

# IDENTIFICATION OF DYEING MORDANTS AND RELATED SUBSTANCES ON TEXTILE FIBERS: A PRELIMINARY STUDY USING ENERGY DISPERSIVE X-RAY SPECTROMETRY

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**Abstract**—Samples of modern wool, silk and cotton woven fabrics were mordanted with five common dyeing mordants: potassium aluminum sulfate, cupric sulfate, ferrous sulfate, stannous chloride and potassium dichromate. Samples were observed by scanning electron microscopy (SEM) and metallic elements detected by energy dispersive X-ray spectrometry (EDS). The results and limitations of the detection process are discussed and compared to other analytical procedures. The application of this procedure to historical textiles for analysis of metallic mordants and certain dyes is discussed.

## 1 Introduction

The analysis of dyes on historical textiles by thin layer chromatography and combinations of thin layer chromatography and ultraviolet and/or infrared spectroscopy is well documented [1–9]. Recently the use of HPLC has been explored [10]. Less frequently, mordants have been analyzed either by wet-chemistry microanalysis [11], by X-ray fluorescence (XRF) [2], or by atomic absorption spectroscopy (AAS) [12]. The use of scanning electron microscopy (SEM) along with energy dispersive X-ray spectrometry (EDS) appears to be easy and convenient for the identification of metallic mordants on fibers, if such instrumentation is available. In this preliminary report we have examined samples of modern wool, silk and cotton fabrics mordanted in our laboratories with common mordants [13, 14]: potassium aluminum sulfate (alum), cupric sulfate, ferrous sulfate, stannous chloride, and potassium dichromate. The quantity of mordants taken was based roughly on recipes indicated in dyers' handbooks.

## 2 Materials and methods

Samples of wool, silk, and cotton fabric were prepared by the Metropolitan Museum's Textile Conservation Laboratory as references for mordant analysis. The mordants used were potassium aluminum sulfate (alum),  $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$ , cupric sulfate,  $CuSO_4 \cdot 5H_2O$ , stannous chloride,  $SnCl_2 \cdot 2H_2O$  (Fischer Scientific Certified ACS Grade), ferrous sulfate,  $FeSO_4 \cdot 7H_2O$  (Mallinkrodt Analytical Reagent Grade), and potassium dichromate,  $K_2Cr_2O_7$  (Mallinkrodt Technical Grade).

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### 2.1 Wool

Wool samples were taken from Merino breed sheep whose fleece was spun without the removal of natural oils. The yarn was woven then cut into 75mm squares and treated as follows:

Merino 1 Untreated

Merino 2 Washed in 3% Orvus WA paste in demineralized water pH 7.3 at 50°C, rinsed once in demineralized water and dried flat on a screen.

3g samples of Merino 2 were heated with mordants in 100ml of demineralized water for one hour at 80°C to produce the following samples:

Merino 3 Merino 2 with 0.562g potassium aluminum sulfate (alum).

Merino 4 Merino 2 with 0.374g cupric sulfate.

Merino 5 Merino 2 with 0.374g ferrous sulfate.

Merino 6 Merino 2 with 0.187g stannous chloride.

Merino 7 Merino 2 with 0.094g potassium dichromate.

### 2.2 Silk

The loosened fiber (*Bombyx mori*) was supplied with some of the sericin already removed. The fiber was then spun and woven. Microscopic examination suggested that the samples were sufficiently 'degummed' to receive a mordant.

Silk 1 Untreated.

Silk 2 Rinsed in demineralized water (pH 7.1) at 23°C.

2g samples of Silk 2 were heated with mordants in 100ml of demineralized water for one hour at 90°C to produce the following samples:

Silk 3 Silk 2 with 0.374g alum.

Silk 4 Silk 2 with 0.249g cupric sulfate.

Silk 5 Silk 2 with 0.374g ferrous sulfate.

Silk 6 Silk 2 with 0.102g stannous chloride.

Silk 7 Silk 2 with 0.015g potassium dichromate.

### 2.3 Cotton

The cotton was American grown; cotton seeds were removed, the fibers spun, and the fabric was woven. An additional treatment of the woven cotton with sodium carbonate [11] was performed to remove wax from the cotton fibers.

