TEKSTİL VE MÜHENDİS

(Journal of Textiles and Engineer)

http://www.tekstilvemuhendis.org.tr

Investigation of the Effect of Turkey Red Oil on Colour, Fastness Properties and HPLC-DAD Analysis of Silk Fabrics Dyed with Madder (Rubia Tinctorium L.) and Gall Oak

Kök Boya (Rubia Tinctorium L.) ve Mazi Meşesi ile Boyanmış İpek Kumaşların HPLC-DAD Analizi ve Türk Kırmızısı Yağını Renk ve Haslık Özellikleri Üzerindeki Etkisinin İncelenmesi

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Bu makaleye atıf yapmak için (To cite this article):

Lale MEYANCI ÖZER, Recep KARADAĞ, Emine TORGAN (2016): Investigation of the Effect of Turkey Red Oil on Colour, Fastness Properties and HPLC-DAD Analysis of Silk Fabrics Dyed with Madder (Rubia Tinctorium L.) and Gall Oak**,** Tekstil ve Mühendis, 23: 103, 197-204.

For online version of the article: http://dx.doi.org/10.7216/1300759920162310305

TMMOB Tekstil Mühendisleri Odası
UCTEA Chamber of Textile Engineers
Tekstil ve Mühendis
Journal of Textiles and Engineer

Yıl (Year) : 2016/3
Cilt (Vol) : 23
Sayı (No) : 103

Research Article / Araştırma Makalesi

INVESTIGATION OF THE EFFECT OF TURKEY RED OIL ON COLOUR, FASTNESS PROPERTIES AND HPLC-DAD ANALYSIS OF SILK FABRICS DYED WITH MADDER (*RUBIA TINCTORIUM* L.) AND GALL OAK

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Received / Gönderilme Tarihi: 27.01.2016
Accepted / Kabul Tarihi: 19.07.2016

***ABSTRACT*:** Madder (*Rubia tinctorum* L.) has been used for dyeing textile materials since the stone age. This plant contains natural pigments in its roots, such as alizarin, pseudopurpurin, purpurin, munjistin, rubiadin, xanthopurpurin, purpuroxanthin, lucidin, chinizarin, christofin and anthragallol. Madder gives a unique red colour to textiles. The aim of this study is to understand the effect of Turkey red oil on silk dyeing by using madder (*Rubia tinctorıum* L.) and gall oak extracts (*Quercus infectoria* Olivier). Alum [$KAl(SO_4)_2.12H_2O$] and $Ca(NO_3)_2.4H_20$ were used as mordant. Mordanting was achieved at 65^{0}C for 120 min, at pH 4-5 with flotte ratio 100:1. The dyeing process was carried out a at 65^{0}C for 60 min. at pH 6-7 with flotte ratio of 100:1. The colour coordinates K/S, as well as washing, light and rubbing fastness values were determined and discussed. Reversed-phase high-performance liquid chromatography with diode-array detection was utilized for the identification of colouring compounds present in the dyed silk fabrics. The effects on the results of gall oak, madder and Turkey red oil was evaluated.

Keywords: Madder; *(Rubia tinctorum* L.*)*, Gall oak; *(Quercus infectoria* Olivier*)*, Turkey red oil; Silk fabric; Colour measurement; Fastness; Alizarin; Purpurin, Rubiadin; HPLC-DAD.

KÖK BOYA (*Rubia tinctorium* L.) VE MAZI MEŞESİ İLE BOYANMIŞ İPEK KUMAŞLARIN HPLC-DAD ANALİZİ VE TÜRK KIRMIZISI YAĞINININ RENK VE HASLIK ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİNİN İNCELENMESİ

