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The Colour Characteristics of Wool Dyed with Plants of Latvia

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Abstract. **Dyeing with natural dyes from plant and other organic sources is known since the prehistoric times. In Latvia, natural dyes have been used for the colouring of natural fibres, such as flax, wool, cotton, silk and leather. Plants for the dyeing were collected in autumn in Latvia, used fresh or dried. Mordant ferrous sulphate, copper sulphate pentahydrate, potassium hydroxide, potassium dichromate and acetic acid were used before, during and after dyeing. The quality of dyeing was evaluated using the RGB system.**

Keywords: **Natural Dyes, Wool Yarn, Mordanting, Colour Evaluation.**

I. Introduction

Dyeing with natural or vegetable dyes from plant and other organic sources is known since the prehistoric times [1]. Throughout history, people have dyed their textiles using common, locally available materials. In Latvia, natural dyes have been used for the colouring of natural fibres, such as flax, wool, cotton and silk, as well as leather [2].

Nowadays, interest in natural dyes is a result of awareness and demand for natural products [3]. Natural dyes are eco-friendly, biodegradable, non-toxic, and less allergenic in comparison with synthetic dyes [4]. The uncontrolled discharge of synthetic dyes into the aquatic ecosystem is a global environmental concern due to their negative ecotoxicological effects. Dyes obtained from different natural sources have emerged as an important alternative to synthetic dyes [5].

With Latvian plants it is easier to dye beige, pale yellow and pale green shades. Most difficult is to get the pink and blue shade, due to the fact that in our plants this pigment is not found. The dyeing is not sustainable from blueberries, chokeberries and blackcurrants [2].

Natural colorant from the plants was extracted under different operating conditions such as extraction time (45–120 min), temperature (60–90 C) [5] as well as conventional method and ultrasonic technique [6].

To improve the intensity of the natural dyes extracted from plants, a mordant is required. The various substances- mineral (salts, crusts, mud, metal oxides) and organic (urine, animal or vegetable fats, plant's juices and broths) can be considered for mordanting [7]. Different mordants allow different colour ranges for each dyestuff.

Some basic techniques of mordanting have been applied. One of them is pre-mordanting it means that the dye-bath is not altered by adding a mordant. The simultaneous mordanting is a quick method and gives good results with wool when light colours are desired. The post–mordanting is possible to intensify, fix more permanently or modify the shades [7].

Latvian handcraftsmen have been using natural dyes for manufacturing crafts since ancient times. In this study, non-toxic and eco-friendly dyes were extracted from Latvian plants collected during the autumn season, used for wool dyeing and the quality of dyeing result was evaluated.

II. Materials and Methods

A. Materials.

100% wool yarn (245Tex) produced by "Klippan Saule" Ltd., Latvia was used. Wool was prewashed with a solution of pH neutral liquid laundry detergent "KASTANIS CLASSIC" (JSC "Spodriba", Latvia) before dyeing (liquor ratio 30; dose-2 g/l at 30°C for 10 min.), rinsed with warm and cold water.

The plants (Tab.1) such as leaves of white chestnut (Ch.), Norway maple (M), apple-tree (A) and vine (V), bush of cowberry (C), heather (H) and plants of common nettle (N) and onion peel (O) were collected in the region of Riga in an autumn and used fresh. Leaves of hemp (He) from experimental fields of Agriculture Science Centre of Latgale, harvested in autumn, were used dried.

B. Chemicals

Mordants such as ferrous sulphate ($FeSO_4$), copper sulphate pentahydrate ($CuSO_4*5H_2O$), potassium hydroxide (KOH), potassium dichromate ($K_2Cr_2O_7$) and acetic acid (CH_3COOH) were used. The doses of mordant were 5 g/l and 33 g/l in case of CH_3COOH.

C. Methods

Preparation of the dyes extract

Chopped plants were soaked in distilled water (ratio 1:10) 24 h at room temperature. After boiling 1.5 h and filtration, dregs were boiled repeatedly at the same water ratio. Both extracts were mixed and used for the dyeing.

