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Weighted Silk: Identification, Characterization, and Photodegradation

by

Shawna Lynne Lemiski ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Clothing and Textiles

Department of Human Ecology

Edmonton, Alberta
Spring 1996

University of Alberta

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ABSTRACT

Weighted silk poses a particular challenge to textile conservators. Metallic weighting agents, especially tin and iron, cause rapid degradation of silk leaving many weighted silk artifacts in very fragile condition. To aid in the identification of historic weighted silks, three identification tests were evaluated. A burning test, a flame test for tin, and a spot test for iron were conducted on unknown samples. These results were consistent with those from energy dispersive x-ray analysis. All three tests can be used successfully with little experience. Also, the effects of ultraviolet and visible light were studied using new unweighted and tin weighted silk. The tin weighted silk showed consistently greater degradation than the unweighted silk when exposed to increasing amounts of ultraviolet plus visible light. Under visible light only, the damage to both unweighted and weighted silks was greatly reduced; however, significant changes in the tin weighted silk still occurred.

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CHAPTER ONE: INTRODUCTION

Preventive conservation is concerned with preserving artifacts by protecting them from sources of harm that accelerate the natural rate of deterioration. The sources of harm that must be controlled are many, and include excessive or improper handling or treatment, and environmental elements such as light, humidity, temperature, air pollutants, and pests. General standards for preventive conservation have been developed by many concerned agencies and institutions, and there are specific guidelines for various classes of artifacts. These guidelines are based on our limited knowledge of the deterioration mechanisms of the materials. All materials have different physical and chemical properties that must be considered when planning for their handling, storage, treatment, and display.

Deterioration mechanisms play an important role in storage and treatment decisions. Prediction of degradation patterns is another important aspect of deterioration studies. "Additional attention must be given to establishing the pattern of deterioration in specific materials and conservation problems, what might be called the pathogenesis of their deterioration" (Feller, 1994). By identifying patterns of degradation specific to a particular material, conservators may be able to identify the material, determine the extent of its degradation, and predict the progression of its degradation.

Textile artifacts make up a significant portion of many museum collections. Unfortunately, textiles are organic materials and therefore highly susceptible to decomposition. Storage and display conditions for textiles are necessarily stricter than for other classes of artifacts, such as metals or ceramics. Many textile materials are highly sensitive, and require stringent controls. Archeological textiles, for example, are often in fragile condition after being buried for hundreds of years, then unearthed into an oxygenated atmosphere. Another class of textiles (weighted silks) fits into this special group and will be the focus of this research

Most collections of historic costumes and textiles contain silk artifacts that have badly deteriorated. Many silk garments and textiles from the period of approximately 1870 to 1940 are in more fragile condition than others from earlier periods. These artifacts often contain *weighted silk*. During the late nineteenth and early twentieth centuries, many silk fabrics were subjected to a manufacturing process that added chemicals to increase the weight and volume of the silk. Various chemicals were used over time, and many have proven to be harmful to silk (especially metal compounds such as tin chloride), causing it to deteriorate more quickly than unweighted silks from the same period.

The deterioration of weighted silk results in fabrics that are extremely fragile, and that fracture and "powder" when handled. The damage is characterized by multiple, straight-edged slits or cracks that may follow the grain of the fabric. According to one textile conservator, weighted silks "are characterized by a shattered, brittle, fragmented silk fabric - a state that has occurred apparently independently of such factors as use, storage, or exhibition conditions" (Ballard, 1987, p. 252-3). Unlike unweighted silks, the damage is not restricted to areas of the garment or textile that received concentrated abrasion or soiling, but rather is distributed throughout the entire artifact.

Although such a description of deteriorated, weighted silks may suggest that weighted silks can be identified easily by their condition, this is not always true. There may be weighted silks that do not show this degree of degradation, just as there are likely to be highly degraded unweighted silks with similar characteristics. Consequently, visual assessment alone, even by experienced conservators, is not sufficient to confirm whether a silk has been weighted. Instrumental methods of identifying weighted silk, such as energy dispersive x-ray analysis are costly and are not accessible to all conservators. However, it is important that conservators know whether they are dealing with weighted or unweighted silk. Simple, quick, and inexpensive tests to confirm the presence of weighting agents on silk and that require only minute samples are needed.

