[Transaction]

Journal of the Korean Society
of Clothing and Textiles
Vol. 29, No. 12 (2005) p.1608~1618

Analysis of Degradation Products in Madder Dyed Fabrics in Selective Degradation Conditions

Cheunsoon Ahn[†] · **S. Kay Obendorf***
Dept. of Fashion & Industry, University of Incheon
*Dept. of Textiles and Apparel, Cornell University

퇴화조건에 따른 꼭두서니 염색물의 퇴화물 연구

안춘순[†] · **S. Kay Obendorf***
인천대학교 패션산업학과, *Dept. of Textiles and Apparel, Cornell University

(2005. 9. 14. 접수)

Abstract

The purpose of this investigation was to investigate the degradation products of the dye component extracted from madder dyed fabrics using the GC-MS analysis and to evaluate the change of color due to degradation treatment. Four different degradation protocols were used in this study; refrigeration at 7°C (LT), room temperature (RT), oven treatment at 100°C (OV), and H_2O_2/UV(PER) method. Degradation times for each thermal system were 6 hour, 24 hour, 48 hour, 1 week, 2 week, 4 week. Alizarin was detected from the control and degraded samples of both alizarin dyed and madder dyed fabrics. Benzoic acid, 2,4-di-tert-butylphenol, phthalic anhydride were detected as the degradation products for both alizarin dyed and madder dyed fabrics. The result suggest that these products can be used as the fingerprints of GC-MS analysis for the identification of madder dye in archaeological textiles. Both alizarin dyed and madder dyed samples became less red and less yellow after degradation. In the PER degradation system madder dyed sample showed the greatest color difference even after 1 week of degradation treatment. Further research is necessary for investigating the color change in the exhumed textiles, which is caused by the dual action of dye fading and the staining of organic matters in the soil.

Key words: Madder dyed fabric, Alizarin dyed fabric, Degradation, GC-MS, Color difference; 꼭두서니 염색물, 알리자린 염색물, 퇴화, 가스크로마토그라피 질량분석, 색차

I. Introduction

A textile artifact is one of the major primary sources for the documentation of past cultural behavior. However, as an organic material its preservation in the burial context is not always guaranteed, and even in a relatively well-preserved piece some degradation of the chemistry of a textile is unavoidable. Color fading is one of the visually detectable degradation which a textile undergoes within the burial context as well as after its exposure to light and atmosphere. Beside the color fading of the fabric itself, fabrics excavated from burial sites are often heavily stained by humic acids and naturally occurring tannins within the soil, and the staining is even more severe when the soil is damp(Walton & Taylor,

---

[†] Corresponding author
E-mail: cssong@incheon.ac.kr

This research was supported by the 2005 Research Fund of University of Incheon.

1991). Due to the loss of original color, it is difficult to identify the dye or the color of the textile piece which otherwise can provide a valuable information on the past costume culture. Without the hint of the original hue it is difficult to select one or a limited number of standard dyestuff for the comparative analysis pertinent for dye identification. However, such problem can be overcome by analyzing each possible dyestuff separately in a simulated degradation condition. The data then can become part of a pool of standard dyes for the forthcoming comparative analysis.

This paper deals with the identification of degradation products in the madder dyed textiles. The investigation is part of our continuing effort for the identification of dyes in badly faded textiles of archaeological origin. In our previous study(Ahn & Obendorf, 2004), we have designed and experimented the two major degradation conditions, thermal and H_2O_2/UV treatments, in order to indirectly simulate the burial induced fading observed in archaeological textiles. The thermal series of degradation treatment included refrigeration near 0°C, room temperature, and oven temperature at 100°C. The thermal series were chosen on the basis of the research on soil microclimate (Child, 1995; Rieger, 1983) and past researches simulating natural ageing of dyed textiles via accelerated thermal treatment(Brushwood, 1988; Needles et al., 1986; Needles & Nowak, 1989; Peacock, 1983, 1996). H_2O_2/UV treatment was chosen on the basis of the advanced oxidation process(Colonna et al., 1999) which was developed to reproduce the microbial decomposition of dye wastewater(Jarosz-Wilkolazka et al., 2002), and the assumption that such oxidation process with H_2O_2/UV occurs in nature from the reduction of humic substances in soil(Scheck & Frimmel, 1995). Alizarin, the major chromophoric substance of madder plant, was chosen in our previous research(Ahn & Obendorf, 2004) as the analytical target in order to establish the comparative standard data for the investigation of madder plant itself. From the above analysis four major degradation products- benzoic acid, 2,4-di-tert-butylphenol, phthalic anhydride, and dimethyl phthalate <Table 1>were identified through GC-MS analysis.

