOCOIU, M., CIOCOIU, M., ANTONIU, GH., Strategia cercetării, Ed. Performantica, Iaşi, 2002

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