

THE DETECTION OF MORDANTS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY

PART I. DYED WOOLEN TEXTILE FIBERS

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ABSTRACT—Twelve mordanted and cochineal dyed modern wool samples were subjected to scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDS) analysis. The analyses for metallic elements matched in all cases those actually used in the preparation. The mordants detected contained the metallic elements: aluminum, chromium, copper, iron, and tin. SEM photomicrographs were also examined for the effects of mordanting on fiber surfaces. Atomic absorption (AA) analysis of the samples is also reported.

INTRODUCTION

IN A PREVIOUS STUDY A GROUP of modern mordanted textile samples was subjected to SEM-EDS analyses to determine the feasibility of identifying mordants on museum textiles.¹ Successful qualitative identification was achieved on silk, cotton, and wool for samples containing the elements aluminum, iron, copper, tin and chromium. Some problems that appeared in that study were the following: significant elements are present very nearly at the limits of detectability of our analytical system; iron sometimes appeared as a trace element even when not used as a mordant; and some analyses of samples mordanted with chromium gave no indication of chromium; the same was true for tin but less frequently. Aside from the difficulties in obtaining unambiguous analyses for some samples, anticipated difficulties for museum and archaeological samples are foreseeable owing to loss of mordant during dyeing, washing, wear and aging that is certain to attend all historical samples. The presence of metallic elements from dust, dirt, soil, stains, treatment, etc., may also constitute a source of metallic elements that is not associated with the mordanting process requiring a cleaning or washing of the samples prior to analysis. Finally, not all mordants contain metallic elements² and the mordants free of metallic elements or elements lighter than sodium would not be detected by EDS.

In the series of analyses described in this study, wool samples were mordanted and dyed with cochineal³ and submitted without identification for SEM-EDS analysis. For each sample analyzed, metallic elements of the mordants actually used were identified unambiguously. The quantity of metallic element present in the mordanted samples, as determined by atomic absorption (AA), was also obtained. SEM photomicrographs of the samples were taken and examined for indications of the effects that mordants and/or additives had on the surface structure.

EXPERIMENTAL

MATERIALS AND METHODS.⁴ Cochineal dyed wool samples were obtained from the Textile Conservation Dept., Metropolitan Museum of Art, New York. These samples were produced in a collaborative exercise during a 5-day workshop conducted by Fred Gerber in September 1978. The samples were stored on ragboard sheets in a bound sample book.

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Although details are ambiguous, mordants were applied before dyeing. The following quantities of mordant were used per pound of wool yarn: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, 4.0 oz; $CuSO_4 \cdot 5H_2O$, 1.0 oz; $FeSO_4 \cdot 7H_2O$, 1.0 oz; $SnCl_2 \cdot 2H_2O$, 0.5 oz; $K_2Cr_2O_7$, 0.5 oz.

Mordants were dissolved in sufficient quantities of water to insure solution of mordants, heated, and the wool yarn was then added to the mordant solution. The yarn was left in the solution for some time depending on the mordants. Dried cochineal insect grains from the Canary Islands were mashed and added to warm water. After the dye was extracted into the water larger dye baths were prepared and the mordanted yarn was added and simmered (90-100°C) *ca.* 1 h. Different dye baths were used for each mordant. The dyed yarns were then rinsed in cold tap water and dried. Some of the mordant/dye solutions contained unspecified amounts of additives other than metallic mordants: cream of tartar, oxalic acid, sumac. The cochineal and the sumac were not purified or refined products but used as received. The sumac was field collected on the morning of use.

ANALYSES. The samples were prepared for scanning electron microscopy and examined in an AMRay 1600T with attached Kevex X-ray spectrometer system. Details of the treatment for analysis and the equipment used has been described previously.¹ In addition, elemental dot mapping and photomicrography were performed on the samples. For atomic absorption analysis (AA), samples were submitted to Schwartzkopf Microanalytical Lab, Woodside, NY 11377.

RESULTS AND DISCUSSION

WIDE COLOR VARIATIONS WERE ACHIEVED by the use of different mordants and additives. The same dye, cochineal, was used for each batch but with a different mordant and/or additive. In the absence of mordant or additive (sample 13) the wool fibers are nearly free of color. Each of the numbered samples was visually distinct. Visual examination of the fibers of each sample other than sample number 13 showed color well dispersed over the fibers. Table I shows the approximate sample size used for the SEM-EDS analyses and the elements observed in EDS scans of the carbon coated samples. At least three scans were performed for each sample. The table is divided into two parts: elements observed during each scan and elements observed in some scans. The frequency with which the elements were observed is also given. As expected for wool samples sulfur is prominently present in each scan. Elements other than those from the mordant may be picked up by the wool from the wash water or the non-uniform wool-mordant-dye-additive system.