Dyeing

Wool was dyed (Tab.1) (liquor ratio 30) at 80-95°C for 60 min, rinsed with warm and cold water, squeezed and dried at room temperature.

Mordanting

Pre- mordanting (B) before dyeing (liquor ratio 30) in separate bath containing a mordant (title B Chemicals) at 30 °C for 45 min. was used. Wool was rinsed with water (warm, cold), squeezed and dried.

Simultaneous mordanting (liquor ratio 30) was done at the time (T) of dyeing in a bath containing a mordant (title B Chemicals) at 80-95°C for 60 min. The samples were rinsed with warm and cold water, squeezed and dried at room temperature.

Post-mordanting (title B Chemicals) was used after the dyeing (A) (liquor ratio of 30) at 30 °C for 45 min

TABLE 1

DESIGNATION OF SAMPLES, USED PLANTS, MORDANTS AND METHOD OF MORDANTING, COLOUR PARAMETERS OF DYED SAMPLES

Nr.	Used Plants	Used Chemicals	Method of Mordanting	Designation of Sample	Degree of Lightness, L*	Coordinate of Colour Vector		Hue, H
						a*	b*	
0	Wool	pH neutral laundry detergent"Kastanis Classic"	Prewashed	0	79.91	3.38	3.90	-
1	Leaves of white chestnut	$CuSO_4*5H_2O$	Post-mordanting	Chl_$CuSO_4$_A	49.75	6.47	16.42	1.47
2		$FeSO_4$	Post-mordanting	Chl_$FeSO_4$_A	56.71	3.98	15.89	1.5
3	Fruits of white chestnut	$CuSO_4*5H_2O$	Post-mordanting	Chs_$CuSO_4$_A	49.82	3.76	7.88	1.33
4		$FeSO_4$	Post-mordanting	Chs_$FeSO_4$_A	54.90	3.60	7.65	1. 52
5	Leaves of Norway maple	-	Without mordant	M	45.80	4.18	2.96	-0.87
6		$FeSO_4$	Simultaneous mordanting	M_$FeSO_4$_T	30.92	3.64	3.29	-1.17
7	Leaves of apple-tree	$CuSO_4*5H_2O$	Post-mordanting	A_$CuSO_4$_A	50.17	3.70	14.45	1.54
8		$FeSO_4$	Post-mordanting	A_$FeSO_4$_A	40.71	2.13	9.27	-1.34
9	Leaves of vine	$CuSO_4*5H_2O$	Post-mordanting	V_$CuSO_4$_A	42.62	8.86	16.21	1.15
10		$FeSO_4$	Post-mordanting	V_$FeSO_4$_A	39.38	4.98	11.71	1.37
11		$FeSO_4$	Pre-mordanting	V_$FeSO_4$_B	38.33	5.79	11.01	1.24
12		$K_2Cr_2O_7$	Simultaneous mordanting	V_$K_2Cr_2O_7$_T	57.79	5.12	12.72	1.38
13	Bush of cowberry	-	Without mordant	C	63.46	5.88	23.70	1.45
14		$CuSO_4*5H_2O$	Post-mordanting	C_$CuSO_4$_A	48.21	4.23	20.85	1.52
15		$K_2Cr_2O_7$	Simultaneous mordanting	C_$K_2Cr_2O_7$_T	44.51	6.53	23.53	1.41
16		$K_2Cr_2O_7$	Pre-mordanting	C_$K_2Cr_2O_7$_B	53.57	7.34	29.47	1.42
17	Bush of heather	-	Without mordant	H	46.78	5.41	16.81	1.41
18		$CuSO_4*5H_2O$	Pre-mordanting	H_$CuSO_4$_B	55.67	2.92	16.98	-1.54
19	Plants of nettle	$CuSO_4*5H_2O$	Post-mordanting	N_$CuSO_4$_A	51.12	5.86	20.08	1.42
20		$FeSO_4$	Post-mordanting	N_$FeSO_4$_A	51.25	3.99	9.23	1.46
21	Onion peel	-	Without mordant	O	54.06	9.73	18.24	1.15
22		KOH	Post-mordanting	O_KOH_A	34.05	12.13	20.24	1.08
23		KOH	Simultaneous mordanting	O_KOH_T	35.58	13.55	23.02	1.08
24	Leaves of Hemp	-	Without mordant	He	69.14	3.07	18.05	-1.51
25		CH_3COOH	Simultaneous mordanting	He_CH_3COOH_T	62,04	5,79	15.01	1.38
26		$K_2Cr_2O_7$	Simultaneous mordanting	He_$K_2Cr_2O_7$_T	61,46	4,56	11.92	1.47
27		$CuSO_4*5H_2O$	Simultaneous mordanting	He_$CuSO_4$_T	59.63	-0.53	10.03	-0.87
28		$FeSO_4$	Simultaneous mordanting	He_$FeSO_4$_T	62.38	5.74	3.52	-0,61

