

WEIGHTED SILKS OBSERVED USING ENERGY DISPERSIVE X-RAY SPECTROMETRY

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Abstract

A group of modern silk fabrics was treated with various weighting agents as standards. These standards were observed using energy dispersive x-ray spectrometry. The standards were compared to untreated samples and to museum specimens of weighted silks. In all prepared specimens the elements expected from treatment were observed; weighting treatments could be distinguished. The analytical procedures are discussed and compared to recent work on mordant analysis using the same techniques.

Introduction

There are two fundamental ways to stiffen the soft and gentle drape of a silk fabric. One method is to adjust yarn properties and fabric construction, making denser textiles and more compact weaving structures. The other method is to apply finishes to the yarn or cloth so that the final product has the appropriate 'hand' or feel, regardless of initial fabrication. The second method has overwhelming economic advantage; it is known as 'weighting' or 'loading' the silk.

Weighted silk has been an aspect of silk production for centuries. The first printed book on dyestuffs, published in 1548, includes a recipe to stiffen silk with gum arabic [14]. A less water soluble result is obtained by using tannins. The leaf extract of a sumach *Rhus coriaria*, native to Sicily, has been calculated to improve the weight on fiber up to 25% [1,3]. In addition, animal glue has been used to stiffen silk already impregnated with tannins. The result can account for a loading of as much as 50% [3]. Another 'vegetable' means of loading silk involved the use of sugar to stiffen light colored silks 10-20% [15]. While these methods may darken the color of the finished fabric and even encourage insect damage, they may not cause the same or as much degradation of weighted fiber as later weighting processes using salts.

Much damage is found in silks that have been weighted with mineral salts. Dark fabrics many times would be pre-treated with tannin and then placed in a bath of an iron salt. Alternatively, a silk intended to be black could be pre-treated with the ammoniacal salt of chlorostannic acid and perhaps a solution of catechu extract (from the leaves and branches of the *Uncaria gambir* plant). The resulting brown silk could then be top-dyed black with an extract of oxidized logwood to reach a loading of 100%. A blue silk can be obtained if the ferric hydrate fixation is followed by a treatment with potassium ferrocyanide, rather than catechu or oxidized logwood [3].

The use of salts of bismuth and of tungsten is also reported [3]. Tribasic lead acetate was used in the early 20th century [1]. However, the most well known methods for loading silks utilize stannic chloride [1]. From the mid-19th century

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until 1938, when the Federal Trade Commission ruled that weighted silk had to be labeled--and the percentage of weighting listed on the label--tin weighting was quite popular among fabric manufacturers and finishers [19]. Even today some garments, such as men's ties, are made with weighted silks.

The first step in the process of tin loading involved the submersion of degummed silk in an aqueous solution containing the ammoniacal salt of chlorostannic acid [$\text{SnCl}_6(\text{NH}_4)_2$]. Because of its color, this solution was commonly called the 'pink bath'. After stannic chloride absorption on the fiber, the silk was first rinsed in water to hydrolyse the salt, and then rinsed in sodium carbonate to neutralize any remaining hydrochloric acid. This process could be repeated four or five times. Each time a weight gain of up to 10% could be obtained. The weight gain has been attributed to the attachment of tin to the amino acid glycine; the total weight gain obtainable by these baths was effectively limited by the diminished luster imparted to the fiber [3,19]. Substituting disodium phosphate provided some improvement [3].

The greatest weight gains were obtained using the "dynamite" method developed by Neuhaus [1,3]. He discovered that tin and phosphate loaded silk could absorb a substantial quantity of silicate when after-treated in a sodium silicate bath. Furthermore, a bath of aluminum sulfate between the last phosphate bath and the sodium silicate treatment could enhance the final percentage of loading even more [1]. Weightings of 400% above that of the degummed silk are reported [19].

For textile conservators working with antique fabrics and costumes in museums, 'mineral' loaded silks present a serious problem. The natural aging of a textile is always cumulative and idiosyncratic; the rate of embrittlement of silks treated with metallic salts is accelerated to a degree uncharacteristic of other fabrics. Procedures to remove water soluble degradation products or solvent soluble soiling are proscribed; normal repair methods--wet cleaning and sewing--and accepted storage practices--rolling or folding--adversely affect mineral weighted silks [1].