- Cotton 1 No treatment.  
Cotton 2 Heated in demineralized water (pH 7.2) for three hours at 95°C to remove wax.  
2.25g samples of Cotton 2 were heated with mordants in 100ml demineralized water for one hour at 90°C.  
Cotton 3 Cotton 2 with 0.561g alum plus 0.144g sodium carbonate.  
Cotton 4 Cotton 2 heated at 90°C in 100ml demineralized water containing 0.144g sodium carbonate for one hour, followed by heating at 90°C in 100ml demineralized water containing 0.280g cupric sulfate.  
Cotton 5 Cotton 2 heated at 90°C in 100ml demineralized water containing 0.144g sodium carbonate for one hour, followed by heating at 90°C in 100ml demineralized water containing 0.280g ferrous sulfate.  
Cotton 6 Cotton 2 with 0.144g stannous chloride plus 0.144g sodium carbonate.  
Cotton 7 Cotton 2 heated at 90°C in 100ml demineralized water containing 0.144g sodium carbonate for one hour, followed by heating at 90°C in 100ml demineralized water containing 0.071g potassium dichromate.

#### 2.4 Analysis

Pieces of the control (untreated), the washed, and the washed and mordanted samples were prepared for analyses in an Amray 1600T SEM with attached Kevex 07000 EDS. Different sample sizes and mounting techniques were tried to determine optimal conditions under which the study should be performed. The sample sizes varied from single fibers to bundles and to 25mm<sup>2</sup> patches. All of the samples were mounted on spectroscopically pure carbon stubs with spectroscopically pure carbon paint, coated with 10–20nm of spectroscopically pure carbon in a vacuum evaporator, and viewed at 20 or 30keV in a scanning electron microscope with attached energy dispersive X-ray spectrometer. The elemental analyses were obtained with the aid of the computational standardless analysis package (with Magic V) for the Digital Electronics Corp. PDP-11/03 computer, both provided by Kevex. This software/hardware combination permits the determination of elemental compositions from sodium to uranium.

Extensive sampling of the wool was undertaken to determine the smallest sample size required for each mordant. Sampling of the silk and cotton was limited to small bundles of 10 to 50 fibers each, 0.5mm long.

### 3 Results and discussion

Table 1 shows the EDS results for the wool samples. Each series of elements represents either a set of observations for different quantities of fibers or for different places on a single fiber sample. The reported order of the elements in each run is given in decreasing concentration (weight percentages). Large differences in weight percentages were observed in different parts of replicate samples. Some elements are observed consistently, but for each wool sample elements are also observed only occasionally. The frequency with which elements are observed in this study is noted in parentheses in column 4 of Table 1 (3–5 scans per sample). Our results suggest that for quantitative analyses a large number of scans might be required as well as an independent external analysis. The EDS method of analysis is particularly sensitive to the non-uniformity of the sample and/or to the non-uniform process of mordanting. Sulfur, as expected, is evident in all samples. There appears to be a detectable difference in washed and unwashed samples: sulfur rather than potassium is the most abundant element in the washed samples (Orvus WA paste). Soluble salts are presumably removed in the washing.

All samples of the alum-mordanted wool examined clearly showed aluminum to be present, even when a single fiber was examined. Varying quantities of calcium and phosphorus were also observed, possibly from the demineralized wash water or detergent contamination on glassware. Copper was detected on all samples mordanted with cupric sulfate, even when a single fiber was examined. Iron was always detected in fiber bundles or square samples mordanted with iron sulfate, but single fibers occasionally failed to indicate the presence of iron unambiguously. A problem that arises with identifying iron as a mordant is that iron is frequently found in water as a contaminant. Other elements closely associated with iron are also frequently observed. In a double-blind experiment (*vide infra*), a sample that was mordanted with tin also contained iron. The analysis for iron can be problematic, not because it is difficult to detect or easily washed out, but because it is ubiquitous. Tin was detected reliably only on fairly large samples. In one set of experiments, tin was detected only in one of three places on a bundle of fibers, suggesting the possibility of aggregation of that element or mordant. Chromium proved to be the most difficult mordant to detect unambiguously. It was detected with reliability only on the largest samples in our study.