Colour Test

The samples representing variations (Tab.1) were carried out in the spectral width from 400 to 700 nm (CQA Easy Color V3.0 Pocketspec Technologies Inc, USA), using CIE L* a* b* measuring system, what allows to determine the

coordinates of colour vectors a*, b* and L*- the degree of lightness in the colour space [8]. (ΔL*), common colour differences (ΔE), chroma (C) and hue (H) were calculated according to the following common formulas [9].

$$\Delta L^* = L^*_{sample} - L^*_{standard} \quad (1)$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

$$C = \sqrt{(a^*)^2 + (b^*)^2} \quad (3)$$

$$H = arctg(\frac{b^*}{a^*}) \quad (4)$$

L^*_{sample}- the degree of lightness of sample,

$L^*_{standard}$- the degree of lightness of standard,

Δa*, Δb*-average of coordinates of colour vector.

Parameters of dyed samples were compared with the prewashed wool as standard was used.

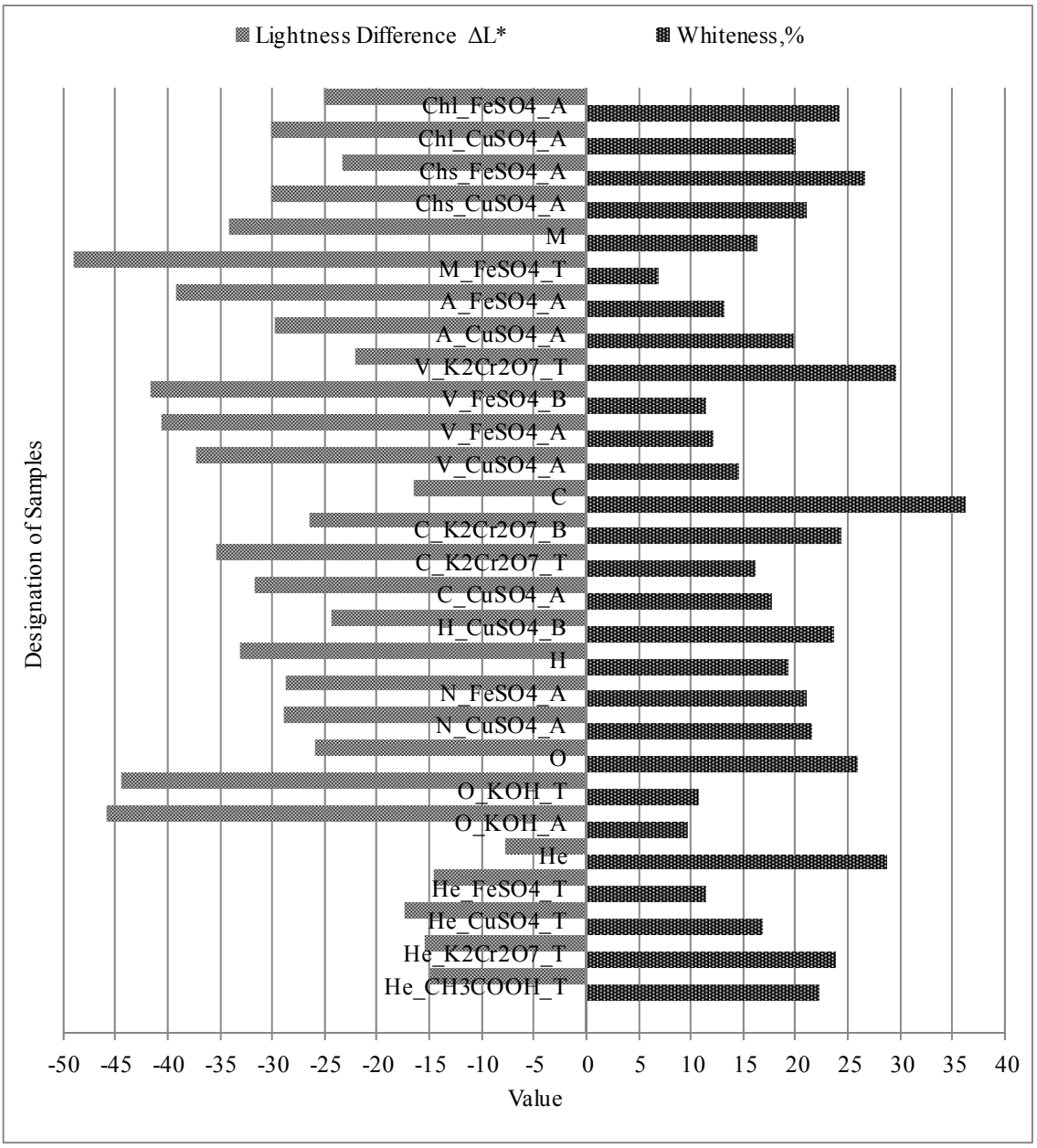

Fig.1. Lightness Difference and Whiteness of Dyed Samples

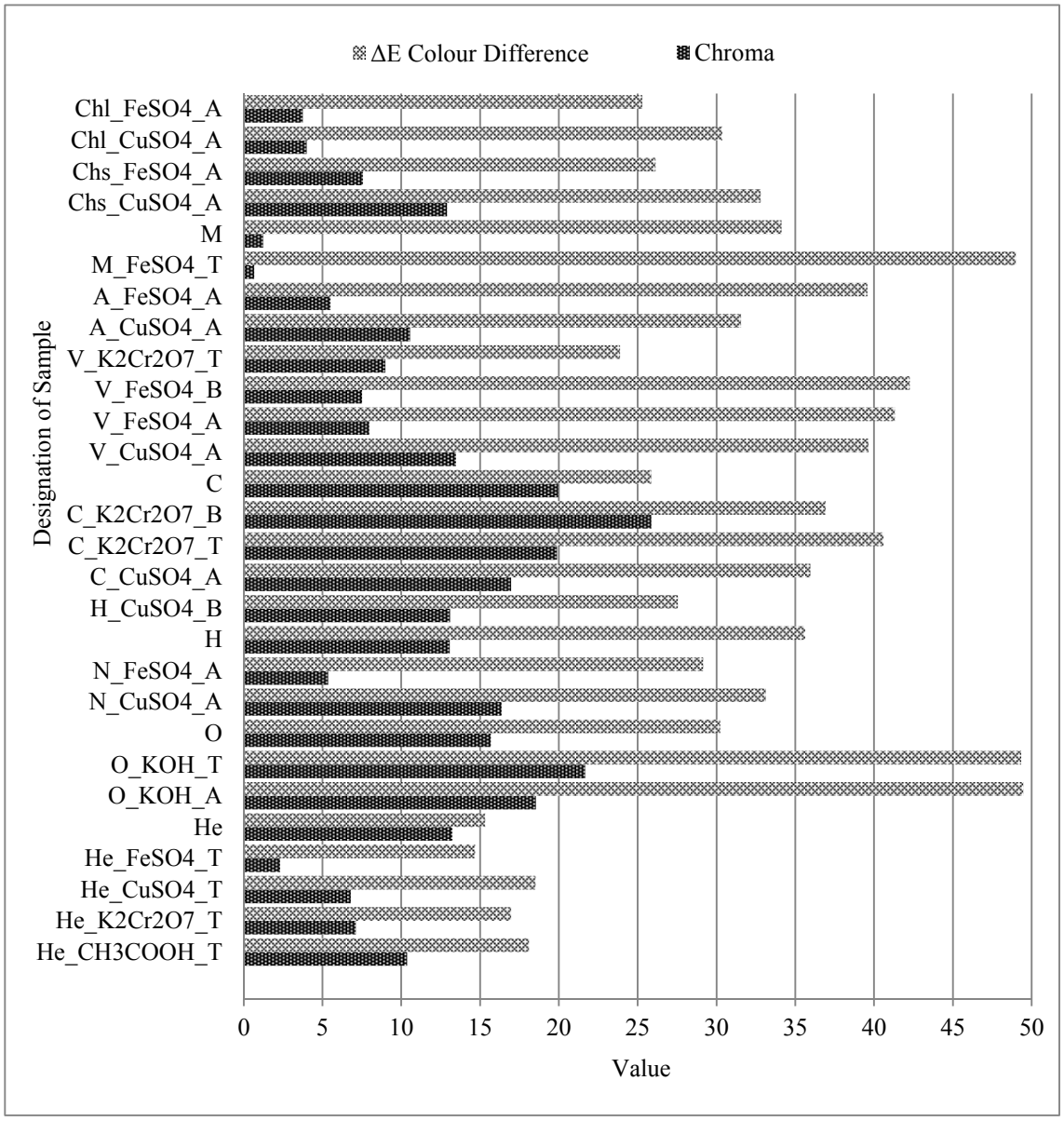

Fig.2 Colour Difference and Chroma of dyed samples

Whiteness Test

Whiteness of dyed samples was determined with Rhopoint Novo-Shade Duo 45/00° reflectometer (Rhopoint Instrumentation Ltd, UK). Preparing and testing of samples according to user manual [10] was performed.

