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THE IDENTIFICATION AND CHARACTERIZATION OF METAL WRAPPINGS IN HISTORIC TEXTILES USING MICROSCOPY AND ENERGY DISPERSIVE X-RAY SPECTROMETRY:PROBLEMS ASSOCIATED WITH IDENTIFICATION AND CHARACTERIZATION

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Abstract

Scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDS) has been employed for the description of metal wrapped yarns. Although considerable detail is obtainable as microphotographs, and elemental analysis is obtained with ease, caution should be exercised in interpreting results. Several unravelled samples should be examined; light microscopy should be employed prior to SEM-EDS analysis. Examination of eight specimens (six from the textile collection of the Metropolitan Museum of Art, New York; two from private collections) is described. The samples were Chinese (5), German (1), Spanish (1), Turkish (1). Difficulties encountered in describing this set of samples are enumerated.

KEY WORDS: Metal wrapped textiles, scanning electron microscopy, energy dispersive x-ray analysis.

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Introduction

The problem of describing the metal wrapping of yarn used in the textile arts has received modest attention [3-5,7,9,13-15]. It is attractive to study variations in wrapping techniques and materials in order to establish place and time indicators for textile identification. Numerous yarns and their metal wrappings have been examined in our laboratories in a manner following procedures developed for the detection of mordants on textile fibers. For earlier studies in this laboratory on textile standards, samples were simply carbon coated and subjected to scanning electron microscopic-energy dispersive x-ray spectrometry (SEM-EDS). Metallic mordants were detected successfully on undyed standards of cotton, silk, wool [11], and dyed wool [8]. The samples had been mordanted with salts containing aluminum, iron, chromium, tin, and copper. In each case, the metal was detected successfully. Weighted silk samples prepared as standards have also been analyzed successfully for the substances used in the weighting process [1,2]. (Mordants are usually metallic salts used in small amounts required in the dyeing process; weighting substances [2] are usually used in larger quantities to increase the weight of silk fabrics.) For wool and silk samples, the sulfur present in the proteinaceous fibers was useful as an internal standard for distinguishing the presence of trace metallic species from metallic species usually introduced as mordant [1,2,8,10]. Organic additives, such as dyes, (6,6' Dibromo-indigo, shellfish purple, has been successfully detected using EDS, see ref. 11.) sumac, oxalic acid, etc., escape detection by EDS analysis (except insofar as trace metallic impurities are present), owing to the fact that the analysis is appropriate only for elements of higher atomic number than NEON [8]. Analysis of historic silk [10] and wool (R.J. Koestler and N. Indictor, unpublished results) samples have been carried out on a limited number of examples. In some instances the presence of metallic species confounds detection of mordants with surface accretions related to the history of the textile (soils, stains, washing, etc.). It is possible that washing or vacuuming the textile prior to SEM-EDS analysis may reduce or eliminate surface accretion without disturbing the mordant. This is a problem suitable for further investigation.

Presence of metal wrapped yarns introduces further complicating features to the analysis [3,6,7,9,12,15]. The variety of metal wrapping techniques [3-5,7,9,13-15] is considerable. In the simplest cases sheet or wire alone is used as embroidered or supplementary elements. Another technique is to use thin, beaten or rolled, metal strips of gold, silver, or baser alloys wrapped around a fiber core; core fibers may be dyed, or undyed, or a mixture. In more complex examples, gold or silver leaf or dust may be applied, with (or without) adhesive or ground, to paper, parchment, membrane, or leather which is then cut into thin strips and used as a weaving element or wound about a core fiber of silk, linen, or cotton. The wrapping may be single or more and may be loosely or tightly wrapped. Some of the metal wrapped specimens submitted for SEM-EDS analysis to this laboratory will be described and some of the problems encountered will be indicated.

Experimental

Specimens were obtained from Metropolitan Museum of Art textiles and textiles in private collections. The samples examined were taken from the specimens submitted. After observing through a light microscope (Wild M8), the samples were carbon coated with about 10nm of spectroscopically pure carbon in an Edwards E306 vacuum evaporator and submitted to SEM-EDS analysis. Samples were viewed in an AMRAY 1600T scanning electron microscope with attached Kevex Model 7000 x-ray spectrometer. Operating conditions were as specified on the micrographs or, for EDS, 20 or 30 kV, 200 s collection time, 1 to 100 μm^2 excitation areas. In each case the metal wrapping was separated from the core fiber in a manner which would permit viewing (either with optical microscopy or scanning electron microscopy) of: 1. Outer metal surface, metal clearly evident; 2. Outer metal surface, worn area; 3. Underside of wrapping material or metal wrap; 4. Core fiber; 5. Cross-section of core fiber. The samples examined are listed in Table 1 along with brief catalog descriptions. Figure 1 shows some of the textiles examined; Figure 2 shows some SEM images obtained.