Table 2 shows a summary of results obtained from small bundles of silk fibers (10–50 fibers per bundle). The presence of sulfur is clearly detectable in

Table 1 Wool: results of EDS scans

Sample no.	Treatment	Elements always observed*	Elements sometimes observed†	Remarks
Merino 1 Bundle of fibers	Untreated	K, S, Si, Cl	Fe (75), P (25)	
Merino 2 Bundle of fibers Square of fabric	Washed	S, K, Ca, Si S, K, Ca, Si	Cl (50), P (50)	
Merino 3 Bundle of fibers Square of fabric	Alum	S, Al, Si S, Ca, Al, P, Si	Ca (33), P (67)	Single fiber sufficient
Merino 4 Bundle of fibers	Cu	S, Cu, Si	Ca (40), Fe (20), Al (20)	Single fiber sufficient
Merino 5 Bundle of fibers Square of fabric	Fe	Si, Fe, Si S, Fe, Si	P (50), Ca (33)	Square of fibers needed
Merino 6 Bundle of fibers Square of fabric	Sn	S, Si, P S, Sn, Si	Sn (33) Al (50)	Square of fibers needed
Merino 7 Bundle of fibers Square of fabric	Cr	S, K S, Si, K, Ca, Cl, Al	Cr (50), Si (67), P (67), Fe (33)	Square insufficient

\*In order of decreasing weight percent.

†Numbers in parentheses are frequency of occurrence (% during 3–5 scans).

Italics denote very small or trace amounts.

all samples, but the actual weight percentages were considerably lower than those for the wool samples. This would be expected when comparing the amount of sulfur-containing amino acid cysteine in wool and silk [15]\*. This group of samples also indicates that washed and unwashed samples show different elemental analyses. Aluminum, iron, copper and tin are clearly and unambiguously detected, while chromium is not, suggesting that the instrumental technique is insufficient to detect this mordant, at least in the concentrations present on the silk in our experiments. Single-fiber mordant identification of the aluminum, iron, copper and tin may be possible and will be tried in the future.

Table 3 shows the data for the cotton mordanted samples. In these samples, sulfur, probably from mordant or wash water, is detectable only in trace amounts on a few of the samples. Some change in elemental distribution is also noted between washed and unwashed samples. Aluminum, iron, copper and tin were readily detected in small bundles but chromium was not.

\*Data from *Handbook of Common Polymers*, The Chemical Rubber Co., Cleveland OH (1971). Sulfur in silk c. 0.05% as cysteine; sulfur in wool c. 3.4% as cysteine (c. 13%) and methionine (c. 0.5%).

Table 2 Silk: results of EDS scans\*

Sample no.	Treatment	Elements observed†
Silk 1	Untreated	Ca, S, K, Si, Fe, Cl, Na
Silk 2	Washed	Ca, S, Si, P, Al, Cl, K
Silk 3	Al	S, Al, Si, Ca, Cl, Fe
Silk 4	Fe	Fe, S, Si, Ca, Cl, P
Silk 5	Cu	Cu, S, Ca, Si, Cl, Ni (?), P, Al
Silk 6	Sn	Sn, Si, Ca, Fe, S
Silk 7	Cr	Ca, S, Cl, Si

\*Small bundles.

†In order of decreasing weight percent.

Table 3 Cotton: results of EDS scans\*

Sample no.	Treatment	Elements observed†
Cotton 1	Untreated	Ca, Si, S, Cl, Mg
Cotton 2	Washed	Ca, Cl, Si, S, Al, Fe
Cotton 3	Al	Al, Fe
Cotton 4	Fe	Ca, Si, Fe
Cotton 5	Cu	Ca, Si, Cu, P, Fe
Cotton 6	Sn	Sn‡
Cotton 7	Cr	K, Fe, Ca, Si, Cl, S

\*Small bundles (10–50 fibers).

†In order of decreasing weight percent.

‡Other elements unrecorded.

Italics denote very small or trace amounts.

Table 4 Limits of sensitivity of mordant detection by EDS: comparison of mordant quantities applied to wool samples with quantities analyzed by AAS

Element	EDS product literature [16]	Maximum % element in wool mordanted sample*	% Element by AAS in wool sample†
Al	0.1% ± 0.07	1.0	0.10
Cu	0.1%	3.2	0.50
Fe	0.1%	2.6	0.28
Sn	0.1%	3.3	0.24
Cr	0.1%	1.1	0.08
Zn	0.1%	no data	no data

\*See experimental section. Assumes textile sample absorbs all added mordant.

†Atomic absorption spectrophotometric analyses done by Schwartzkopf Microanalytical Labs, Woodside, NY 11377 (uncertainty ±10%).