Since many silk fabrics can acquire splits and tears, even without a degradative finish, there is a need to know whether or not the fabric in question is a mineral weighted silk before proposing treatment to repair existing damage. Previous methods to determine the agents used in loading silk are destructive, crude, dangerous, or otherwise inappropriate. Ashing a sample is the analytical method most often described [1,3,5,9,18]. For this, 2-3 g of silk or 0.2-0.3 g of ash is required (about 45 x 15 cm for degummed unweighted silk) and spot testing methods are used [2,5,9]. Another method is a Kjeldahl nitrogen analysis requiring 0.5-1.0 g of silk [2,3]. It compares favorably with the extraction method (2% hydrofluoric, heated and 2% sodium carbonate, heated) [2,3]. Again a 2-3 g sample of silk is required. Comparison with known denier at known weightings either by microscopy or x-radiography has also been sug-

gested [16,18]. The choice, then, for textile conservators seeking knowledge of the finish without appreciable loss, has been limited. By and large, textile conservators with accessioned museum objects forego technical analytical assistance in describing the chemical finish on antique silks. The aim of this project has been, therefore, to ascertain whether or not samples of portions of single threads could be analyzed for metal salts using energy dispersive x-ray spectrometry (EDS) [11].

Following procedures established earlier for the detection of mordants on prepared standards [7,11] and on historical silks [6,10], a group of modern silk fabrics was treated with various weighting agents and subjected to EDS analysis. The EDS analyses were performed without prior knowledge of treatment. In each case all the elements characteristic of the treatments were observed and each of the treatments could be determined.

Experimental

Sample Preparation

Standard silk fabrics, one a crepe de chine and one a plain silk were purchased from Test-fabrics, Inc. These were used as sample series #20-29 and #30-39 respectively. (Japanese silk habutae, style #604, 37.6 denier warp, 32.1 denier weft; 1.11 07/yd² or 8 mommie. crepe de chine, style #601 20-22 denier yarn size; 14 mommie. Test fabrics, Inc. P.O. Drawer 0, 200 Blackford Avenue, Middlesex, New Jersey, 08846). A third sample series #1-10 was taken from a balanced plain weave fabric, tan in color, donated by The Boston Museum of Fine Arts' Research Department. It was a modern fabric of unknown origin. Silk yarn, an organzine 2-ply 20/22 denier, was obtained from Zwicky & Co., (CH-8304 Wallisellen, Switzerland). Skeins of this yarn formed sample series #40-49. All sample fabrics were cut, notched for identification and weighed to a tenth of a mg, with a gross weight of ca. 2 g. Skeins were reeled off the silk yarn and identified with cotton threads; they were individually weighed prior to the cotton tagging.

All the samples were treated with a degumming solution although samples from the series #1-10, 20-29, and 30-39 showed indications of previous degumming. Only series #40-49, the silk yarn, had the characteristic handle of gummed silk. Sodium lauryl sulfonate was used instead of the usual carboxylate soap ('Marseilles soap'). A 0.7% w/w solution with deionized water was made. The liquor ratio (sample: solution) was 1:30-40. The samples were maintained in baths of this solution for 1½ h at 96°C. Samples were then rinsed continuously and individually with running deionized water for 10 to 20 min., air dried and conditioned to 45% RH (relative humidity) and 20°C (68°F) before re-weighing to a tenth of a mg.

In addition, samples of degraded, deaccessioned silk were obtained from The National Museum of American History. The historic silks were not treated chemically but rather held in reserve and subsequently analyzed.

Weighting

Samples were divided into groups and variously treated as indicated in Tables 1 & 3. Samples #4, 24, 34, and 44, (Treatment V) were set aside as controls. Samples #3, 23, 33, 43, 6, 36, and 46, (Treatment I) were pinked and neutralized once. Samples #22, 32, and 42 were pinked and neutralized twice (Treatment I'). Samples #21, 26, 10, 20, 30, and 40, were pinked and neutralized twice and subsequently treated with both aluminum sulfate and sodium silicate baths (the modified Neuhaus method, Treatment II).