Unlike the standard alizarin which has been highly purified to be used as reagent chemical, the madder dye used in archaeological textiles is a composite mixture of natural compounds comprising not only major coloring substance but also a large amount of its derivatives and other extraneous matters inherent in the plant. Schweppe(1989) reported that there are more than 22 different hydroxyanthraquinone type components in madder root besides alizarin. Numerous small peaks in the gas chromatogram of madder compared to the single major peak in the gas chromatogram of standard alizarin which were the result of our previous investigation are good representation of the composite nature of madder extraction(Ahn & Obendorf, 2003). Considering the complex nature of the madder extraction, the question rises to whether the same degradation products of standard alizarin reported in the previous literature(Ahn & Obendorf, 2004) are observed in madder dyed textiles, which is the ultimate form of standard comparable to archaeological textiles. Based on the above questions, the purpose of this investigation was to investigate the degradation products of the dye component extracted from madder dyed fabrics and to evaluate the change of color due to degradation treatment. Comparisons will be made between the degradation products detected from the present investigation and those identified in our previous research on the degradation of standard alizarin. The result of this study, together with our previous results will become part of the cumulative collection of analytical data which can then be used as the fingerprint for the identification of madder dye in badly faded archaeological textiles.

II. Experimental

1. Materials

Alizarin(1,2 dihydroxyanthraquinone, 97% purity) was purchased from Sigma Aldrich(Milwaukee, WI) and used without further purification. Dried madder root was purchased from Korean traditional medicinal market. Alizarin(1,2 dihydroxyanthraquinone, 97 % purity) was purchased from Sigma Aldrich(Milwaukee, WI) and used without further purification. Methanol(HPLC grade) was purchased from Mal-linckrodt

Baker(Paris, KY). 30% H_2O_2(ACS reagent grade) was purchased from J. T. Baker(Phillipsburg, NJ). Reagent grade H_2SO_4 and HCl were purchased from EM Science(Darmstadt, NJ). Potassium aluminum sulfate was purchased from Shinyo Pure Chemicals(Osaka, Japan). Benzoic acid, 2,4-di-tert-butylphenol, phthalic anhydride, and dimethyl phthalate were all ACS reagent grades purchased from Sigma Aldrich(Milwaukee, WI). Silk fabric used for dyeing was standard silk fabric(KS K0905) purchased from Korea Apparel Testing & Research Institute. Deionized distilled water was used throughout the experiments. A 0.45 μm glass fiber enhanced syringe filter (Alltech, Deerfield, IL) was used for filtering samples for GC-MS analysis.

2. Methods

1) Preparation of standard alizarin dye

The standard specimen of alizarin was prepared by making a 0.3wt % dye solution in water, evaporated to dryness using a rotary evaporator(50°C), and the residue dissolved in methanol for GC-MS analysis. Same procedure was followed for preparing standard specimen of madder dye after its extraction.

2) Extraction of madder dye

Madder extraction was carried out following the procedure in Ahn & Obendorf(2003). Dry roots of madder were thoroughly washed and powdered before use. 20g of powdered madder was soaked in 400ml water for 90min at room temperature. The water was decanted and the remaining madder powder was extracted with fresh 400ml water, adjusted to pH 3 using 10% H_2SO_4, heated for 90min at 80°C. The extraction was filtered using the büchner funnel with glass fiber filter paper(Fisher Scientific). The extraction was evaporated to dryness using a rotary evaporator(50°C), and the residue dissolved in methanol for GC-MS analysis.

3) Fabric dyeing

Silk fabric was dyed with madder extraction and alizarin standard separately. Approximately 2g of silk fabrics were treated in 200ml of 10% o.w.f. potassium aluminum sulfate solution for 30min at 80°C prior to dyeing, rinsed and dried. The fabrics were dyed with either 200ml of madder extraction or alizarin control solution for 90min at 80°C, rinsed, dried, and the dye liquor saved. The same fabrics were mordanted the second time with a fresh potassium aluminum sulfate solution and dyed again using the dye solution saved from the previous step.

4) Degradation of dyed fabrics

The study utilized thermal and H_2O_2/UV degradation systems, the same degradation conditions employed in our previous research(Ahn & Obendorf, 2004b). The thermal series degradation included refrigeration at 7°C(labeled 'LT' in the following), room temperature with minimal light exposure(RT), and oven treatment at 100°C(OV). For each degradation system, fabric dyed from different madder or alizarin dye batch were used, thus creating different control sample for each degradation system. 2cm ×10cm size dyed fabrics were arranged for each degradation time/ degradation system combinations. Degradation times for each thermal system were 6 hour, 24hour, 48hour, 1week, 2week, 4week. For H_2O_2/UV degradation, 2cm×10cm size dyed fabrics were immersed in separate vials with 30% H_2O_2 solution and the vials were placed under the UV lamp (365nm, UVL-18, UVP, Upland CA) at room temperature for 6hour 24hour, 1week, and 2week.

5) GC-MS sample preparation

Extraction of dye from alizarin dyed and madder dyed fabrics were carried out following Kharbade & Agrawal(1985). Approximately 0.02g of dyed fabric was treated in simmering 10% HCl for 30min, the solvent evaporated and the residue was dissolved in methanol for GC-MS analysis. The 'control' specimens of no degradation treatment were also prepared in the above manner and analyzed using the GC-MS.