Table 1: DESCRIPTION OF TEXTILES SAMPLED

Acc. No.*	Catalog Description of Textiles
Banner[a]	Banner Heading, Yuan Style, Chinese.
44.136.2	Robe, Imperial Court, Chinese, K'ang Hsi(?)
64.39	Robe, Imperial Court, Chinese, First half 18th C.
54.14.2	Robe, Emperor's 12-Symbol, Chinese, Early 18th C.
35.84.8	Robe, Emperor's 12-Symbol, Chinese, Late K'ang Hsi.
53.35.4	Altar (?) Frontal. Esther before Ahasuerus. South German, 16th C. (The Cloisters Collection).
1984.344	Silk with adorsed and regardant griffins in circles. Spanish 13/14th C.
Cotton[a]	Towel with metal embroidery. Turkey, 20th C.

* Metropolitan Museum of Art Accession Number.

[a] Private collections.

Results and Discussion

Table 2 is a description of the samples taken from the specimens on examination with the light microscope. Observations are made on: (1) the identity and color of the core fibers; (2) the identity of the wrapping material; (3) differences between the inside and the outside of the wrapping material; (4) differences between worn and unworn areas of the metallic surface; (5) corrosion and loss at metal surface; (6) appearance of ground, if any, between the metal surface and the wrapping material; (7) twists of core fibers and wrapping; (8) width of wrapping; (9) closeness or openness of wrapping (exposure of core fibers).

Table 3 lists the EDS results of the components of the metal wrapped specimens. Here are listed the major metallic species detected on the several surfaces as well as other elements of higher atomic number than NEON. An attempt is made to estimate the range of compositions observed at the surfaces and to indicate the presence or absence of gold or silver.

Table 4 is a summary of the observations. A number of important kinds of observations are possible using the light microscope, SEM and EDS analysis: 1. Mechanical structure of the wrapped fiber; single or double wrapping, twist of core and wrapping, width of wrapping, closeness or openness of wrapping (extent to which core fibers are exposed). 2. Identity of the core fibers. 3. Color of the core fibers. 4. Metallic elements within the core fibers. 5. Identity of wrapping material. 6. Metallic composition of the wrapping; presence or absence of gold, silver; alloy composition. 7. Metallic components in the ground of the wrapping. 8. Condition of the wrapping and core.

Some of the difficulties and limitations encountered in the analyses are:

1. For the most part the presence or absence of mordant on core fibers cannot be determined. Metallic species found on the wrapping material is invariably found in the core fibers also. Exhaustive washing or vacuuming of the core fibers after separating this from the wrapping material might resolve this difficulty. Color of the core fiber sometimes resists definitive description. It is difficult to distinguish between a light yellow (which may have faded) and an undyed fiber which may have yellowed from deterioration or interaction with the wrapping material. Since yellow fibers may have been used

Table 2: SAMPLES EXAMINED (LIGHT MICROSCOPE)

Acc. No.	Description of Specimens
Banner[a]	Single wrapped fibers (silk). Wrapping: fibrous substrate (paper?) to which thin gold metal (leaf or dust) is attached through brown ground.
-A	Core fibers, trace metal.
-B	Outer metal surface.
-C	Worn area of outer surface.
44.136.2	Double-wrapped two-color fibers (undyed and yellow silk). Wrapping: fibrous substrate (paper?) to which thin gold metal (leaf or dust?) is attached through red ground.
-A	Outer surface, metallic area.
-B	Inner surface of wrapping.
-C	Inner surface of wrapping.
-D	Core fibers.
-E	Outer surface, metallic area.
64.39	Single wrapped yellow fibers (silk). Wrapping: fibrous substrate (paper?) to which thin gold metal (leaf or dust?) is attached through red ground.
-A	Outer surface, metallic area.
-B	Inner surface, metallic area.
-C	Inner surface, metallic area.
-D	Core fibers.
54.14.2	Single wrapped undyed fibers (silk). Wrapping: silver metal.
-A	Metal wrapping.
-B	Core fibers.
35.84.8	Single wrapped amber fibers (silk). Wrapping: fibrous substrate (paper?) to which thin gold metal (leaf or dust?) is attached through red ground.
-A	Inner surface of wrapping.
-B	Outer surface, metallic area.
-C	Outer surface, worn area.
-D	Core fibers.
53.35.4	Thin metal sheet wrapping (no organic fibers).
1984.344-A	Outer surface, metallic area.
-B	Outer surface, worn area.
-C	Inner surface of wrapping.
-D	Core fibers.
Cotton[a]	
-A	Outer surface of wire thread.
-B	Cross-section of wire thread.