ÖZET: Kökboya ilk çağlardan beri tekstil materyallarinin boyanmasında kullanılmaktadır. Bu bitki köklerinde alizarin, pseudopurpurin, purpurin, munjistin, rubiadin, xanthopurpurin, purpuroxanthin, lucidin, chinizarin, christofin, and anthragallol gibi doğal pigmentleri içerir. Kökboya, tekstil ürünlerine eşsiz bir kırmızı renk verir. Bu çalışmanın amacı; kökboya (*Rubia tinctorıum* L.) ve mazı meşesi (*Quercus infectoria* Olivier*)* ekstratları kullanılarak boyanmış ipek kumaşlar üzerindeki Türk kırmızısı yağının etkilerini incelemektir. Mordanlama işleminde alum [$KAl(SO_4)_2.12H_2O$] ve $Ca(NO_3)_2.4H_20$ mordanları olarak kullanıldı. Mordanlama, banyo oranı 100:1 alınarak pH 4-5 de 65 ^{0}C sıcaklıkta 120 dakikada yapıldı. Boyama işlemi, banyo oranı 100:1 alınarak pH 6-7 de 65 ^{0}C de 120 dakikada yapıldı. Renk koordinatları K/S oranı ile birlikte yıkama, ışık ve sürtünme haslıkları bulundu ve değerlendirildi. Boyanmış kumaşlarda bulunan renkli maddelerin tanımlanması için Ters Fazlı Yüksek Performanslı Sıvı Kromatografisi (RP-HPLC) kullanıldı. Türk kırmızısı yağı, mazı meşesi ve kökboya'nın sonuçlar üzerindeki etkileri incelendi.

***Anahtar Kelimeler*:** Kökboya; *(Rubia tinctorum* L.*)*, mazı meşesi; (*Quercus infectoria* Olivier), İpek kumaş, Renk ölçümü, Haslık, Alizarin; Purpurin, Rubiadin; HPLC-DAD.

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DOI: *10.7216/1300759920162310305, www.tekstilvemuhendis.org.tr*

1. INTRODUCTION

Natural dyes are obtained from dye plants and dye animals in nature [1-9]. They were the primary colour source of textiles until the mid to late 19th century [10-13]. Natural dyes can be sorted into three categories: natural dyes obtained from plants, animals and minerals. Although some fabrics such as silk and wool can be coloured simply by being dipped in the dye, others such as cotton require a mordant. Dyes do not interact directly with the materials, they are intended to colour. Natural dyes are substantive and require a mordant to fix to the fabric, and prevent the colour from either fading with exposure to light or washing out. These compounds bind the natural dyes to the fabrics. There are three types of mordant: Metallic mordants: Metal salts of aluminium, chromium, iron, copper and tin are used. Tannins: Myrobalan and sumach are commonly used in the textile industry. Oil mordants: These are mainly used in dyeing Turkey red colour from madder[14]. Dyer's madder is one of the oldest and most popular red dyestuff found in nature on the Eurasian super-continent extracted from dried roots of *Rubia tinctorum L.*, madder has been used since antiquity for dyeing textiles (in particular in Europe, the Middle East and India [15] where the plant was indigenous. Belonging to the group of mordant dyes, madder requires a pre-treatment of textile fibres with a solution of mordant The metal salt most frequently used as mordant was alum often together with cream of tartar.

By using different metal ions and varying the dyeing recipes, a wide scale of shades can be obtained: pink, red, purple and black [16]. The colouring compounds of *R. tinctorum* L. roots consist of antraquinone dyes.

The main colouring compounds are alizarin and purpurin. Together with alizarin and purpurin, a number of anthraquinones such as xanthopurpurin, pseudopurpurin, rubiadin and munjistin are present. In the drying process of madder roots, pseudopurpurin is probably converted into purpurin. In addition, the metal compound used for mordanting, such as aluminium or iron, will influence the uptake of the various colouring components [17].

High Performance Liquid Chromatography (HPLC) using Diode-Array Detection (DAD) is ideally suited for identification of natural dyestuffs present in these materials [18-22]. In this study, the first 20 of the 40 pieces of silk fabrics were mordanted with alum the other 20 of them were mordanted with $Ca(NO_3)_2$ using various dyeing procedures then the mordanted silk fabrics were dyed with *Rubia tinctorium* L. and gall oak extracts with varying amount of Turkey red oil. High performance liquid chromatography (HPLC) with a diode-array detection (DAD) was used to examine natural dyestuffs in the silk fabrics, the colourimetric and fastness properties of the silk fabricswere also investigated.

Because of the harmful effect of the synhtetic dyes to the environment, this study was chosen asan alternative dye for the dyeing process.

2. MATERIALS AND METHOD

2.1 Materials

In this experimental work, 100% silk sateen weave S 4/1 (3) ready for dyeing, fabric was used. The weight of the fabric was 74 g m-2 (160 ends/cm and 60 picks/cm).

Madder (Rubia tinctorum L.) and gall oak (Quercus intectoria Olivier) were obtained from Turkish Cultural Foundation, Cultural Heritage Preservation and Natural Dyes Laboratory, 34775, Istanbul, Turkey. Alum $[KAl(SO_4)_2.12H_2O]$ and $Ca(NO_3)_2.H_2O$ were obtained from Merck.