A double-blind series of experiments was performed for the wool mordanted samples. The elements of the mordant were invariably detected with the EDS scans. The alum, copper and iron mordanted samples were unambiguously identifiable. Although the tin and chromium samples gave clear indications of tin and chromium respectively, other elements (aluminum and/or iron) were also observed. The limits of detection for the elements of interest in this study are given in Table 4 and are reported according to the manufacturer's product literature [16]. The instrumentation used in this study dates from 1978 and 1982; it is our experience that newer EDS instrumentation is more sensitive.

Fibers from our wool sample batch were also analyzed by AAS (Table 4). It is possible to use data so obtained in conjunction with EDS scans to estimate mordants quantitatively in order to produce series of EDS standards. The AAS data suggest that only about 10% of the metallic element of the mordant is incorporated into the fibers in the process of mordanting. Subsequent dyeing, washing and deterioration probably cause further loss of mordant in real textiles. Table 4 also indicates a major source of difficulty that may arise in EDS detection of mordants. The detection limit of the EDS to the mordants in our study is 0.1%. Therefore, if the mordant of interest is present in smaller percentages it may not be detected. The AAS analyses indicate that the amount of aluminum and chromium mordant actually adhering to our wool samples was at or below the detection limits of our EDS.

Colors that contain only the elements carbon, hydrogen, nitrogen and oxygen, and organic mordants (e.g. tannins, fatty acids), cannot be detected directly by our EDS. Newer EDS equipment has windowless detectors that make possible the determination of hydrogen, nitrogen, oxygen and carbon, but applicability to dye analysis has yet to be explored. Metallic salt mordants are amenable to window-type EDS detectors. The direct dye 6,6'-dibromoindigo, owing to the presence of the easily detected bromine atom, should also be observable.

Scans of a modern cotton sample known to have been dyed with shellfish purple, which contains this dye, gave positive indications for bromine both by EDS scans and bromine microanalysis.\* The sample taken for EDS was a single fiber of less than 1mg. The sample analyzed colorimetrically was c.15mg and indicated the presence of 0.075% bromine. Purples achieved with other dyes or dye combinations should give completely different analyses.

Another method for mordant identification—proton induced X-ray emission (PIXE)—is also under investigation [17].

The successful identification of mordants on dyed modern textiles has been completed in our laboratory and will be reported shortly. A study of mordant identification on historical textiles is under way.

#### 4 Conclusions

Modern samples of wool, silk and cotton mordanted with potassium aluminum sulfate, ferrous sulfate, cupric sulfate, stannous chloride and potassium dichromate were analyzed successfully for Al, Fe, Cu, Sn and Cr by EDS. Occasional EDS scans for Sn and Cr failed to indicate these elements. AAS analyses of mordanted wool samples indicated that the level of mordant present is at or near the limits of detectability for our instruments. EDS analysis was capable of detecting the presence of 6,6'-dibromoindigo on cotton samples.

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\*Schwartzkopf Microanalytical Laboratory, Woodside NY 11377. Colorimetric determination of bromine.

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- Résumé**—Divers échantillons modernes de tissus en laine, soie et coton ont été traités par cinq agents mordants courants: le sulfate double d'aluminium et de potassium, le sulfate de cuivre, le sulfate ferreux, le chlorure stanneux et le bichromate de potassium. Les échantillons ont été examinés par microscopie électronique à balayage, et les éléments métalliques ont été détectés par spectrométrie X dispersive. Les résultats et les limites de sensibilité de l'analyse sont discutés et comparés aux autres procédés analytiques. On discute de l'application de ce procédé à des textiles historiques pour l'analyse des mordants métalliques et de certaines teintures.
- Auszug**—Es wurden Muster moderner Woll-, Seide- und Baumwoll-Webstoffe mit fünf gewöhnlichen Färbebeizmitteln gebeizt: Kalium-Aluminium-Sulfat, Kupfersulfat, Eisensulfat, Stannochlor und Kaliumdichromat. Die Muster wurden durch Elektronenabtastmikroskopie (SEM) beobachtet, und metallische Elemente wurden durch Energieerztreuungs-Röntgenspektrometrie (EDS) aufgefunden. Die Ergebnisse und Beschränkungen des Detektionsprozesses werden erörtert und mit anderen analytischen Prozeduren verglichen. Die Anwendung dieser Prozedur auf historische Textilien für die Analyse metallischer Beizmittel und bestimmter Farbstoffe wird erörtert.