III. Results and Discussion

The wool samples dyed with the above- mentioned Latvian plants without and with different mordants using and applying the three mordanting methods, gave mainly yellowish, brownish, greenish and grey colours.

Colour coordinates (Tab.1) a* (-0.5-13.6) and b*(2.9-29.5) characterise redness (+a*), greenness (-a*), yellowness (+b*) and blueness (-b*) [11]. Higher values of a*, b* were obtained with mordant K2Cr2O7 use and pointed at ruddy and yellowy shade of the colour of the sample.

Values of degree of lightness (Tab.1) are positive. The colour of hemp without mordanting (69.14) is a bit darker, than prewashed wool, but maple (45.80) is still darker than the preliminary sample. However, the lightness of hemp with FeSO4 (62.38) use is slightly deeper than without mordanting (69.14). The major decrease of lightness (30.92) has been observed with maple and same mordant application. It indicates that the main factor is used plant.

The value of hue (Tab.1) indicates the variety of colour shades of dyed wool. The sample with hue value (-0.87) indicates dark grey colour with maple as well as the dun colour with hemp with FeSO4 use (simultaneous-mordanting). The value of hue (-1.5) points at greenish-grey colour of heather with the same mordant and method use, as well as light yellowish colour of hemp sample. Positive values of hue (1.5) point at snuff colour (hemp with K2Cr2O7 simultaneous-mordanting), green hay colour (cowberry and apple with CuSO4) as well as dark straw colour (chestnut with CuSO4). The significant change of hue has been observed with one plant use with different mordants. It indicates, that important for hue is both- use of plant and mordant.

Values of the lightness difference (Fig.1) characterize the difference between lightness of the sample and lightness of the standard (prewashed wool). For samples without mordant use the lowest difference of lightness (-7.74) is for hemp (beige colour), the higher (34.11) is for maple (medium grey colour). For samples with mordant use, lower difference of lightness is (-14.49) for samples dyed with white chestnut (hay colour) with ferrum sulphate (simultaneous mordanting). The greater difference of lightness (-49.0) is for maple (dark gray) with ferrous sulphate use (simultaneous mordanting), as well the lower whiteness index (6.9 %) has been set for this sample, due to dark colour.