2.2 Method

2.2.1 The Mordanting and Dyeing of Silk Fabrics

The selected (1-20) 100% silk fabric samples were mordanted with 6% alum andother selected (21-40) 100% silk fabric samples were mordanted in a bath containing 6% alum and 2% $Ca(NO_3)_2$at 65°C for 120 min, at pH 4-5 with a flotte ratio 100:1 before dyeing. The silk samples were extracted by using water for 60 min at 80°C with madder and gall oak.

Natural materials (madder roots, gall oak and Turkey red oil) used for dyeing are given in Table 1. The dyeing process was carried out a at 65° C for 60 min. at pH 6-7 with a flotte ratio of 100:1. Then, the dye bath was cooled. At the end of the dyeing process, the all dyed fabrics were washed at 45-50 °C with pure water. Washed fabrics were rinsed and allowed to dry at the room temperature (25 °C). The results of area percentage of the dyestuffs are given in Table 2.

The dyed fabrics were hydrolysed by using water/methanol/ 37 % hydrochloric acid mixture in conical glass tubes for precisely 8 min in a water-bath at 80°C to extract the organic dyes. After rapid cooling under cold running water, the solution was evaporated just to dryness in a water-bath at 50-65 °C under a gentle stream of nitrogen. The dry residues were dissolved in 400 µL the mixture of methanol/water (2/1 v/v). Then 95 µL of the supernatant were injected into the HPLC apparatus.

Table 1. Dyeing properties for silk fabrics dyed according to the different procedures.

Dyeing number	Mordanting						Dye plant		Ekstraction		Dyeing				
	Alum %	Ca(NO$_3$)$_2$ %	Time (min.)	Tem.(0C)	pH	Bath ratio	Madder %	Gall oak %	Tem. (^{0}C)	Time (min.)	Tem. (^{0}C)	Time (min.)	pH	Bath ratio	Add Oil (mL.)
1	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	-
2	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	-
3	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	1.0
4	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	2.0
5	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	5.0
6	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	7.5
7	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	10.0
8	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	12.5
9	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	15.0
10	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	17.5
11	6	-	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	20.0
12	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	1.0
13	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	2.0
14	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	5.0
15	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	7.5
16	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	10.0
17	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	12.5
18	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	15.0
19	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	17.5
20	6	-	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	20.0
21	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	-
22	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	1.0
23	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	2.0
24	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	5.0
25	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	7.5
26	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	10.0
27	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	12.5
28	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	15.0
29	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	17.5
30	6	2	120	65	4-5	1/100	100	-	80	60	65	60	6-7	1/100	20.0
31	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	-
32	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	1.0
33	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	2.0
34	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	5.0
35	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	7.5
36	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	10.0
37	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	12.5
38	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	15.0
39	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	17.5
40	6	2	120	65	4-5	1/100	100	10	80	60	65	60	6-7	1/100	20.0

Table 2. Area percentages of the colouring compounds.

Trial No	Ellagic acid %	Alizarin %	Purpurin %	Rubiadin %	Unidentified %
1	0	42,638	38,685	3,313	15,365
2	55,421	17,063	22,365	0,361	4,79
3	0	44,447	36,19	3,796	15,566
4	0	43,759	38,182	2,838	15,221
5	0	42,926	40,401	1,522	15,151
6	0	50,479	34,101	2,725	12,695
7	0	40,55	43,004	1,634	14,813
8	0	36,303	44,334	1,039	18,324
9	0	54,42	35,874	2,138	7,568
10	0	57,964	33,881	1,403	6,753
11	0	52,095	26,768	0	21,137
12	21,33	49,473	19,51	0	9,687
13	29,13	32,965	34,31	0,436	3,16
14	27,472	46,369	18,584	0	7,575
15	32,083	45,85	17,051	0	5,016
16	24,276	36,28	35,504	0	3,94
17	25,035	35,078	35,909	0	3,977
18	21,351	33,284	41,543	0,24	3,582
19	17,229	38,728	39,844	0,263	3,935
20	22,542	39,311	34,92	0,197	3,029
21	0	41,99	53,604	0,704	3,702
22	0	45,945	49,448	0,978	3,629
23	0	49,456	46,384	0,892	3,268
24	0	47,513	46,309	0,837	5,342
25	0	40,404	55,955	0,391	3,251
26	0	39,79	49,842	1,452	8,916
27	0	45,778	42,782	1,651	9,789
28	0	43,373	45,661	1,601	9,365
29	0	45,557	44,692	0,968	8,783
30	0	44,36	47,96	0,795	6,884
31	21,96	29,951	46,271	0,295	1,523
32	16,803	30,37	50,756	0,307	1,765
33	16,822	33,04	48,222	0,322	1,594
34	13,575	34,098	50,098	0,257	1,971
35	17,002	28,709	52,474	0,159	1,656
36	22,539	30,696	44,481	0	2,284
37	16,437	27,515	53,75	0,128	2,17
38	15,966	28,509	53,963	0,038	1,524
39	13,504	32,155	52,391	0,083	1,867
40	9,843	40,151	48,086	0	1,92