Table II summarizes the mordants identified by EDS analysis. Samples 13 and 15 gave such small weight percentages (approx. 1%) of aluminum and iron in *some* EDS scans that they were reported as probably absent. Samples 20, 24, 25, 27 and 28A gave trace analyses for aluminum or iron (about 1-2%) in all EDS scans and are reported as possibly present. Samples 23A and 26 had aluminum (4-6%); samples 14 and 24 had copper (16-70%); samples 16 and 27 had iron (9-19%); samples 17 and 28A had tin (about 70%); samples 25 and 26 had chromium (17-32%). The decision to report the presence or absence of elements was based on the peak heights of these elements relative to that of sulfur, the element persistently present in all of the scans. "Yes" values were reported when EDS scans showed the mordant element to be always present in amounts greater than 2% relative to sulfur. Variation in weight percent relative to sulfur was often greater than 100% from scan to scan emphasizing the

already noted difficulty in using EDS analysis for quantitative assay.¹ The percentages indicated above represent only the weight percents of elements above the atomic weight of fluorine detected in an individual scan and not the weight percent present in the sample.

Table I
WOOL. Results of EDS Scans

Sample #	Elements Always Observed ^a	Elements Sometimes Observed ^b
13	S, Ca	<u>Si</u> (.8), <u>Fe</u> (.6), <u>Al</u> (.2)
14	S, Cu	<u>Si</u> (.5)
15	S, Ca	<u>Fe</u> (.66), <u>Al</u> (.66), <u>K</u> (.33) <u>P</u> (.33)
16	S, Fe, <u>Si</u>	<u>Ca</u> (.5), <u>P</u> (.5), <u>Al</u> (.5)
17	Sn, S, <u>Cl</u> , <u>Si</u> , <u>P</u>	
20	S, Ca, <u>Al</u> , <u>Fe</u> , <u>Si</u> , <u>P</u>	
23A	S, Al, <u>Ca</u> , <u>Fe</u> , <u>P</u> , <u>K</u>	
24	S, Cu, <u>Al</u> , <u>Si</u> , <u>Ca</u>	<u>Fe</u> (.66)
25	S, Cr, Ca, <u>Al</u> , <u>Si</u>	<u>Fe</u> (.66)
26	S, Cr, Al, Ca	<u>K</u> (.33), <u>Cu</u> (.33)
27	S, Fe, <u>Ca</u> , <u>Si</u> , <u>Al</u>	
28A	Sn, S, <u>Cl</u> , <u>Al</u>	

^a In order of decreasing weight percent.

^b Nos. in parenthesis are frequency of occurrence (3-5 scans)

Underline denotes very small or trace amounts.

The reporting of absolute weight percents for the elements under discussion would require: preparation of known samples with controlled quantities of additives uniformly distributed on the sample; or an independent elemental microanalysis of the samples of levels greater than the 10% obtained by AA (see below). It would also be necessary to perform replicate scans to account for non-uniformity of the surface and non-uniform attachment of the additives.

Table III shows the mordants and additives used in the preparation of the samples of Table I. It is seen that all the mordants actually used were unambiguously detected (*cf.* Table II). The presence of traces of aluminum and iron in some of the EDS scans suggests a small problem. Continued experience and information concerning the context of samples will help the analyst to know when to disregard trace element values. In this connection the assistance of the curator or conservator cannot be overestimated. It should be noted that sample 26 had a double mordant (aluminum and chromium) and each was detected unambiguously. No difficulty at all was encountered in the detection of Sn or Cr (*cf.* ref. 1).

Table IV provides data obtained independently by AA analyses for the elements present in the mordant and detected by EDS scans. The data of column 3 is calculated from the recipes and assumes that all mordant used was incorporated into the yarn. As expected from our previous study¹ the quantity of mordant found in the dyed fabric is

Table II
Detection of Metal Elements on Cochineal Dyed Wool Samples by EDS

Sample #	METAL ELEMENTS				
	Al	Cu	Fe	Sn	Cr
13	(-)	-	(-)	-	-
14	-	yes	-	-	-
15	(-)	-	(-)	-	-
16	-	-	yes	-	-
17	-	-	-	yes	-
20	?	-	?	-	-
23A	yes	-	-	-	-
24	?	yes	-	-	-
25	?	-	-	-	yes
26	yes	-	-	-	yes
27	?	-	yes	-	-
28A	?	-	-	yes	-

(-) Probably absent (not detected in all scans)