6) Instrumentation

Control and degraded samples were analyzed on the Hewlett-Packard GC 6890 Series coupled to the Agilent Technologies 5973N MSD system. Operating conditions were as follows: Front inlet was kept at splitless mode with initial temperature at 250°C. The products were separated on a Hewlett Packard 190915-433 capillary column(30m×250 m i.d., 0.25m nominal film thickness) programmed from 50°C to 305°C, column flow 1.3ml/min at initial temperature. Initial temperature at MSD was 310°C. Mass spectra were recorded at scan range 80-250*m/z*. The assignment of possible degradation products was based on the match with standard mass spectrum available in the GC-MS library database(Agilent Technologies, 2000). The structural assignments of four main degradation products identified by GC-MS analysis were verified further by comparing their MS spectra with those of known chemicals. Color of madder and standard alizarin dyed fabrics were evaluated in terms of CIE Lab data(D65/10) measured with the Macbeth Color-eye 1500/PLUS Color Measurement System with Optiview software version 2.0f.

III. Results and Discussion

1. Analysis of the Standards

The gas chromatogram of standard alizarin dye <Fig. 1> showed a strong peak in the 10.1min retention time(r.t.) range that is consistent with alizarin (Table 1). Mass spectrum of the peaks in the 10.1 min range matched well with alizarin in the NIST

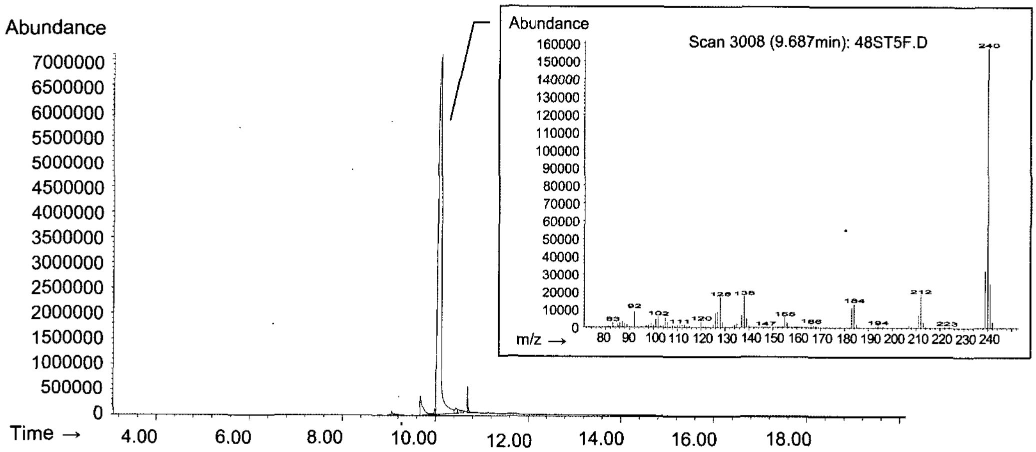


Fig. 1. Gas chromatogram of the standard alizarin dye (Inlet: Mass spectrum of alizarin 1)

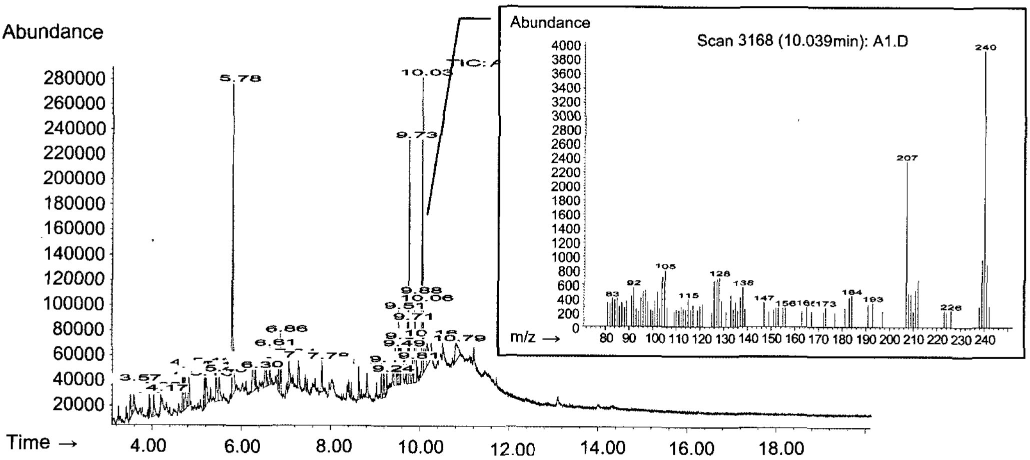
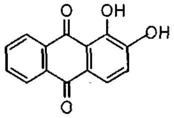
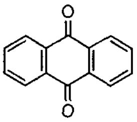
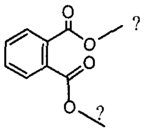
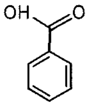
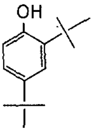
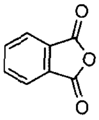
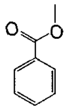
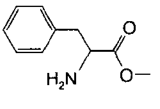
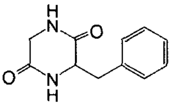
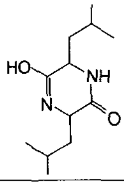