In order to compare this series as tin weighted samples with another type of silk weighting, samples #9, 29, 39, 49, 7, 27, 37, and 47, were brightened with a solution of dilute sulphuric acid and then treated in an iron liquor bath. Samples #9, 29, 39, and 49, were bathed once (Treatment III); samples #7, 27, 39, and 47, twice (Treatment III'). The iron liquor bath produced a mid-brown color on the fabric. Samples #8, 28, 38, and 48, were also treated once with the iron liquor but subsequently treated with potassium ferricyanide, which yielded samples royal blue in color (Treatment IV).

Procedure

Several texts discuss the mineral weighting of silk; the formulations used were those of Carboni [3]. It should be noted that many of the solutions are hygroscopic, and silk finishers have found it practical to describe the strengths of solutions in terms of the density of the mixed solution rather than in weight per volume or volume per volume. The units used, then, are described in degrees Baumé (°Be). Comparison between °Be and specific gravity are found in Trotman [17].

Tin Loading. Stannic chloride was mixed in deionized water until the solution reached 28°Be. Pink liquors were discarded if they fell below 21°Be. Wetted samples were immersed in the pink bath at a 1:40 liquor ratio, and stirred for 1½ to 3½ h at room temperature. Tap water was used to rinse the samples; washed samples had a surface pH of approximately 3.6.

After washing, pinked samples were neutralized in a disodium phosphate solution made with deionized water. The solution had a density of 5°Be at room temperature. The samples were immersed in the bath with a 1:40 liquor ratio. The temperature of the bath was raised to 60°C and maintained there for 1 h, while the samples were stirred. At the end, the pH of the bath was 9.0-9.2. The samples were removed from the bath and rinsed individually with deionized water for 10 to 20 mins. Disodium phosphate baths must be replenished in alkalinity to a pH of 11 after use, or made up anew.

The aluminum sulfate bath employed had a density of 3.5-4.5°Be. A liquor ratio of 1:40 was used; the temperature raised to 50°C, and the samples then immersed for 1 h. Once rinsed, the samples were treated in a sodium silicate bath of 4°Be at 42°C for 1 h. They were subsequently soaked in the 0.7% degumming solution described above at about 80°C for another hour and then given a final rinse.

Iron Loading. Samples were dipped into a dilute solution (3%) of sulfuric acid and then submerged into an iron liquor at room temperature for an hour. The iron liquor was composed of 83 parts ferrous sulfate, 5 parts sulfuric acid at 66°Be, 13 parts concentrated nitric acid; the mixture was diluted with deionized water to 33°Be. The liquor to sample ratio was approximately 1:12. The samples were then rinsed in deionized water, and simmered in the spent liquor of the original degumming bath for one hour before final rinsing in deionized water. The weight of those samples to be treated with the potassium ferricyanide solution was tallied. A solution containing 10% of that weight in potassium ferricyanide and 10% of that weight of hydrochloric acid was prepared with a liquor ratio of about 1:18. The samples were immersed in the bath, the temperature was raised to 50°C. After that temperature had been maintained for one hour, the samples were removed and rinsed.

Antique Samples

In addition to the modern silks loaded with mineral salts, four samples of shattered silk were donated by the Natural Museum of American History. These samples came from a de-accessioned painted silk flag of the 1860's; the flag had been formally declared beyond repair. Whether or not weighting agents had contributed to the demise of the object was unknown.

EDS Analyses

Patches of fibers were affixed to carbon stubs with carbon paint; coated with about 10 nm carbon (all carbon was ultra-spectroscopically pure) and subjected to energy dispersive x-ray spectrometric analysis in a scanning electron microscope (AMRay 1600T equivalent with attached KeveX EDS). Generally the operating conditions for the collection of EDS data were as follows: 20 or 30 kV, 200 s collection time, 1 to 100 µm² excitation areas. One group of samples (#40-49) was taken as single fibers. No noticeable difference in results was observed. Sample preparation and treatment of data has been described [4,6,7,10,11].