Once identified, weighted silk continues to pose challenges to the conservator. Handling of objects made from weighted silk is difficult because of their weakened structure. Furthermore, satisfactory treatments have not been found for either improving the condition or retarding the degradation of weighted silks. Preventive conservation, therefore, is the conservator's main alternative for the present time, as "most often little can be done to correct the results of inherently poor materials and craftsmanship; much can be done, however, to lengthen the life of an object by controlling its environment" (Bachmann & Rushfield, 1992, p. 5). It is clear that special criteria are necessary for the handling, storage, display, and treatment of weighted silk in order to achieve the goals of preventive conservation. These criteria should be based on a sound understanding of how weighted silk reacts to environmental conditions.

While a full understanding of the process of weighted silk degradation requires the study of all physical, chemical and environmental factors for the many types and levels of weighting, this project will be limited to one factor and one type of weighted silk. As will be discussed in the review of the literature, light is commonly considered to be the most harmful of all the environmental factors on weighted silk. Many researchers in the past century have proposed that the severe degradation of weighted silks is due to the effect of light. There are, however, numerous examples of highly degraded, weighted silks that would not have received much light exposure, such as garment linings and facings. This raises the question of whether light is really the main factor affecting weighted silk. Hence, light has been chosen as the primary focus of this research on the degradation of weighted silk. Light also can be easily controlled to minimize its effects on artifacts.

Statement of the Problem

The purpose of this study was to investigate methods for identifying weighted silk, and to study the effect of tin weighting on the photodegradation of silk under visible and ultraviolet light. Visual examination of silk artifacts was used as the primary means by which many conservators have identified weighted silk, but definite patterns of damage due to weighting have not been established. Simple, inexpensive tests to positively identify weighted silk are lacking. Furthermore, the effect that tin weighting has on the degradation of silk with exposure to light is not understood. It cannot be assumed that tin weighted and unweighted silks react to light in the same way.

Objectives

Several objectives were pursued through this study. These objectives may be divided into parts I and II of the research project:

Part I:

1) to test the validity of three simple, non-instrumental techniques for identifying the presence of metallic weighting agents in historic silk artifacts;

2) to characterize the visual appearance of weighted silk degradation and to identify patterns of damage that are common to historic weighted silk artifacts;

Part II:

3) to examine a selected tin weighting procedure for its immediate effect on silk; and

4) to determine quantitatively the different effects of visible and ultraviolet light on selected physical and chemical properties of unweighted and tin weighted silk.

Definition of Key Terms

Degradation: refers to chemical and photochemical damage of the silk fibroin, whereby the protein molecules undergo destruction and formation of bonds that change the chemical formula or structure of the silk (Bresee, 1986). While the degradation is chemical in nature, it may be revealed as changes in physical properties, such as colour change, weakening or embrittlement.

Energy to rupture: (also called work of rupture) is the "energy or work required to break the specimen" (Booth, 1969, p. 361), or the "toughness" of the fabric. It is represented graphically as the area under the load-elongation curve.

Extension at break: is a percentage calculated from *elongation*, which is "the amount of stretch or extension that a fibre, yarn, or fabric will accept" (Hudson, Clapp, & Kness, 1993, p. 380) before it breaks. Breaking extension is calculated as shown in Equation 1.

$$\text{extension at break } (\%) = \frac{\text{change in length } (\Delta L)}{\text{original length } (L_o)} \times 100 \qquad (1)$$

Flexural rigidity: is a measure of the stiffness of a fabric, where a 10 % change represents a barely noticeable change in the stiffness of the fabric (ASTM test method D1388-64). Flexural rigidity is calculated as follows:

$$\text{flexural rigidity, } G \text{ (mg-cm)} = W \times (O/2)^3 = W \times c^3 \qquad (2)$$

where

W = weight per unit area (mg/cm^2),

O = length of overhang as measured in centimetres (cm), and

c = bending length in centimetre (cm), which = $O/2$

Habutae: (also *habutai or habutaye*), is a lightweight, closely woven plain weave silk fabric that is slightly irregular due to hand reeled weft yarns; habutae is usually woven in the gum, then the fabric is degummed as a piece (Kolander, 1985).