Fig. 2. Gas chromatogram of the standard madder dye (Inlet: Mass spectrum of alizarin 1)

Table 1. Products detected from madder and alizarin dyed samples

Retention Time (min)	Cpd No.	Product Assignment	Chemical Structure	Major Ion Fragments (m/z)	Relative Abundance Library	Relative Abundance Experimental
10.1	*1*	alizarin (1,2-dihydroxy anthraquinone)		240 212 138	100 23.7 15.5	100 12
9.0	*2*	9,10-anthraquinone		208 180 152 126	86.8 100 92.9 13.8	100 89.1 70.6 10.3
10.7	*3*	unidentified phthalate		167 149	32.2 100	29.2 100
4.7	*4*	benzoic acid		122 105	78.5 100	67.5 100
6.8	*5*	2,4-di-tert-butylphenol		206 191	15.4 100	14 100
5.8	*6*	phthalic anhydride		148 104	13.4 100	16.4 100
4.0	*7*	benzoic acid, methyl ester		136 105	32.8 100	32.8 100
6.9	*8*	l-phenylalanine, methyl ester		120 88	77.5 100	77.5 100
9.7	*9*	2,5-piperazinedione, 3-(phenylmethyl)-		204 114 91	205 36 100	20.5 100
8.8	*10*	2,5-piperazinedione, 3,6-bis(2-methylphenyl)-		170 140 86	100 20.5 49.3	

MS library(Agilent Technologies, 2000). In repeated analyses, small peaks were detected consistently at retention times of 9.07 and 10.71min. The mass spectrum of the product at 9.07min r.t. was consistent with the ion fragmentation pattern of 9,10-anthraquinone($C_{14}H_8O_2$) (Table 1). The identity of the product at 10.71min is not as clearly identified, but due to the ion fragmentation pattern it is believed to be a phthalate compound. The presence of 9,10-anthraquinone and the phthalate compound is believed to be due to solvent and evaporation procedures used in the preparation of standard specimen.

Compared to the standard alizarin, the standard specimen of madder extraction displayed numerous small peaks and a large number of notable peaks in its chromatogram(Fig. 2). The peak at 10.05min was relatively strong and its ion fragmentation pattern matched well with that of alizarin in the NIST MS library, and also that of alizarin peak in standard alizarin(Table 1). The standard specimen of madder extraction showed peak at 5.8min which matched the ion fragmentation pattern of phthalic anhydride ($C_8H_4O_3$) in the MS library. This product was not detected in standard alizarin, but it was identified as one of the four major products found after degradation of standard alizarin in our previous research (Ahn & Obendorf, 2004). Another much smaller peak was found at 4.7 min, and the ion fragmentation pattern matched that of benzoic acid($C_7H_6O_2$) in the MS library. Product 4 also was identified as one of the main degradation products of alizarin in our previous research(Ahn & Obendorf, 2004). Two other products, 9,10-anthraquinone(r.t. 9.0min) and a type of phthalate compound(r.t. 10.7) which were detected throughout the analyses of standard alizarin were rarely detected from madder extraction. Purpurin, which is known as another important chromophoric substance in some madder species, was not detected in the standard specimen of madder extractions.

2. GC-MS Analysis of the Dye Extracted from Fabric Samples

The gas chromatogram of the dye extracted from the control samples of alizarin dyed fabrics exhibited a large number of peaks, some of which were present in standard alizarin and some which were newly introduced(Fig. 3). The gas chromatogram of the dye extracted from the control samples of madder dyed fabrics showed numerous peaks from which only several number of prominent, characteristic peaks could be singled out(Fig. 4).

Alizarin was detected from the control samples of both alizarin dyed and madder dyed fabrics, a more prominent peak observed in the former(Table 2). From the control samples of alizarin dyed and madder dyed fabrics, benzoic acid and 2,4-di-tert-butylphenol were detected besides alizarin(Table 2).

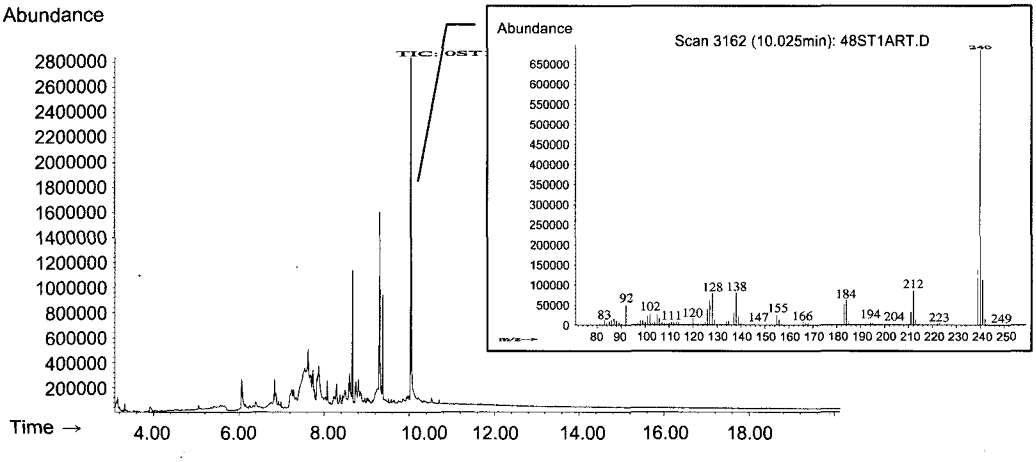


Fig. 3. Gas chromatogram of the control sample of alizarin dyed fabric (Inlet: Mass spectrum of alizarin 1)