Results

Table 1 lists the chemicals used in treatments and the elements expected in EDS analyses for each treatment. Table 2 gives weight changes in grams observed for treatments including the degumming treatments. Also included are the % changes after treatments. Table 3 summarizes the results of weight changes according to treatments. Table 4 gives qualitative EDS results of the treated silks; the last column of Table 4 gives the actual sample treatments. Table 5 lists average normalized quantitative values obtained by EDS analysis for tin and iron observed in the treatments; the values are listed as % of all elements above atomic no. 10.

Samples #4, 24, 34, and 44, were found to contain only silicon, calcium, and sulfur. These samples were correctly identified as unweighted, degummed (untreated) specimens. Samples from the series #3, 23, 33, 43, 6, 36, and 46, were all found to contain substantial amounts of tin as well as smaller amounts of sodium, phosphorus,

TABLE 1. CHEMICALS USED IN WEIGHTING SILK.

| TREATMENT | CHEMICALS USED | ELEMENTS |
|--|--|------------------------------------|
| | | EXPECTED IN EDS |
| I, I' PINKED, NEUTRALIZED | SnCl_4 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ | S, Sn, P, (Na) |
| II NEUHAUS | SnCl_4 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3$, Na_2SiO_3 | S, Sn, Al, Si, (Na) |
| III, IRON III' LIQUOR | FeSO_4 , H_2SO_4 , HNO_3 , ORVUS | S, Fe, (Na) |
| IV IRON LIQUOR, POTASSIUM FERRI- CYANIDE | FeSO_4 , H_2SO_4 , HNO_3 , ORVUS $\text{K}_3\text{Fe}(\text{CN})_6$, HCl | S, Fe, K, (Na) |
| V NONE | | S, Ca, Si (other tr. elements)* |

*see ref. 11.

sulfur, and silicon. The group of samples that were treated by the modified Neuhaus process, #21, 26, 10, 20, 30, and 40, were found to contain tin, aluminum and very substantial amounts of silicon and sodium, along with phosphorus and sulfur.

Iron weighted samples #7, 27, 37, 47, 9, 29, 39, and 49, were correctly identified. The series that was topped with potassium ferricyanide, #8, 28, 38, and 48, were shown to contain potassium; all other samples did not contain potassium.

For the nineteenth century silks, the results were as follows: The two blue silk samples were found to contain iron and tin, and very small amounts of copper and aluminum. The red silk was observed to have no copper or tin, only a small amount of iron and less aluminum than the blue. The white silk had higher quantities of sulfur and barium than any of the untreated modern samples.

Discussion

Elements were detected on the silk samples in accordance with their presence in weighting treatments. Such congruence, combined with the small sample size, indicates that energy dispersive x-ray spectrometry can be used to assist textile conservators in future analyses of degraded silk.

The "add-ons" or gains in weight for silk are usually determined by comparing the original weight to the final weight as a percentage. The term *rendita* or yield is employed [3]. Because the silk is degummed during processing, "above par" normal refers to a gain in weight over and beyond that lost through degumming, "below par" under the degumming loss, and "at par" restitu-

TABLE 3. WEIGHTING TREATMENTS OF SILK: SUMMARY

| TREATMENT | | TIN TREATMENTS | | | | | | |
|-----------|--|-----------------|-------|------|-------|------|-------|-------|
| I | PINKED AND NEUTRALIZED ONCE | | | | | | | |
| # | | 3 | 23 | 33 | 43 | 6 | 36 | 46 |
| Wt.gn%* | | (8.4 | 10.8 | 11.2 | 11.4 | 11.8 | 14.9 | 15.3) |
| I' | PINKED AND NEUTRALIZED TWICE | | | | | | | |
| # | | | 22 | 32 | 42 | | | |
| Wt.gn% | | | (20.1 | 20.3 | 16.7) | | | |
| II | NEUHAUS | | | | | | | |
| # | | 21 | 26 | 10 | 20 | 30 | 40 | |
| Wt.gn% | | (9.5 | 7.5 | 13.8 | 22.5 | 19.4 | -1.7) | |
| | | IRON TREATMENTS | | | | | | |
| III | TREATED WITH IRON LIQUOR ONCE | | | | | | | |
| # | | 9 | 29 | 39 | 49 | | | |
| Wt.gn% | | (4.3 | 6.4 | 7.7 | 4.2) | | | |
| III' | TREATED WITH IRON LIQUOR TWICE | | | | | | | |
| # | | 7 | 27 | 37 | 47 | | | |
| Wt.gn% | | (3.0 | 4.3 | 6.0 | 1.2) | | | |
| IV | TREATED WITH IRON LIQUOR TWICE AND POTASSIUM FERRICYANIDE | | | | | | | |
| # | | 8 | 28 | 38 | 48 | | | |
| Wt.gn% | | (10.6 | 13.7 | 14.6 | 8.6) | | | |
| V | NO TREATMENT | | | | | | | |
| | | 4 | 24 | 34 | 44 | | | |