Scroop: Hudson, et al. (1993) define scroop as "the characteristic rustling or whispering sound of silk as it moves". This feature can be enhanced by weighting of silk, or produced through other chemical treatments.

Silk: for the purposes of this research will refer to degummed silk fibroin fibres cultivated from the *Bombyx mori* moth larvae. Silk in its unadulterated form consists of two components:

Fibroin: the fibrous protein that is extruded by the silkworm as two filaments (brins) which are bound together by the sericin, and constitutes approximately 75% of the weight of the silk cocoon (Robson, 1985).

Sericin: the nonfibrous protein gum that is extruded with the fibroin and binds the two brins together into a single thread (bave), and accounts for only about 25% of the weight of the cocoon (Robson, 1985). The amino acid compositions of the fibroin and sericin are quite different, as are the properties of the two substances.

Stiffness: is the resistance of a fabric to bending (ASTM test method D1388-64), calculated as *flexural rigidity* (see above).

Tensile (breaking) strength: is the "maximum tensile force observed during a test in which the specimen is stretched until it breaks " (CAN/CGSB-4.2 No. 9.1, p. 2).

Weighting: has been defined as "the process of adding weight or body to fabric or yarn by chemical or mechanical addition of various materials" (Tortora & Merkel, 1996). More specifically, ***weighted silk*** is a silk that has been treated with metal salts to increase its weight and body.

CHAPTER TWO: REVIEW OF THE LITERATURE

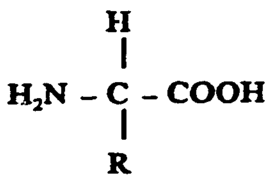
A review of the literature on silk structure, causes of silk degradation, and the weighting of silk provided a strong theoretical base for the study. This review explores in detail the theoretical background that guided the investigation. First, the chemical structure of silk (especially fibroin) are examined. Then, factors that contribute to the degradation of unweighted and weighted silk are studied, including chemical agents as well as environmental conditions. Tests that have been and can be used to assess the degradation of silk are discussed. The section on silk weighting covers the history of weighting, as well as the various agents used over time, and methods of application.

Silk Structure

Silk as spun by the *Bombyx mori* larva is composed of two filaments of fibroin (called brin) held together by a gum-like sericin coating (Denny, 1980). Becker, Willman, & Tuross (1995) note that "a fundamental distinction between fibroin and sericin is the composition of amino acids that make up these two proteins"

Chemical Composition of Fibroin

As a protein fibre, the molecular composition of silk fibroin is similar to that of other proteins. "Proteins consist of a large number of units linked together by amide (—CO—NH—) groups" (McIntyre, 1971, p. 31). The basic units of a protein are α-amino acids which are linked together by peptide bonds:



$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-COOH$$

α-amino acid

$$-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle H}{\overset{|}{N}}-$$

peptide bond

This peptide link results from the elimination of water between the amino group on one amino acid and the carboxyl group on another.

The polypeptide chains formed by the condensation of many amino acids have a variety of side groups (R) along the length of the chain. In silk fibroin, there are approximately sixteen α-amino acids with different side groups linked together into a polymer (Otterburn, 1977). Table 1 shows the distribution of α-amino acids in fibroin and sericin. The three amino acids that make up the majority (80-85%) of the polymer are glycine (–H), alanine ($-CH_3$), and serine ($-CH_2OH$) (Robson, 1985; Trotman, 1970; Truter, 1973).

Several researchers have tried to determine the order of the amino acids in the fibroin molecule. Otterburn (1977) found that the majority of the molecule is composed of crystalline regions with the following sequence of amino acids:

Gly-Ala-Gly-Ala-Gly-[Ser-Gly-(Ala-Gly)$_n$]$_8$-Ser-Gly-Ala-Ala-Gly-Tyr

where n = 2 (p. 60). Because the glycine, alanine, and serine side chains are relatively small, fibroin molecules can pack closely together to form a fibre that is highly crystalline (approximately 60 %) with few areas of disorder (McIntyre, 1971; Robson, 1985). A smaller proportion of the molecule contains groups of four and eight peptide groups linked together, including glycine, alanine, tyrosine and valine (Otterburn, 1977). Tyrosine and valine are bulkier than glycine, alanine, and serine, and therefore form areas of disorder as the chains cannot pack together closely. A small fraction of fibroin is truly amorphous, having amino acids with large side groups such as arginine, lysine, histidine, and tryptophan (Otterburn; Truter, 1973).