[a] Private collections.

Table 3: EDS RESULTS

Acc. No.		Elements Observed*
Banner[a]	-A	Au, Fe, Al, S.
	-B	Au, tr. metals, No Ag.
	-C	Au, Fe, Al. No Ag or S.
44.136.2	-A	Au/Ag ca. 1:6; Pb, Fe, Al, tr. metals.
	-B	Pb, Fe, Al, tr. metals.
	-C	Pb, Fe, Al, tr. metals.
	-D	Pb, Fe, Al, tr. metals.
	-E	Au/Ag ca. 1:3; Pb, Fe, Al, tr. metals.
64.39	-A	Au/Ag ca. 7:1; tr. Fe and Al.
	-B	S, Fe, Al, tr. metals. No Au or Ag.
	-C	S, Fe, Al, tr. metals. No Au or Ag.
	-D	S, Fe, Al, tr. metals. No Au or Ag.
54.14.2	-A	Ag (more than 95%)
	-B	Ag, S, tr. metals.
35.84.8	-A	Fe, Al, Pb, S, tr. metals.
	-B	Au, Al, tr. Fe. No Ag or S.
	-C	Fe, Al, Au, tr. S.
	-D	Fe, Al, S, tr. metals.
53.35.4		Cu/Zn 4:1; no other elements.
1984.344	-A	Ag, Au, S, tr. Si and Cl. Au/Ag ca. 0.3-0.15.
	-B	Ag, Au, S, Ca, Si, Na, Al, Cl, Mg, K.
	-C	Ca, Si, S, K, Fe, Al, Cl, Na.
	-D	Ag, Cl, K, Ca, S, Al, Fe.
Cotton[a]	-A	Ag, Cu.
	-B	Cu core, Ag surface.

[a] Private collections.

* "tr." (trace) refers to elements detected at << 5% of the normalized analysis. Numerical values refer to intensity ratios or percentage of normalized total analysis.

to enhance the effect of the metallic surfaces, particularly for loosely wrapped examples, and since yellow dyes are among the most fugitive, visual examination may be inconclusive.

2. Identification of core fibers by elemental analysis can be unreliable. In one case, where the core fibers appeared to correspond closely to textbook examples of cotton fibers under the light microscope, the EDS analysis clearly indicated the presence of sulfur. The sulfur in the core fiber may have come from proteinaceous wrapping material, or the presence of some silk in the core fibers. Conceivably, exhaustive vacuuming or washing could obviate this difficulty.

3. Identification of the wrapping material when other than metal or metal alloy is possible only by light microscopic examination or SEM imaging. Comparison with known examples and experience with typically deteriorated specimens is essential. EDS cannot be used to identify the materials, except by inference or as a fingerprint indicator. The multiplicity and variability of metallic species in the ground material of several specimens of wrapping material suggests numerous possibilities for materials used as ground. As the domain of observations is enlarged, elemental analysis may become diagnostic as a

Fig. 1. Some textiles from which metal threads were taken. 1a. Metropolitan Museum of Art 64.39. 1b. Metropolitan Museum of Art 54.14.2. 1c. Turkish Towel (private collection). (Fig. 1b and 1c on facing page).

means of identifying different types of metal wrapping. Consultation with experienced conservators and curators is an invaluable accompaniment to this type of analysis, essential for the scientist unfamiliar with textile technology.