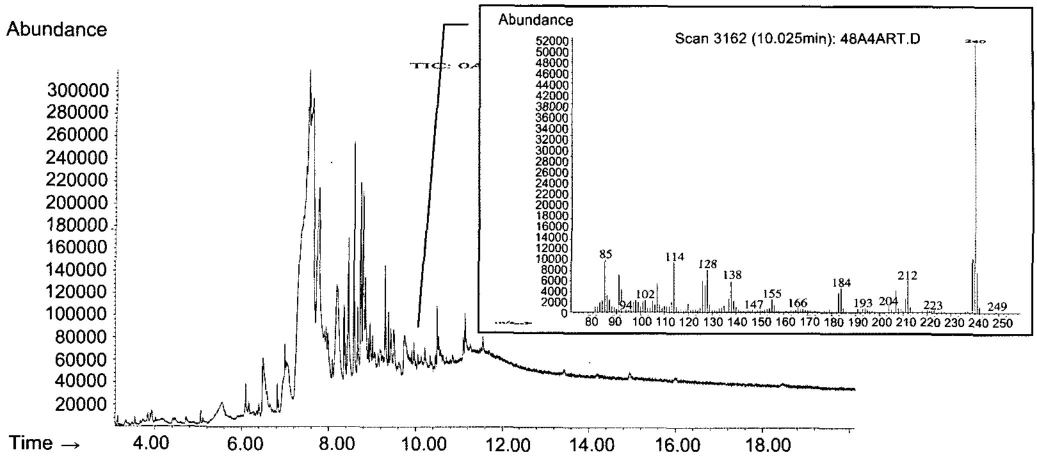


Fig. 4. Gas chromatogram of the control sample of madder dyed fabric (Inlet: Mass spectrum of alizarin 1)

Table 2. Presence of major products in alizarin and madder dyed samples

	Retention Time (min)	Cpd	Alizarin dyed sample							Madder dyed sample						
			Con	6hr	24h	48h	1wk	2wk	4wk	Con	6hr	24h	48h	1wk	2wk	4wk
LT	9.7-10.1	*1*	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	10.7	*3*	-	-	-	-	-	Y	-	-	-	-	-	-	-	-
	4.7	*4*	Y	-	-	Y	Y	-	-	Y	Y	Y	-	-	Y	-
	6.8	*5*	Y	Y	-	-	-	Y	-	Y	-	Y	-	-	-	-
	5.8	*6*	-	-	-	-	-	Y	-	-	-	-	-	-	-	-
RT	9.7-10.1	*1*	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	9.0	*2*	-	-	-	-	-	-	Y	-	-	-	-	-	-	-
	10.7	*3*	-	-	-	-	-	Y	-	-	-	-	-	-	-	-
	4.7	*4*	-	-	-	Y	-	-	-	Y	Y	-	Y	-	-	-
	6.8	*5*	-	Y	-	-	-	-	-	Y	Y	-	Y	-	-	-
OV	9.7-10.1	*1*	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	10.7	*3*	-	-	-	-	-	Y	-	-	-	-	-	-	-	-
	4.7	*4*	-	Y	-	-	-	-	-	Y	-	-	-	Y	Y	-
	6.8	*5*	-	-	-	-	-	Y	-	Y	-	-	-	-	-	-
	5.8	*6*	-	-	-	-	-	Y	-	-	-	-	-	-	-	-
PER	9.7-10.1	*1*	Y	Y	Y	Y	Y	Y		Y	Y	Y	-	Y		
	9.0	*2*	-	-	-	-	Y	-		-	-	-	-	-		
	10.7	*3*	-	-	-	-	-	-		-	-	-	-	Y		
	4.7	*4*	-	-	-	-	Y	-		Y	-	-	-	-		
	6.8	*5*	Y	-	-	Y	-	-		-	-	-	Y	Y		

When the fabrics were degraded in the four degradation systems, alizarin was detected from all the samples of LT, RT, and OV degradation systems and most samples of PER degradation system in both madder dyed and alizarin dyed fabrics(Table 2). Benzoic acid and 2,4-di-tert-butylphenol were most often detected in LT degradation in both standard alizarin dyed and madder dyed fabrics. Phthalic anhydride was detected in alizarin dyed fabrics only in 2week LT and OV degradation. Unidentified phthalate was observed in 2week LT, RT, and OV degradation of alizarin dyed fabrics and 1 week PER degradation of madder dyed fabrics. In just a few occurrences, 9, 10-anthraquinone was observed in alizarin dyed fabrics only. Dimethyl phthalate which was one of our major degradation product found in the most accelerated degradation of the aqueous extracts in our previous investigation(Ahn & Obendorf, 2004) was not detected from the extractions of the present dyed fabrics. However, except for dimethyl phthalate same degradation products found in our aqueous degradation samples were also observed in our silk fabrics dyed with either madder or standard alizarin. And such result suggest that the degradation products identified in our previous research can be used as the fingerprints of GC-MS analysis for the identification of madder dye in archaeological textiles.