Table 1
Amino Acid Composition (Residues/1000) of *Bombyx mori* Silk.

Amino Acid	Fibroin	Sericin
Glycine	445	147
Alanine	293	43
Serine	121	373
Tyrosine	52	26
Valine	22	36
Aspartic acid	13	148
Glutamic acid	10	34
Threonine	9	87
Isoleucine	7	7
Phenylalanine	6	3
Leucine	5	14
Arginine	5	36
Lysine	3	24
Proline	3	7
Cystine (half)	2	5
Histidine	2	12
Tryptophan	2	
Methionine	1	
NH_3 or amide		86

(Adapted from Lucas and Rudall, 1968, p. 484, 494).

The packed fibroin chains form a parallel β-pleated sheet arrangement with hydrogen bonding holding adjacent sheets together (Robson). Figure 1 shows this structure of pleated sheets held together by hydrogen bonds. The amorphous regions are not as well ordered, and are the parts of the fibre that are accessible to water and other chemicals, including weighting agents (Truter). Crighton (1993) states that the *voids* are the sites where hydrolysis occurs when the fibre is subjected to acid or alkali, and that tin is likely absorbed in those areas during weighting. These *voids* are more commonly referred to as "free volume" (Rodriguez, 1989).

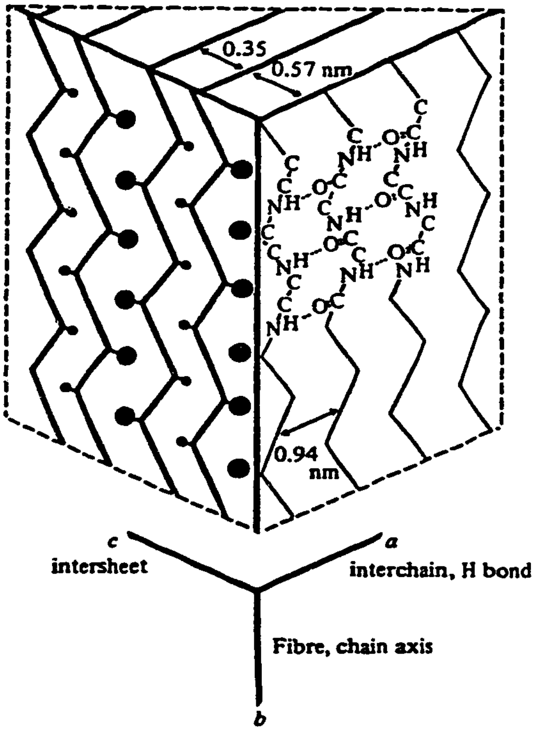


Figure 1. Parallel β-pleated conformation of *Bombyx mori* silk fibroin (Denny, 1980, p. 258, after Marsh et al., 1955, "An investigation of the structure of silk fibroin", *Biochimica et Biophysica Acta, 16,* p. 13-18). Reprinted with permission.

Chemical Composition of Sericin

Sericin, like fibroin, is a protein composed of a series of amino acids held together by peptide bonds. In sericin, the most abundant amino groups are serine, aspartic acid, glycine, and threonine (Otterburn, 1977). Aspartic acid and threonine have large side groups, preventing the protein chains from packing close together, creating a more amorphous polymer than fibroin. Thus, rather than forming a fibre, sericin is a yellowish, gum-like substance that coats the fibroin and makes it feel harsh (Hartsuch, 1950). The sericin gum is easily removed by hot soapy solutions and weak acids and bases (Hartsuch).

Degradation of Silk

According to Crighton (1993), "[s]ilk, of all the natural animal (protein) fibres, is that which is most sensitive to degradation" (p. 96). Many agents and factors are known to cause damage to silk fibres and fabrics. The effects of the damage may be noticeable immediately, or only when these effects are combined with natural aging. Agents and factors which cause damage to silk may be chemical or environmental conditions, or a combination of both. These elements will be explored as they relate to the degradation of tin weighted silk.