2.2.2 Colour measurements

The colour measurements were performed using a Datacolor SF 600 plus spectrophotometer coupled to a PC under D65 illuminant/10° observer with a specular componenet included. The untreated was taken as standard. The color differences according to the CIELab (1976) equation, were obtained from the colour measuring software. Colour strengths of fabrics were determined by using the Kubelka-Munk formula (Eq. 1), which is shown below.

$$K/S= (1-R)^2/2R \qquad (1)$$

K is the scattering coefficient

S is the absorption coefficient

R is the reflectance

The colours are given in CIELab coordinates: L* corresponding to brightness (100 = white, = black) a* to the red-green coordinate (+ = red, - =green), b* to the yellow-blue coordinate (+ = yellow, - = blue) and C* to vividness- dulness(100 = vivid, 0 = dull). The results of the colourimetric measurements are given in Table 3.

2.2.3 Fastness properties

Washing fastness, light fastness and rubbing fastness of the samples were tested according to [23-26]. The spesific tests were applied using the following instruments: Atlas Xenotest Alpha for light fatness (SDL Atlas USA). James H. Heal Crockmaster rubbing fastness tester and Gyrowash James. H. Heal for wash fastness. The Standard grey scale (where 1 is poor and 5 is excellent) is used to identify the changes in shades and staining to adjacent multifiber fabrics. The unmordanted and dyed samples were exposed to the light for 90 h. by xenon arch lamp (250 W). The change in shades under artificial light were examined according to standard blue fabric The Society of Dyers and Colourists (SDC) protocols. ECE non- phosphate standard detergent was used in wash fastness experiments. The results of the fastness standard tests are given in Table 4.

Table 3. Colorimetric dataof the dyed silk fabrics.

Samples	L*	a*	b*	C*	h	λ	K/S
Standart	93.37	0.87	2.87	3	73.03	360	0.14
1	58.19	39.35	29.78	49.35	37.11	360	7.04
2	41.96	42.44	27.26	50.44	32.72	360	14.36
3	53.25	41.09	32.54	52.41	38.38	360	9.24
4	50.01	43.54	34.06	55.28	38.04	360	11.79
5	51.25	42.80	33.40	54.29	37.97	360	11.35
6	54.15	41.97	33.29	53.57	38.42	360	9.76
7	49.74	44.94	32.75	55.65	36.06	360	11.68
8	52.62	43.94	32.66	54.75	36.62	360	10.41
9	50.38	44.69	31.79	54.84	35.43	360	10.90
10	50.98	44.97	31.80	55.08	35.26	360	11.00
11	51.93	43.59	31.02	53.50	35.44	360	10.25
12	43.58	41.90	27.12	49.91	32.92	360	16.73
13	44.39	42.08	25.65	49.28	31.37	360	13.52
14	42.91	44.00	26.88	51.56	31.42	360	14.98
15	44.70	43.27	26.35	50.66	31.34	360	14.28
16	45.43	43.22	27.11	51.02	32.10	360	14.45
17	47.26	42.99	26.50	50.08	31.95	360	13.14
18	45.77	43.42	26.02	50.62	30.94	360	13.63
19	45.36	44.13	26.65	51.55	31.13	360	14.02
20	46.31	42.95	25.19	49.79	30.40	360	11.31
21	52.93	42.09	25.02	48.97	30.73	360	6.33
22	56.54	38.33	25.23	45.89	33.36	360	5.27
23	59.42	37.06	26.49	45.55	35.55	360	4.94
24	59.28	38.33	23.67	45.05	31.70	360	4.16
25	51.97	43.17	32.39	53.97	36.88	360	10.32
26	50.74	44.57	31.02	54.30	34.84	360	10.97
27	54.32	43.17	32.39	53.97	36.88	360	10.32
28	55.14	42.54	31.18	52.75	36.24	360	9.18
29	49.53	45.50	30.57	54.82	33.90	360	11.96
30	47.37	46.28	31.16	55.79	33.95	360	14.70
31	46.34	41.50	23.04	47.46	29.04	360	8.63
32	48.53	40.83	21.68	46.23	27.97	360	6.79
33	47.34	41.09	23.04	47.11	29.28	360	7.95
34	44.41	43.4	23.88	49.55	28.83	360	9.01
35	49.37	40.91	20.76	45.88	26.91	360	7.26
36	47.33	42.51	20.90	47.37	26.18	360	7.80
37	48.80	42.75	20.00	46.30	25.80	360	7.33
38	46.74	42.97	20.66	47.68	25.35	360	7.96
39	45.55	43.81	22.87	49.42	27.56	360	9.89
40	47.11	42.41	20.41	47.06	25.70	360	8.94