Sample number.

* Wt.gn increase based on initial weight of textile.

tion to the weight of the sample before degumming [3]. It should be noted that the samples here were calculated on the basis of their degummed weights, since the series #1-10, 20-29, and 30-39, were all apparently degummed as received. The add-on from the first pinking averaged 12.4%, that for no pinking, 24.6%. However, the average for two pinkings and an aluminum sulfate bath and sodium silicate bath, followed by "soaping" averaged only a gain of 9.2%. The reduction of weight gain may have resulted from high temperature (80°C) of the final "soaping" or from the removal of fillers present in the silk which the modified Neuhaus treatment removed.

It is evident from Tables 2 & 3 that the extent of weighting was small, rarely more than 20% (based on the original undegummed textile), implying that sodium lauryl sulfonate was a poor degumming agent, compared to the soap treatments traditionally used. The process of degumming obviously encourages the subsequent loading of

Weighted Silks

TABLE 2. WEIGHT CHANGE OF SILK SAMPLES (% CHANGE COMPARED TO ORIGINAL WEIGHT).

| Sample No. | Original wt. g (%) | After degumming g (%) | Treatments | | | | | | Final wt. g (%) |
|------------|--------------------|-----------------------|------------------|------------------|------------------|------------------|-----------------|------------------|-------------------|
| | | | I | I' | II | III | III' | IV | |
| 3 | 2.1098 (0) | 2.1268 (0.8) | 2.2880 (8.4) | - | - | - | - | - | 2.2880 (8.4) |
| 4 | 2.3605 (0) | 2.3876 (1.14) | - | - | - | - | - | - | 2.4478 |
| 6 | 2.1900 (0) | 2.2044 (0.66) | 2.4478 (11.8) | - | - | - | - | - | 2.4478 |
| 7 | 2.1962 (0) | 2.2001 (0.2) | - | - | - | 2.2438 (2.2) | 2.2621 (3.0) | - | 2.2621 (3.0) |
| 8 | 2.0583 (0) | 2.0687 (0.5) | - | - | - | 2.2279 (10.7) | - | 2.2755 (10.6) | 2.2755 (10.6) |
| 9 | 2.2748 (0) | 2.2910 (0.7) | - | - | - | 2.3731 (4.3) | - | - | 2.3731 (4.3) |
| 10 | 1.9906 (0) | 1.9939 (0.2) | 2.208 (11.6) | 2.5117 (26.2) | 2.2660 (13.8) | - | - | - | 2.2660 (13.8) |
| 20 | 1.4342 (0) | 1.4384 (0.3) | 1.6390 (14.3) | 1.8905 (31.8) | 1.7566 (22.5) | - | - | - | 1.7566 (22.5) |