- Absent

yes Present

? Possibly present (detected in all scans)

substantially less than the amount actually used except for the tin mordanted samples. The AA results suggest that a larger amount of tin compound was used than was reported in the experimental section. The data of Table IV also suggests that the process of dying after mordanting may produce a greater retention of mordant in the fiber than simply applying mordant. Previous studies showed retention of mordants to be approximately 10%.¹ The entries under % Element by AA are replicates (since each mordant is applied according to the same recipe each time it is applied). It is seen that the values are excellent replicates in some cases but in other cases differences considerably exceed the experimental error of the analysis. One reason for the differences may be non-uniform sample preparation. The procedures for mordanting and dying maintained constant proportions among the ingredients but quantities of water were not measured in the mordant or dye baths or for the washing. The additives and impurities, furthermore, may have contributed differently to the partitioning of mordant between the textile and the aqueous phase. Another reason for the differences may be non-uniformity of the samples. Wool structure may vary considerably microscopically and macroscopically.⁵ Animal breed, treatment, processing, aging, differences in exposure to the environment, etc., all contribute to structural, mechanical and chemical variations in wool and its ability to interact with mordants, other additives, and impurities. Dot mapping scans of our samples indicated that the individual samples were quite uniform with respect to the metallic elements in the fiber surfaces.

Table III
Mordants and Additives Used for Cochineal Dyed Wool Samples

Sample #	Mordant ^a (wt ratio of mordant to wool)					Additive
	Al (1/4)	Cu (1/16)	Fe (1/16)	Sn (1/32)	Cr (1/32)	
13	—	—	—	—	—	—
14	—	+	—	—	—	—
15	—	—	—	—	—	cream of tartar
16	—	—	+	—	—	—
17	—	—	—	+	—	—
20	—	—	—	—	—	sumac
23A	+	—	—	—	—	cream of tartar
24	—	+	—	—	—	cream of tartar
25	—	—	—	—	+	cream of tartar
26	+	—	—	—	+	cream of tartar
27	—	—	+	—	—	oxalic acid
28A	—	—	—	+	—	oxalic acid

^a Mordants: $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$; $CuSO_4 \cdot 5H_2O$; $FeSO_4 \cdot 7H_2O$; $SnCl_2 \cdot 2H_2O$; $K_2Cr_2O_7$.

+ Present

— Absent

Table IV
Comparison of Mordant Quantities Applied to Cochineal Dyed Wool
Samples with Quantities Analysed by AA

Sample No.	Element	Maximum % Element in Mordanted Sample ^a	% Element by AA ^c
13,15,20,24,25,27	Al	? ^b	$<0.065 \pm 0.025$
23A, 26	Al	1.2	0.09, 0.09
14,24	Cu	1.5	1.0, 0.6
13,15,20	Fe	? ^b	$<0.04 \pm 0.02$
16,27	Fe	1.2	0.24, 0.24
17,28A	Sn	3.2	3.65, 3.95
25,26	Cr	2.3	0.85, 0.31

^a See Experimental Section. Assumes textile sample absorbs all added mordant.

^b Samples prepared with no added Al or Fe.

^c Schwartzkopf Microanalytical Lab, Woodside, NY 11327. All values $\pm ca.$ 10%.

Each of the samples was examined by SEM photomicrography and the samples retained. Although not prepared with this investigation in mind, the samples examined in this study represent a good standard series since the same wool and dye were used throughout; the only difference in the samples should arise from the use of different mordants and/or additives. No clear-cut distinctions in surface appearance could be made among the various mordanted and dyed wool fibers. It is possible that surface characteristics of aged fibers provide a better indication of treatment.

The distribution of the mordant on fibers is an excellent subject for the elemental dot-mapping⁶ capabilities of SEM. Preliminary results indicate complete delocalization of elements without discernible pattern in the surfaces of the mordanted wool fibers. This result suggests that representative EDS results ought to be obtainable even with sample sizes as small as a single fiber.

CONCLUSIONS

1. The use of different mordants and additives in the cochineal dyeing of wool produced a wide variety of color.

2. The elements aluminum, iron, copper, tin and chromium were unambiguously matched respectively with wool samples which were mordanted with $K_2O_4Al_2(SO_4)_3 \cdot 24H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $SnCl_2 \cdot 2H_2O$ and $K_2Cr_2O_7$, and dyed with cochineal.

3. Some samples gave trace analyses in EDS scans for iron and aluminum (although not actually used in the mordanting procedure) but *far less* than when these elements were actually used in the mordanting procedure. The ratio of the weight percent, metallic element/sulfur, appears to provide a useful criterion for deciding whether or not a mordant has been applied to wool. The criterion may also be extended to the analysis of silk samples (see Part II).

4. Atomic absorption analyses confirm the presence of metallic elements in greater than trace quantities as detected by EDS scans. EDS scans indicating trace quantities of elements (Al and Fe) are also confirmed.

5. The presence or absence of mordants or additives could not be inferred from differences in the appearance of fibers examined in this study by SEM photomicrographs.

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