For comparison and explaining the obtained results, the whiteness index, % (Fig.1) of wool samples was determined from black (0%-no reflectance) to brilliant white (100%-full reflectance). The value of whiteness of prewashed wool (36.5) as standard was used. With ferrous sulphate and cowberry has been observed whiteness index 36.3% (light hay colour), while about 19% with use of vine (dark beige colour) and potassium dichromate (simultaneous mordanting). It indicates, that a greater influence on the lightness difference and the whiteness was observed from the used mordant.

The value of colour difference (Fig.2) denotes a common colour difference of the sample. Without mordant use the lowest difference (15.33) is for hemp, the highest (35.61) is for heather. For samples with mordant use, the lower value (14.67) is obtained for hemp with FeSO4 use (simultaneous mordanting). The influence of ferrum sulphate use on colour difference value in this case is about 18%, while with maple use, the same mordanting method - about 30%. With potassium hydroxide and onion (post-mordanting) use the highest difference of colour (40%) was observed. The influence of copper sulphate pentahydrate with hemp is about 18%. For potassium dichromate with cowberry- 39%, while with hemp- 10% difference of colour was observed. The most significant influence on colour difference value has been achieved from the used mordant.

Chroma (Fig.2) is a measure of intensity or saturation of any hue. The lowest value of chroma (Fig.2) of the sample without mordanting is for maple (1.23) greyish beige colour, whereas light hay colour is with cowberry (16.96). For maple mordanted simultaneously with ferrous sulphate the lowest value of chroma (0.66) has been observed, the dark gray shade of sample. The higher parameter of chroma (25.9) is for cowberry, mordanted with potassium dichromate before dyeing (green shade) and onion (21.7) with potassium hydroxide (brown shade). By the reduction of the saturation of hue, the colour turns into different grey shades due to the used mordant. From the used plants the intensity of chroma observed as different shades of green, yellow or brown colour.

IV. Conclusion

The plants of Latvia were used for wool dyeing without and with the use of different mordants and application of three mordanting methods.

The main factor of influence on lightness is a used plant. The darkness of all samples indicated the negative lightness difference.

The most significant influence on colour difference has been achieved from used mordant and the positive values of colour difference are due to the distinction of common colour difference of each colour.

The whiteness index indicates, that greater influence on the lightness difference and the whiteness has been observed from the used mordant.

Positive and negative values of hue pointed at various shades (yellowish, brownish, greenish and grey colours) of colouring.

The value of chroma pointed at influence of mordant and plant use on colour saturation of dyeing as different shades of green, yellow or brown colour, but by decrease of saturation the colour turns into different grey shades.

The colour parameters are dependent on used plants and mordants more than applying of mordanting method.

The use of the RGB system for the evaluation of quality of dyeing is a new method for craftsmen of Latvia for the dyeing colour characterization.