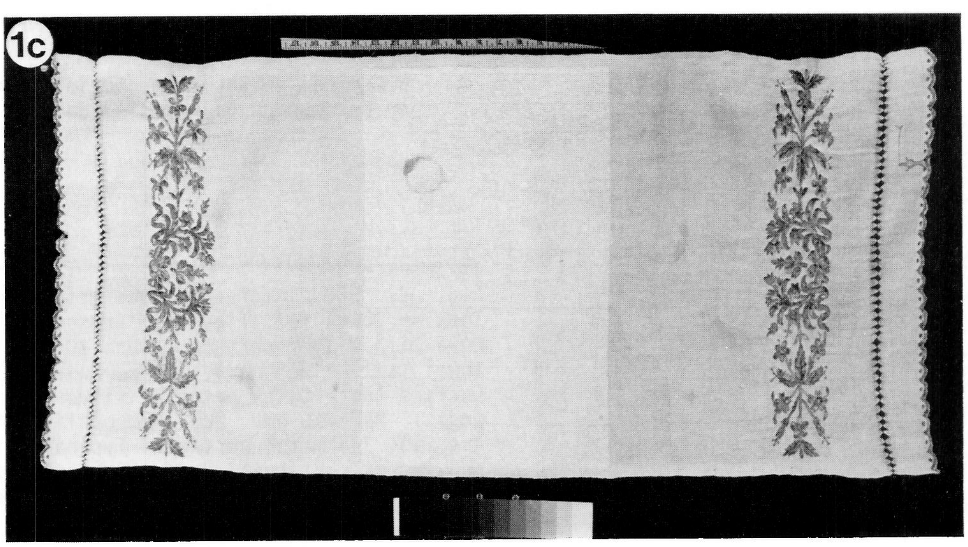
4. Homogeneity of the metallic surface may be altered by corrosion or wear. Hoke and Petrascheck-Heim [7] studied the compositional homogeneity by microprobe analysis of gilded silver lamellae (metal wrapping not attached to a substrate, but wound around a silk core). Homogeneity in the surface composition is used as part of the evidence in assigning workshop origin. A comparable effort for metal wrapped threads in which the lamellae are of more complex structure (paper, membrane, leather substrates for metallic material) suggests that it is impossible to characterize metal surfaces according to simple standards of homogeneity for many historic samples. Corrosion and deterioration are visibly greater on the more complex wrappings with very clear areas of metallic loss. Even in protected places, where the metallic surfaces appear bright and shiny, the surface, unless nearly pure gold, has a mottled (inhomogeneous) appearance. The method of manufacture may produce an inherently inhomogeneous metal surface; but wear and corrosion tend to confound any estimate of homogeneity. The extent of (in)homogeneity is still worth noting, especially when samples are procurable that have undamaged surfaces.

Summary

Some examples of metal wrapped fibers examined with a light microscope and with SEM-EDS are described. Important structural details that can be observed are: identity and color of the core fibers; elemental composition of the metal wrapping; presence or absence of gold or silver and approximate composition; identity of wrapping material; metal components in the ground of the wrapping; mechanical structure of the wrapped fiber (single or double wrapping, metal wrapped core or metal applied to a wrapping material which is then wound about a core, twist, width of wrapping, closeness or openness of wrapping).

Limitations and difficulties encountered are: identifying mordants on core fibers (confused by the presence of metallic species from wrapping material); failure to distinguish between cotton and silk if wrapping material


1b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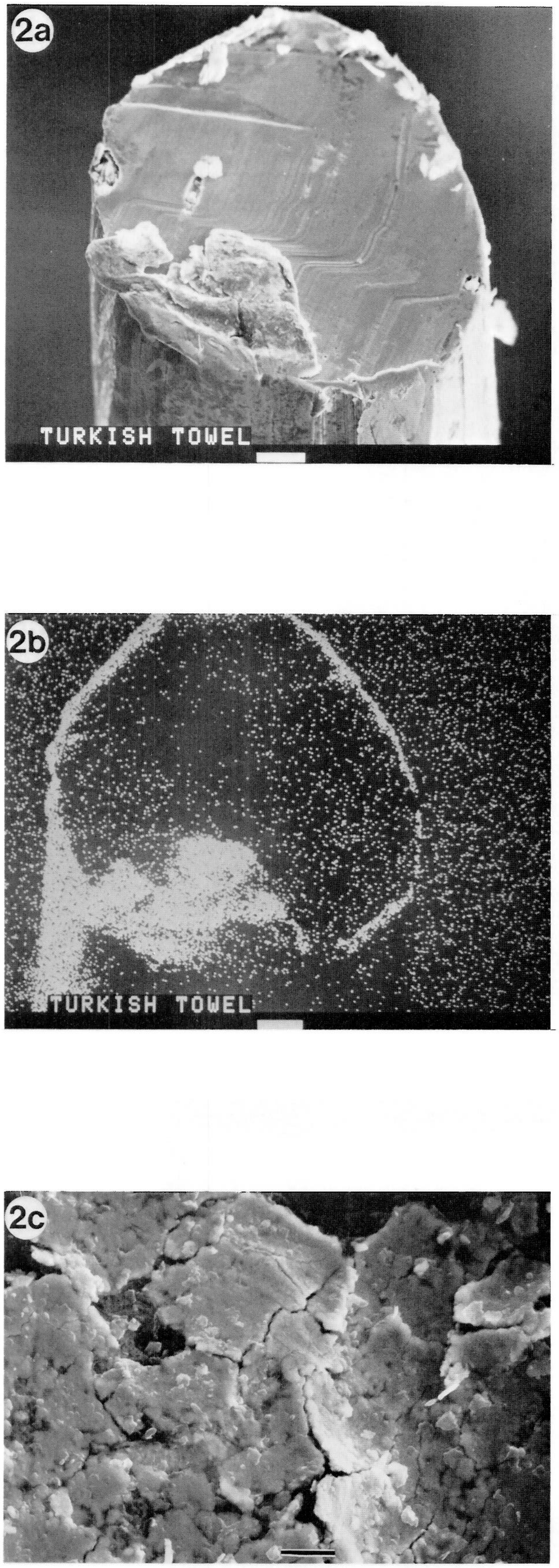