Several new, small but high probability, peaks were observed after the degradation of dyed fabrics. The mass spectrum of the peak found at 4.0min of RT and PER samples of standard alizarin dyed fabrics matched well with the ion fragmentation pattern of benzoic acid, methyl ester(M.W.=136) in the MS library(Table 1). This product appears to be due to some reaction between our methanol solvent and one of our degradation product benzoic acid. High temperature treatment with methanol solvent while the dye component was extracted from fabric samples may have induced such product formation. Other new peaks formed at 6.9min, 8.8min, and 9.7min, are likely to be some reaction between silk protein and the dye component. Each were assigned as 1-phenylalamine, methyl ester(r.t.=6.9 min, M.W.=179), 2,5-peperazinedione, 3-(phenylmethyl)-(r.t.=9.7, M.W.=204), and 2,5-piperazinedione, 3,6-bis(2-methylphenyl)-(r.t. 8.8min, M.W.=226) according to the MS library(Table 1). These products were usually found at later degradation times, and although they appear sparingly they were detected throughout different degradation systems of both madder dyed and standard alizarin dyed fabrics. The usefulness of 1-phenylalamine, methyl ester, 2,5-peperazinedione, 3-(phenylmethyl)-, and 2,5-piperazinedione, 3,6-bis(2-methylphenyl)- in the identification of badly faded archaeological textiles dyed with madder is yet uncertain. However it is important to note their detection in the degradation of our madder and standard alizarin dyed fabrics for further comparative research on silk fabrics dyed with other natural dyestuffs. There were several other products repeatedly detected from our degraded fabric extracts. However, they were excluded from the present discussion since they were also detected from the extractions of undyed, and(or) unmordanted silk fabrics degraded and extracted in the same manner as our dyed fabric samples.

3. Color Measurement of Dyed Fabrics

Color difference (ΔE) of the degraded fabrics were obtained according to the equation $\Delta E=[\Delta(L)^2+(\Delta a)^2+(\Delta b)^2]^{1/2}$.

In both control and degraded samples, madder dyed fabrics were brighter than the alizarin dyed fabrics(Table 3). The control sample of madder dyed fabric showed L value 56.8~64.3, whereas that of the alizarin dyed fabric showed L value 34.5~36.8. Upon degradation both fabrics became brighter, greater change observed among the alizarin dyed fabrics. ΔL (calculated as $\Delta L=L^*-L$) was 22.0~29.3 for alizarin dyed fabrics whereas it was 8~24 for madder dyed fabrics. However, the overall brightness of the degraded samples was greater in the madder dyed fabrics. Among the four degradation systems, the increase of brightness was the greatest in the PER degradation for both alizarin dyed and madder dyed fabrics, with fabrics becoming brighter with degradation progression; ΔL of 6hour was 22.5 whereas that of 2 week was 29.3 for alizarin dyed samples. The color measurement of the present investigation showing the increase of brightness after degradation raises question concerning the color usually observed in the textiles exhumed from the Korean burial sites, which in most cases is light to dark brownish tone upon excavation. However, such color in the exhumed textiles are due not only to the fading of dye but also to the stain-