| 21 | 1.7298 (0) | 1.8034 (4.3) | 2.0391 (17.9) | - | 1.8934 (9.5) | - | - | - | 1.8934 (9.5) |
| 22 | 1.7762 (0) | 1.7912 (0.8) | 1.9668 (10.7) | 2.1337 (20.1) | - | - | - | - | 2.1337 (20.1) |
| 23 | 1.6834 (0) | 1.6994 (0.95) | 1.8658 (10.8) | - | - | - | - | - | 1.8658 (10.8) |
| 24 | 1.6439 (0) | 1.6593 (0.93) | - | - | - | - | - | - | - |
| 26 | 1.9895 (0) | 2.0117 (1.1) | 2.2865 (14.9) | - | 2.1382 (7.5) | - | - | - | 2.1382 (7.5) |
| 27 | 2.3476 (0) | 2.3660 (0.8) | - | - | - | 2.4310 (2.3) | 2.4481 (4.3) | - | 2.4481 (4.3) |
| 28 | 2.3824 (0) | 2.4110 (1.2) | - | - | - | 2.639 (10.7) | - | 2.7070 (13.7) | 2.7070 (13.7) |
| 29 | 2.2272 (0) | 2.2514 (1.1) | - | - | - | 2.3687 (6.4) | - | - | 2.3687 (6.4) |
| 30 | 2.1495 (0) | 2.2010 (2.4) | 2.4201 (12.6) | 2.7414 (27.5) | 2.5662 (19.4) | - | - | - | 2.4602 (19.4) |
| 32 | 2.0459 (0) | 2.0903 (2.2) | 2.2760 (11.2) | 2.4602 (20.3) | - | - | - | - | 2.4602 (20.3) |
| 33 | 2.0938 (0) | 2.1392 (2.2) | 2.3288 (11.2) | - | - | - | - | - | 2.3288 (11.2) |
| 34 | 2.1665 (0) | 2.2158 (2.3) | - | - | - | - | - | - | - |
| 36 | 2.3094 (0) | 2.3680 (2.5) | 2.6545 (14.9) | - | - | - | - | - | 2.6545 (14.9) |
| 37 | 2.8430 (0) | 2.9144 (2.5) | - | - | - | 2.9839 (5.0) | 3.0125 (6.0) | - | 3.0125 (6.0) |
| 38 | 2.6517 (0) | 2.7154 (2.4) | - | - | - | 2.9344 (10.7) | - | 3.0388 (14.6) | 3.0388 (14.6) |
| 39 | 1.8762 (0) | 1.9227 (2.5) | - | - | - | 2.0210 (7.7) | - | - | 2.0210 (7.7) |
| 40 | 1.6536 (0) | 1.5116 (0) | 1.7371 (14.9) | 1.9785 (30.9) | 1.4856 (-1.7) | - | - | - | 1.4856 (-1.7)* |
| 42 | 1.9906 (0) | 1.6813 (0) | 1.8310 (8.2) | 1.9613 (16.7) | - | - | - | - | 1.9613 (16.7)* |
| 43 | 1.9015 (0) | 1.6540 (0) | 1.8424 (11.4) | - | - | - | - | - | 1.8424 (11.4)* |
| 44 | 2.3590 (0) | 2.1400 (0) | - | - | - | - | - | - | - |
| 46 | 2.1793 (0) | 1.9468 (0) | 2.2439 (15.3) | - | - | - | - | - | 2.2439 (15.3)* |
| 47 | 2.5031 (0) | 2.3190 (0) | - | - | - | 2.3312 (0.5) | 2.3469 (1.2) | - | 2.3469 (1.2)* |
| 48 | 1.8975 (0) | 1.7039 (0) | - | - | - | 1.8767 (10.1) | - | 1.8505 (8.6) | 1.8505 (8.6)* |
| 49 | 2.2598 (0) | 2.1092 (0) | - | - | - | 2.1968 (4.2) | - | - | 2.1968 (4.2)* |

* % change based on wt. after degumming.