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Aina Bernava. Ar Latvijas augiem krāsotas vilnas krāsojuma raksturojums.
Pasaulē krāsošana ar dabas krāsvielām ir zināma kopš aizvēsturiskiem laikiem. Latvijā tās pielieto dabisko šķiedru- linu, vilnas, kokvilnas un zīda, kā arī ādas krāsošanai. Dabas krāsvielas ir videi un cilvēkam draudzīgākas nekā sintētiskās krāsvielas. Mūsdienās interese par dabiskiem produktiem palielina pieprasījumu krāsošanai ar dabas krāsvielām.
Pētījumā krāsota 100% vilna (245 Tex, SIA ”Klippan Saule”, Latvija), kas mazgāta ar pH neitrālu mazgāšanas līdzekli “KASTANIS CLASSIC”(AS ”Spodrība”, Latvija). Augu lapas- (kļavu, ābeles, mežvīteņu, kaņepju un kastaņas), mētras (brūkleņu un viršu), kā arī sīpolu mizas ievāktas rudenī. Krāsošanas šķīduma sagatavošanai nepieciešams 1.0 kg svaigu vai 0.5 kg kaltētu augu uz 0.1 kg dzijas (Vannas modulis 30). Tos sasmalcina, pārlej ar aukstu ūdeni (1:10) un notur 24h istabas temperatūrā, tad 1.5h vāra. Augu izvilkumu nokāš, atkārtoti pārlej ar tādu pat ūdens daudzumu un procedūru atkārto. Abus augu novārījumus salej kopā. Dziju krāso 80-95°C temperatūrā, 60 min. Kodina, atbilstoši receptūrai (5 g/l) ar dzelzs sulfātu, vara sultātu (5 hidrātu), kālija hidroksīdu un kālija dihromātu vai etiķskābi (33 g/l) pirms, pēc krāsošanas (30°C, 45 min), vai krāsošanas laikā.
Paraugu krāsu atšķirības analizē ar CQA Easy Color V3.0 Pocketspec (Technologies Inc, ASV) krāsu testeri, izmantojot RGB sistēmu, kas ļauj noteikt krāsu vektoru koordinātes CIElab-76 krāsu telpā. Pēc iegūtajiem mērījumiem aprēķina gaišuma atšķirību (ΔL*), krāsu atšķirību (ΔE), nokrāsu (C) un krāsu toni (H). Krāsojuma baltuma pakāpi (%) nosaka ar virsmas atstarošanas mērītāju Rhopoint Novo-Shade Duo 45/00^0 (Rhopoint Instrumentation Ltd, UK).
Secinājumi: Visi izpētē izmantotie Latvijas augi ir piemēroti vilnas krāsošanai, Krāsojot iegūtas zaļganas, pelēcīgas vai dzeltenīgas nokrāsas izkrāsojumi. Krāsu atšķirību, kā arī krāsu toni vairāk ietekmē pielietotais augs nekā izvēlētais kodinātājs vai kodināšanas metode, ko apliecina vilnas izkrāsojumu primārā krāsu kvalitātes pārbaude. Krāsa ir atkarīga no izmantotajiem augiem un kodinātājiem.

Айна Бернава. Цветовая характеристика шерстяной пряжи, окрашенной природными красителями Латвии.
Крашение с природными красителями известно с доисторических времён. В Латвии природные красители примененяются для крашения природных волокон - льна, шерсти, хлопка и шелка, а также кожи. Эти красители более экологичны по сравнению с синтетическими красителями. В наше время повышается интерес к экологическим продуктам, и в связи с тем к использованию природных красителей.
Для крашения применена 100% шерстяная пряжа (245 текс, Латвия "Klippan Saule"), которая выстирана pH-нейтральным моющим средством “KASTANIS CLASSIC” (Латвия, "Spodriba"). Листья (клён, яблоня, ломонос, конопля, каштан), мята (брусника и вереска), также шелуха луковиц собранных осенью, применяют в высушенном виде. Для подготовки красильного раствора необходимо 1 кг свежих или 0.5 кг высушенных растений на 0.1 кг пряжи (модуль ванны 30), которые измельчают, заливают холодной водой (1:10), выдерживают 24 часа при комнатной температуре, кипятят 1,5 часа. Получают отвар, и процесс снова повторяют. Оба раствора сливают вместе. Крашение шерстяной пряжи производят при тепературе 85-90^{0}C в течение 1 часа, полощут тёплой и холодной водой, сушат при комнатной температуре. Для травления шерсти применяют сульфат железа, сульфат меди 5- водный, дихромат и гидроксид калия (5 г/л), а также уксусную кислоту (33 г/л) перед/после (при температуре 30^{0}C, 45минут) или во время крашения шерсти.
Для оценки окрашенной пряжи использован прибор CQA Easy Color V3 Pocketspec (Technologies Inc, США) и система RGB, которая позволяет установить координаты цветовых векторов в цветовом пространстве CIELAB-76. Полученные результаты измерений использованы для расчетов светлого тона (ΔL*) цветового различия (ΔE), оттенка (C) и тона цвета (H). Степень белизны (%) окрашенной пряжи измеряет аппаратом Rhopoint Novo-Shade Duo 45/00^0 (Rhopoint Instrumentation Ltd, UK).
Вывод: все использованные растения Латвии применяются для крашения шерстяной пряжи. Первичная проверка качества окрасок показывает, что цветовые параметры зависят от применяемых растений и протрав.