Table 3. Color measurement of alizarin and madder dyed samples

	Alizarin dyed samples					Madder dyed samples				
LT	Time	L*	a*	b*	E	Time	L*	a*	b*	E
	6hr	57.49	11.91	7.74	31.33	6hr	68.66	9.21	15.15	18.54
	24hr	57.41	11.75	7.73	31.37	24hr	68.49	9.26	15.00	18.50
	48hr	57.80	12.23	7.88	31.32	48hr	67.84	9.63	14.62	18.16
	1wk	57.79	12.17	7.83	31.36	1wk	68.67	9.28	14.66	18.81
	2wk	57.41	11.73	7.84	31.35	2wk	68.70	9.15	15.16	18.59
	4wk	57.70	11.84	7.55	31.58	4wk	68.67	9.43	15.06	18.49
	Control	*L (34.53) a (31.24) b (16.72)*				*Control*	*L(56.83) a (18.14) b (26.29)*			
RT	Time	L*	a*	b*	E	Time	L*	a*	b*	E
	6hr	58.24	12.47	8.33	30.06	6hr	68.69	9.37	15.40	17.43
	24hr	58.31	12.51	8.29	30.09	24hr	68.52	9.48	15.29	17.35
	48hr	58.42	12.51	8.21	30.20	48hr	68.72	9.39	15.34	17.48
	1wk	58.33	12.26	8.15	30.30	1wk	69.26	9.28	15.69	17.64
	2wk	58.32	12.44	8.19	30.17	2wk	68.58	9.51	15.41	17.29
	4wk	58.20	12.38	8.18	30.13	4wk	68.80	9.69	15.53	17.24
	Control	*L (36.13) a (30.76) b (17.28)*				*Control*	*L (58.21) a (17.62) b (26.63)*			
OV	Time	L*	a*	b*	E	Time	L*	a*	b*	E
	6hr	57.51	11.25	7.52	30.53	6hr	72.62	6.60	16.91	15.16
	24hr	57.84	11.47	7.49	30.62	24hr	72.48	6.56	16.98	15.05
	48hr	58.13	11.82	7.72	30.51	48hr	72.88	6.29	17.07	15.31
	1wk	58.35	12.05	7.81	30.49	1wk	72.75	6.25	17.63	14.87
	2wk	59.11	12.97	8.56	30.23	2wk	73.07	6.13	18.12	14.78
	4wk	59.11	12.87	8.68	30.26	4wk	73.35	6.15	18.75	14.53
	Control	*L (36.89) a (31.32) b (17.73)*				*Control*	*L (64.30) a (12.86) b (27.94)*			
PER	Time	L*	a*	b*	E	Time	L*	a*	b*	E
	6hr	57.96	12.06	7.74	30.71	6hr	73.03	10.24	13.66	22.51
	24hr	59.70	13.91	8.65	30.71	24hr	75.72	8.85	11.18	26.42
	48hr	60.49	14.50	8.60	31.03	48hr	80.56	3.45	9.65	32.97
	1wk	63.89	16.37	6.92	33.43	1wk	81.29	0.002	3.90	38.33
	2 wk	64.76	16.33	6.90	34.19	2wk				
	Control	*L (35.42) a (30.88) b (16.78)*				*Control*	*L (56.71) a (18.31) b (26.92)*			

ing of organic substances in the soil. In this research, only the fading of dye itself is investigated.

Alizarin dyed fabrics were redder and less yellower than the madder dyed fabrics(Table 3). The control samples of alizarin dyed fabrics exhibited a value 30.7~31.3, b value 16.7~17.7, whereas the control samples of madder dyed fabrics showed a value 12.8~18.3, and b value 26.2~27.9. After degradation treatment both alizarin dyed and madder dyed samples became less red and less yellow. Except for PER degradation, the loss of red was more prominent in alizarin dyed fabrics than madder dyed fabrics; Δa (calculated as Δa=a*–a) of alizarin dyed sample was -18.2~-20.0, whereas as a of madder dyed sample was -6.2~-8.9. However, loss of yellow was more prominent in madder dyed fabrics than alizarin dyed fabrics, Δb(calculated as b=b*–b) of alizarin dyed sample was -8.1~10.2 whereas Δb of madder dyed sample was -9.1~-23.0. Overall, the color difference was more prominent in alizarin dyed fabrics in the LT, RT, and OV degradation system. ΔE of alizarin dyed sample was 30.0~31.5, and ΔE of madder dyed sample was 14.5~18.8. However, in the PER degradation system which is the most accelerated degradation system of the present investigation, madder dyed sample showed the greatest color difference after 1 week of degradation treatment(ΔE=38.3).

IV. Conclusion

The purpose of this investigation was to investigate the degradation products of the dye component extracted from madder dyed fabrics using gas chromatography mass spectroscopy and to evaluate the change of color of the dye fabrics after degradation treatment. The results were as follows:

1. Alizarin was detected from the control and degraded samples of both alizarin dyed and madder dyed fabrics, a more prominent peak observed in the former.
2. Benzoic acid and 2,4-di-tert-butylphenol, and Phthalic anhydride which were the degradation products identified in the previous research were detected from the alizarin dyed and madder dyed fabrics after degradation.
3. In both madder dyed and alizarin dyed fabrics, the samples became brighter after degradation treatment and the increase of brightness was greater with degradation progression.
4. After degradation treatment both alizarin dyed and madder dyed samples became less red and less yellow.
5. The color difference was more prominent in alizarin dyed fabrics. In the PER degradation system which is the most accelerated degradation system of the present investigation, madder dyed sample showed the greatest color difference even after 1 week of degradation treatment.

The result of the present investigation suggest that the four degradation products identified in our previous research can be used as the fingerprints of GC-MS analysis for the identification of madder dye in badly faded archaeological textiles. However, further research needs to be carried out in order to investigate the color change in the exhumed textiles which is caused by the dual action of dye fading and the staining of organic substance in the soil.

References

Agilent Technologies. (2000). *National Institute of Standards and Technology 98 Mass Spectral Libraries, NIST 98, Rev. D.02.00.*

Ahn, C., & Obendorf, S. K. (2003). Separation of chromophoric substance from madder plant under different extraction and analytical conditions. *Journal of the Korean Society of Clothing and Textiles, 27*(11), 1350–1357.

Ahn, C., & Obendorf, S. K. (2004). Dyes on archaeological textiles: Analyzing alizarin and its degradation products. *Textile Research Journal, 74*(11), 949–954.

Brushwood, D. E. (1988). Effects of heating on chemical and physical properties and processing. *Textile Research Journal, 58*(6), 309–317.