TABLE 4. QUALITATIVE EDS RESULTS

| SAMPLE | ELEMENTS | | | | | | | | | | * |
|--|--|----|-----|-----|----|-----|-----|-----|----|--|------|
| | Na | Al | Si | P | S | K | Ca | Fe | Sn | | |
| PLAIN WEAVE DEGUMMED SILK (BOSTON). | | | | | | | | | | | |
| 3 | + | - | (+) | + | + | - | - | - | ++ | | I |
| 4 | - | - | + | - | ++ | - | ++ | - | - | | V |
| 4 | - | - | + | - | ++ | - | ++ | - | - | | V |
| 6 | + | - | (+) | + | + | - | - | - | ++ | | I |
| 7 | - | - | (+) | - | ++ | - | - | ++ | - | | III' |
| 8 | - | - | (+) | - | + | + | - | ++ | - | | IV |
| 9 | - | - | (+) | - | ++ | - | - | ++ | - | | III |
| 10 | + | + | ++ | - | + | - | - | - | ++ | | II |
| SILK HABUTAE (JAPAN). | | | | | | | | | | | |
| 20 | + | + | ++ | - | + | - | - | - | ++ | | II |
| 21 | + | + | ++ | - | + | - | - | - | ++ | | II |
| 22 | + | - | (+) | + | + | - | - | - | ++ | | I' |
| 23 | + | - | (+) | + | + | - | - | (+) | ++ | | I |
| 23 | + | - | (+) | + | + | - | - | (+) | ++ | | I |
| 23 | + | - | (+) | + | + | - | - | - | ++ | | I |
| 24 | - | - | + | - | ++ | - | ++ | - | - | | V |
| 26 | + | + | ++ | - | + | - | - | (+) | ++ | | II |
| 27 | - | - | (+) | (+) | ++ | - | - | ++ | - | | III' |
| 28 | - | - | (+) | - | + | + | - | ++ | - | | IV |
| 29 | - | - | (+) | (+) | ++ | - | - | ++ | - | | III |
| CREPE de CHINE (JAPAN). | | | | | | | | | | | |
| 30 | + | + | ++ | - | + | - | - | - | ++ | | II |
| 32 | + | - | (+) | + | + | - | - | - | ++ | | I' |
| 33 | + | - | (+) | + | + | - | - | - | ++ | | I |
| 34 | + | - | + | - | ++ | - | - | - | - | | V |
| 34 | + | - | + | - | ++ | - | - | - | - | | V |
| 36 | + | - | - | + | + | - | - | - | ++ | | I |
| 37 | - | - | - | - | ++ | - | - | ++ | - | | III' |
| 38 | - | - | (+) | - | + | + | - | ++ | - | | IV |
| 39 | - | - | - | - | ++ | - | - | ++ | - | | III |
| UNDEGUMMED SILK TWO-PLY ORGANZA (SWITZERLAND). | | | | | | | | | | | |
| 40 | + | + | ++ | - | + | - | - | - | ++ | | II |
| 42 | + | - | (+) | + | + | - | - | - | ++ | | I' |
| 43 | + | - | (+) | + | + | - | - | - | ++ | | I |
| 44 | - | - | ++ | - | ++ | + | + | - | - | | V |
| 46 | + | - | + | + | + | - | - | - | ++ | | I |
| 47 | - | - | + | - | ++ | - | - | ++ | - | | III' |
| 48 | - | - | + | - | + | + | - | ++ | - | | IV |
| 49 | - | - | + | - | ++ | (+) | (+) | ++ | - | | III |
| ++ | Present in significant amounts (>30% of elements of atomic no. >11). | | | | | | | | | | |
| + | Present. | | | | | | | | | | |
| - | Absent (not detected). | | | | | | | | | | |
| (+) | Possibly present (<5% of elements of atomic no. >11). | | | | | | | | | | |
| * | Treatment cf. Table 1. | | | | | | | | | | |

the silk. The decrease in weight observed in the modified Neuhaus treatment suggests that the treatment itself produced degumming (i.e., loss of matter) in competition with the weighting that took place. Measurements of weight change after degumming with sodium lauryl sulfonate suggest

TABLE 5. EDS RESULTS OF WEIGHTED SILKS FOR TIN AND IRON.

| TREATMENT | NO. OF SPECIMENS | %* ELEMENT FOUND (AVE) |
|-----------|------------------|------------------------|
| I Sn | 7 | 66 ± 8 |
| I' Sn | 3 | 72 ± 2 |
| II Sn | 6 | 34 ± 5 |
| III Fe | 4 | 65 ± 7 |
| III' Fe | 4 | 66 ± 7 |
| IV Fe | 4 | 71 ± 9 |
| V -- | 4 | --- |

*Of elements greater than atomic no. 10;

Standardless, ZAF corrections via MAGIC V, Normalized to 100% (see ref. 4).

not only that the detergent is a poor agent for degumming but also that it resists removal by aqueous washing [8,12]. There was a small increase in weight as a result of the degumming treatment for the three degummed silks (0.2-2.5%) and a decrease in weight for undegummed samples (7.5-15%). This subject is worthy of further investigation because of the possible long-term effects of wet cleaning textiles; sodium lauryl sulfonate is a commonly used detergent in conservation labs.