Table 4. Fastness properties of the dyed silk fabrics.

Samples	Fastness to Light	Rubbing Fastness		Colour Fastness to Washing					
		Dry	Wet	Colour Change	Staining				
					CA	Co	PES	PAC	Wo
1	6-7	5	4	3-4	4	3-4	4-5	4-5	4
2	7-8	4	3-4	4-5	4-5	3-4	4-5	4-5	4
3	7-8	3-4	3	4-5	4	4	4-5	4	4
4	7	3-4	3-4	4	4	3-4	4	4-5	4
5	7	3-4	3-4	3-4	4-5	3	4-5	4	4
6	7	4	4	4	4	3	4	4	4
7	7	4	4	4-5	4	3-4	4-5	4-5	4
8	7-8	4-5	4	3-4	4-5	3-4	4	4-5	4
9	7	4-5	4	4	4-5	3-4	3-4	4-5	4
10	7-8	4-5	4	4	4-5	3-4	3-4	4-5	4
11	7	5	4-5	4	4	4	3-4	4	4
12	7	5	4-5	3-4	4	4	4	4-5	4-5
13	7	5	4-5	4	3-4	4	4	3-4	4
14	6-7	3-4	3-4	3-4	4	3-4	4	4	4-5
15	7	4	3-4	4	4	5	4-5	4-5	4
16	6-7	4	3-4	3-4	4	4	4-5	4-5	4
17	7-8	4-5	4	4	4-5	3-4	4	4	4
18	7-8	4	4	4	4-5	3-4	4	4	4
19	7	4	3-4	4	4-5	4	4	4	4
20	7	4	3-4	4	4	4	4	4	4
21	6-7	3-4	3	3	4	4	4	4	4
22	7	4-5	4	3	4	4	4	4	4
23	6-7	4	4	3	4-5	4	4-5	4	4
24	6-7	3-4	3-4	3-4	4	3-4	4-5	4-5	4-5
25	7	3-4	3-4	3	4	3-4	4	4	4
26	7-8	5	4-5	3-4	4-5	3-4	4-5	4-5	4-5
27	7	5	4-5	4	4-5	4	4-5	4-5	4-5
28	7	5	4-5	4	4-5	4	4-5	4	4-5
29	7-8	5	4-5	4-5	4-5	4-5	4	4-5	4-5
30	7-8	5	4-5	4	4-5	3-4	4	4-5	4-5
31	7	5	4-5	4-5	4-5	4	4-5	4	4
32	7-8	4	4	4-5	4-5	4	4	4-5	4
33	7-8	5	4-5	4	3	4-5	4	4-5	4
34	7-8	5	4-5	4-5	4-5	4	4	4	4
35	7-8	4	4	4-5	3	4-5	4	4-5	4
36	7-8	4-5	4	4-5	4	4	4	4	4
37	7	4-5	4	4-5	4-5	4	4-5	4-5	4-5
38	7	5	4-5	4-5	4-5	4	4-5	4-5	4-5
39	7	4-5	4	4-5	4-5	4	4-5	4	4-5
40	7	4	4-5	4-5	4	4	4	4	4

2.2.4. HPLC Instrumention

Chromatographic experiments were carried out an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including a G1329 A ALS autosampler and a G1322 A diade-array detector. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 255 nm. A G1322A vacuum degasser and a G1316A thermostatted column comparment were used. The data were analyzed using Agilent Chemstation. A Nova-Pak C18 analytical column protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30 °C. Chromatographic separations of the hydrolyzed samples were performed using a gradient elution program that utilizes two solvents: solvent A: H_2O-0.1% TFA (trifluoroacetic acid) and solvent B: CH_3CN-0.1 %TFA. The flow rate was 0.5 mL/min. The HPLC elution program was performed as described Table 5.