Table 4: SUMMARY OF FINDINGS

Acc. No.	
Banner[a]	Core: undyed silk, Z-twist. Wrapping: single wrapping, Z-twist of paper(?) substrate to which Au (leaf or dust) is attached through brown ground rich in Fe and Al. Tightly wrapped. Surface shows Au but no Ag.
44.136.2	Core: yel. & undyed silk, Z-twist. Wrapping: double wrapping, Z-twist of paper(?) substrate to which Au (leaf or dust) is attached through brick-red ground rich in Pb, Fe, and Al. Tightly wrapped. Surface shows Ag:Au, ca.3:1-6:1*.
64.39	Core: yel. silk sl. Z-twist. Wrapping: single wrapping, Z-twist of paper(?) substrate to which Au (leaf or dust) is attached through brick-red ground rich in Fe, and Al. Closely wrapped. Surface shows Ag:Au ca. 1:7*.
54.14.2	Core: undyed silk, sl. Z-twist. Wrapping: single wrapping, Z-twist, thin metal sheet. Tightly wrapped. Ag greater than 95%*.
35.84.8	Core: amber silk, Z-twist. Wrapping: single wrapping, Z-twist paper(?) substrate to which Au (leaf or dust) is attached through brick-red ground rich in Fe and Al. Tightly wrapped. Surface shows Au, but no Ag.
53.35.4	Thin metal sheet. Cu:Zn ca. 4:1*. No Au or Ag.
1984.344	Core: cotton. Wrapping: single wrapping, membrane or parchment substrate to which a metallic surface has been applied. Surface shows Ag:Au ca. 3:1-6:1*.
Cotton[a]	Thin wire, Cu core with thin Ag surface.

[a] Private collections.

* Numerical values refer to intensity ratios or percentage of normalized total analysis.

Fig. 2. SEM pictures of some metal threads. 2a. Turkish Towel (cf. fig. 1c). Cross-section of copper wire with silver surface. Bar= 10 µm. 2b. Turkish Towel (silver dot map). Copper wire with silver surface (note thick patch of silver from jagged edge). Bar= 10 µm. 2c. Metropolitan Museum of Art 1984.344 metal surface. Typical metal surface showing discontinuities for samples in which metal is attached to a substrate and then wrapped around a fiber core. Bar= 10 µm.

contains sulfur (e.g., metal corrosion products, proteinaceous adhesives, proteinaceous wrapping material); incomplete elemental analysis (no elements detected below atomic number 11 with EDS window-type detectors); estimates of surface homogeneity may be an indication of deterioration or wear rather than manufacture.

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Discussion with Reviewers

E.R. Walters: Fibers mounted in an embedding medium can be cut to give an excellent cross-section surface for SEM/XRS analytical studies using elemental distributions. Was this done for any of these materials? This should separate the concentration of surface accretions from mordants and from elements contained internally in the fibers. Studies on cut surfaces, done in this way, may also help to elucidate how the metals were applied.

Authors: No, but we plan to do these studies in order to obtain some insights into the various methods of fabrication of metal wrapping. The Turkish towel sample was done in cross-section with very clear results.

E.R. Walters: Does the yarn twist and metal wrap always have the same handedness (S or Z), and, are double wraps always the same or may they have opposing twists?

Authors: No, we have now seen examples of different twists in the core from that of the wrapping. Usually it is the same. So far we have not had much experience with double wraps. These are the kinds of questions we hope to be able to answer by examining a large corpus of textiles.