Table 4 shows clear distinctions among the treatments. Twice treated (treatments I' and III') compared to once treated (treatments I and III) samples containing either tin or iron could not be distinguished by EDS analysis. Distinction between the two different tin weightings (treatments I, I', and II) and the two different iron weightings (treatments III, III', and IV) is clear from elemental analysis (presence of Al and Si in treatment II; presence of K in treatment IV).

Table 5 shows EDS results for percent tin or percent iron detected for all tin treated and all iron treated samples. Treatment I and I' are clearly distinguishable from treatment II, but III and III' are not distinguishable from IV.

It should be noted that the sulfur that is detected may arise from the degumming treatment and most of the weighting treatments as well as from the sulfur present in the proteinaceous backbone of the silk. The use of sulfur as an internal standard [7,10] in weighting analyses as compared to mordant analyses may require completely different assumptions. In the present study the use of sulfur as an internal standard was not attempted.

More broadly, EDS may detect elements used in associated textile processes. For example, in the series where silk samples were pinked, the auxiliary neutralization with disodium phosphate was apparent since both sodium and phosphorus were observed. This bath could have been replenished with calcium carbonate, or calcium carbonate could have substituted for sodium diphosphate in actual weighting procedures. To explain the

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presence of adventitious elements, the textile conservator and the scientist must be cognizant, then, of auxiliary processes, and alternate sources of elements; calcium could also be in the tap water rinse during the pinking process.

Sometimes EDS results can be used to explain textile processing. The high sulfur content in the antique white silk may be interpreted as resulting from the contemporary method used to bleach silk; skeins were soaped and placed in a chamber with sulfur which was burned to produce anhydrides. The quantity of sulfur was calculated at 4-6% of the yarn weight. A peroxide bath would subsequently oxidize the anhydrides but the sulfur would remain in the fiber [3]. The barium on the antique white silk may come from the use of barium sulfate as a filler, loading agent, or colorant [13].

This study has not addressed the distinction between silk weighting and mordanting, which we intend to examine in the future.

Conclusions

The usefulness of EDS to detect the mineral salts associated with weighted silks has been established. Tin, silicon, iron, potassium, phosphorus, and calcium can all be unequivocally observed with this analytical technique. In addition, EDS can provide indications of other, associated textile processing, both recent and historic.

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Discussion with Reviewers

Reviewer I: Are the "patches of fibers" you examined actually "swatches" of cloth? If so you might have an accumulation of weighting deposit in the spaces of the weave and these might show a higher detectable elemental concentration if analyzed in "spot mode".

Authors: Yes. We were unable to distinguish significant differences between EDS results obtained from fibers or "swatches". We plan to examine weighted fibers in cross-section.

B.A. Wood: One wonders whether significant differences in composition exist between the fiber surface and the interior. Could ion milling techniques be applied to the textiles to permit analysis below the surface? Perhaps concentration gradients in fiber cross-sections could be more readily detected using x-ray microanalysis in a STEM instrument.

Authors: We intend to compare some cross-sections of historic and modern weighted silks.

E. Williams: I would be interested to know the diameter of the electron beam used in the analysis (i.e., the size of the spot on each fiber that was analysed) and whether the samples were scanned to see if the metal content of the fibers was uniform or varied from place to place on the fibers.

Authors: Usually the beam diameter is between 0.1 and 1.0 μm . We have used single fibers and swatches up to 1 mm^2 . Qualitatively replication is good. Occasionally stray elements are detected upon replication.

Reviewer II: Why was tap water used.

Authors: All reagents were made up using deionized water. All final rinses were done with deionized water. Some of the intermediate rinses (see tin treatments) were done with tap water.