Child, A. M. (1995). Towards an understanding of the microbial decomposition of archaeological bone in the burial environment. *Journal of Archaeological Science, 22*, 165–174.

Colonna, G. M., Caronna, T., & Marcandalli, B. (1999). Oxidative degradation of dyes by ultraviolet radiation in the presence of hydrogen peroxide. *Dyes and Pigments, 41*, 211–220.

Jarosz-Wilkolazka, A., Kochmanska-Rdest, J., Malarczyk, E., Wardas, W., & Leonowicz, A. (2002). Fungi and their ability to decolourize azo and anthraquinonic dyes. *Enzyme and Microbial Technology, 30*, 566–572.

Kharbade, B. V., & Agrawal, O. P. (1985). Identification of natural red dyes in old Indian textiles: Evaluation of thin-layer chromatographic systems. *Journal of Chromatography, 347*, 447–454.

Needles, H. L., Cassman, V., & Collins, M. J. (1986). Mordanted, natural-dyed wool and silk fabrics: Light and burial-induced changes in the color and tensile properties. In S. H. Needles & S. H. Zeronian (Eds.), *ACS Symposium Series 212* (pp.· 199–210). Washington, DC: American Chemical Society.

Needles, H. L., & Nowak, K. C. J. (1989). Heat-induced aging of linen. In S. H. Zeronian, & H. L. Needles (Eds.), *ACS Symposium Series 410* (pp. 159–167). Washington, DC: American Chemical Society.

Peacock, E. E. (1983). Deacidification of degraded linen. *Studies in Conservation, 28*, 8–14.

Peacock. E. E. (1966). Characterization and simulation of water-degraded archaeological textiles: A Review. *International Biodeterioration & Biodegradation, 1996*, 35–

47.

Rieger, S. (1983). *The genesis and classification of cold soils.* NY: Academic Press.

Scheck, C. K., & Frimmel, F. H. (1995). Degradation of phenol and salicylic acid by ultraviolet radiation/hydrogen peroxide/oxygen. *Water Research, 29*(10), 2346–2352.

Schweppe, H. (1989). Identification of red madder and insect dyes by thin-layer chromatography. In S. H. Zeronian, & H. L. Needles (Eds.), *ACS Symposium Series 410* (pp. 188–219). Washington, DC: American Chemical Society.

Walton, P., & Taylor, G. (1991). The characterization of dyes in textiles from archaeological excavations. *Chromatography and Analysis, June*, 5–7.

요 약

본 연구는 꼭두서니와 그 표준 색소인 알리자린으로 염색한 직물에 조건적 퇴화를 유도하고, 가스 크로마토그라피 질량분석기(GC-MS)를 이용해 퇴화물을 분석하여 이를 선행연구에서 밝혀진 표준 알리자린 색소의 퇴화물과 비교함으로써 대조구로서의 꼭두서니 염료의 정보를 완성하는데 그 목적을 둔다. 아울러 퇴화 전후 염직물의 색차를 측정하여 조건퇴화에 따른 색의 변화를 조사하였다. 퇴화조건은 상온(RT), 저온(7°C) (LT), 고온(100°C) (OV)의 세 종류의 온도 조건과 염료 폐수처리 용도로 활용되고 있는 H_2O_2/UV법 (PER)을 사용하였다. 퇴화시간은 6시간, 24시간, 48시간, 1주, 2주, 4주 각각을 측정하였다. 꼭두서니와 알리자린 염직물 모두 퇴화 전후의 시료에서 alizarin(10.1분)이 검출되었다. 꼭두서니와 알리자린 염직물 모두 퇴화 후 benzoic acid(4.7분), 2,4-di-tert-butylphenol(6.8분), phthalic anhydride(5.8분)가 검출되었다. 꼭두서니와 알리자린 염직물 모두 퇴화 후 붉은색과 노란색이 감소하였다. 꼭두서니 염직물보다 알리자린 염직물의 경우 퇴화 전후의 색차가 더 심하였다. 그러나 가장 퇴화조건이 강한 PER 퇴화조건 하에서는 꼭두서니 염직물의 색차가 1주 경과 후에도 매우 심하게 나는 것을 볼 수 있었다. 본 연구의 결과 꼭두서니와 그 표준 색소로 염색한 직물이 퇴화할 경우에도 선행연구에서 밝혀진 알리자린의 퇴화물인 benzoic acid, 2,4-di-tert-butylphenol, phthalic anhydride가 검출됨을 확인하였다. 따라서 이들 화합물은 갈변되어 고유의 색을 알 수 없는 출토복식의 염료를 판정할 때 꼭두서니 염료의 사용여부를 확인할 수 있는 대조구 화합물로 사용될 수 있을 것으로 사료된다. 퇴화 전후의 색차에 대한 측정결과는 퇴화에 따른 염료의 색 변화에 대한 결과이다. 출토복식의 갈변현상은 염료의 변색과 더불어 토양 유기물에 의한 착색도 기인하므로, 출토복식의 색상 변화를 실질적으로 조사하기 위해서는 본 연구의 결과와 함께 토양 유기물에 의한 착색에 대한 연구가 병행되어야 할 것으로 본다.