Table 5. Gradient elution program of HPLC analysis.

Time (min.)	Flow rate (mL/min.)	H_2O-0,1% TFA (v/v)	CH3CN-0,1% TFA (v/v)
0.0	0.5	95	5
1.0	0.5	95	5
20	0.5	70	30
25	0.5	40	60
28	0.5	40	60
33	0.5	5	95
35	0.5	5	95
40	0.5	95	5
45	0.5	95	5

3. RESULTS AND DISCUSSION

According to the results obtained from applied different procedures, it was seen that the amount of ellagic acid was found to be quite high in dyeings without Turkey red oil(Table 1). The best example of this was seen in procedure 12.

It was also observed that $Ca(NO_3)_2.4H_2O$ used in mordanting caused an increase of the purpurin rate bounded with fiber. $Ca(NO_3)_2.4H_2O$ has not affected in binding of fibre with ellagic acid. It was also seen that the undefined colouring compounds showeda decrease with use of $Ca(NO_3)_2.4H_2O$.

The area percentages of the colouring compounds were givenin Table 2.The alizarin and purpurin's rations are quite close, the percentage of purpurin was higher than alizarin in dyeings made using goal oak, this affects the lightfastness. When the results of light fastness properties were examined, the highest values were observed in procedure numbers 17, 18, 32, 33, 34, 35 and 36. Light fastness was the best in the these procedures which consist of ellagic acid and the high area percentage of alizarin and purpurin rather than in the dyeings alizarin and purpurin without ellagic acid (Table 2).

Although the lowest area percentage of purpurin was observed in procedure number 12, the highest K/S value was obtained from procedure number 12.

The highest L* value was observed in procedure numbers 23 and 24. Ellagic acid was notused inthese dyeings. The highest a* values (red colour)were observed with the addition of 17,5 and 20,0 mL. Turkey red oil. Therefore, no asignificant variation was seen between the concentration of amounts of Turkey red oil in spite of alizarin and purpurin the redness of the dyed fabrics. Rubiadin has yellowness incolour. Decreasing of concentration of rubiadin effected the values of b^*.The darkness hue was obtained by adding of 5 mLred oil.

It was observed that dry and wet rubbing fastness values of the samples had moderate gradings (grade 3-5). The colour change ranges in general gave good values; ranging from 3 to 5. The light fastness ratings were good to very good (grade 6-8).The results of wash/light and rubbing tests are given in Table 4.

4. CONCLUSIONS

It is seen that, the color strenght of the fabrics was increased with the increased ellagic acid concentration. It depends on amount of hydroxyl groups. Alizarin has two hydroxyl groups and purpurin has three hydroxyl groups but ellagic acid has four hydroxyl groups. Thus alum can have more chance to bind with purpurin rather than the alizarin.

By using gall oak, ellagic acid binds to fiber, it causes a decrease of L^* value. By increasing the amount of oil, L^* value can be increased relatively.

By using gall oak, ellagic acid bounded with fiber increases K/S value.

It is observed that Turkey red oil has caused to increase of K/S values in the dyeings.It was also seen that K/S values have an increase in procedures between21and 30 that weremade with $Ca(NO)_3.4\ H_2O$ and alum.

It is seen that K/S values are directly related with amounts of elagic acid, purpurin and alizarin in the procedures made with alum.

Due to the alizarin and purpurin rates are close to each another in procedures between 25 and 30, K/S values decreased.

When we examine the procedures from 31 to 40,thepurpurin percentage is found much more than alizarin percentage and it was seen that purpurin has made a strong complex with $Ca(NO_3)_2.4H20$.

Color measurements are performed on four different areas of each fabric andany color differencewas not observed. Turkey red oil causes dyeings without abrage. Increasing the amount of red oil doesn't affect the quality of the dyeing, With increase of the amount of red oil, the percentage of alizarin have shown an decrease but the percentage of purpurin have shown an increase (Table 2). HPLC Analysis isimportant to evaluate the relationship between fastness and colour values and percentage of amounts of dyeing compounds.

Our work on this issue continues. It is concluded that the fabric's colour and fastness values increased significantly compared to earlier studies worked with this method. Based on the overall results It can be said that this study will be an advantage for dyeing silk fabrics.

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