Effects of Chemical Agents on Fibroin

Silk is susceptible to damage from both acids and bases (Hudson et al., 1993; Mauersberger, 1947; McIntyre, 1971). The harm caused by each to the silk fibres is different but both are destructive. Silk is subjected to acids and alkalies in many forms during its normal manufacturing, finishing, and use. Weighting is a finishing process which exposes silk to various chemicals.

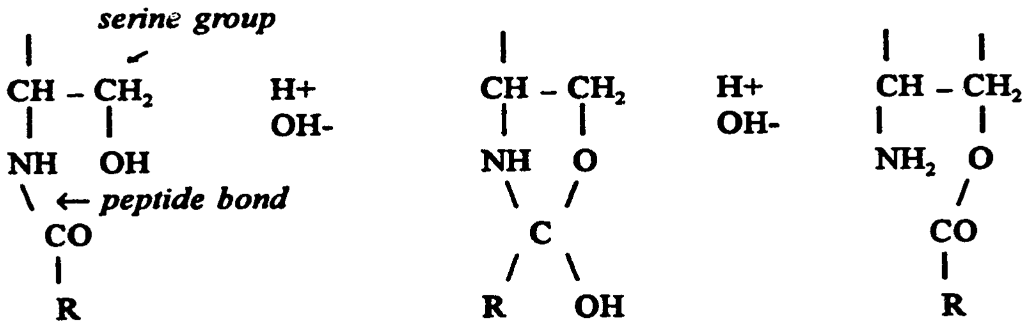
Hydrolysis by Acids

Organic acids do not damage silk. However, concentrated mineral acids attack silk, and can dissolve the fibres (Hartsuch, 1950; Peters, 1963; Robson, 1983). The attack is a hydrolysis reaction (3), and tends to occur randomly in the amorphous regions of the fibre, causing breakage of the peptide bonds in the main chain of the protein molecule (Robson). Initially, this causes weakening of the chain, but if the molecule segments become too short the fibre eventually dissolves.

Hydrolysis of peptide bond by aqueous acids or bases:

---NH — CO--- + water + strong acid or hot base → ---NH_2 + HOOC--- (3)

Another important reaction in fibroin caused by concentrated acids is the N → O peptidyl or acyl shift (Otterburn, 1977; Robson,1985). Equation 4 shows peptide bonds along the main chain being broken and the bond shifting to an adjacent amino acid side group.



(4)

Acid may be encountered during weighting. The stannic chloride in the tin-phosphate-silicate weighting procedure can be converted into hydrochloric acid (HCl) when the tin is deposited into the fibres as tin hydroxide [$Sn(OH)_4$] (Howitt, 1946). Hydrochloric acid in moderate concentrations is known to degrade silk (Hudson et al., 1993), while in high concentrations it will dissolve the fibres (Mauersberger, 1947). Mauersberger further states that "chlorine destroys silk" and that "strong solutions of stannic chloride (70° Tw.) will dissolve silk" (p. 724). According to Trotman and Bell (1935), "Silk weighted with tin chloride frequently develops tenderness, partly owing to unremoved hydrochloric acid but chiefly due to the presence of chlorides" (p. 142T).

Other sources of acid may be cleaning solutions. In a study on the effect of dry cleaning on silk, Clair and Mack (1929) found that acidic spotting agents caused a decrease in the breaking strength of both unweighted and weighted silks. Certain acidic stains, such as tannin, ink, and perspiration also caused lower breaking strengths if left in the silk for three weeks without cleaning (Clair & Mack).

Hydrolysis by Alkalies

Bases are also harmful to silk and cause hydrolysis, although the attack is somewhat different from that of acids. Alkalies tend to initiate hydrolysis sequentially from the end of the protein chain rather than randomly at amorphous regions (Crighton, 1993; Otterburn, 1977; Peters, 1963; Robson, 1985). This suggests that the effect of hydrolysis by acid is greater than hydrolysis by a base because the breakages due to acids are distributed along the length of the chain (Peters) and therefore shorten the overall length of the chain more quickly. However, in a study comparing the effects of acids and alkalies on weighted silks, Ross, Johnson, and Edgar (1936) found that alkalies caused more damage than did acids to samples of silk that was weighted by five different methods, including tin weighting.

Alkalies are present in the tin-phosphate-silicate weighting process. The sodium phosphate and sodium silicate baths can produce alkaline conditions that are dangerous for silk. In fact, the alkalinity of the sodium phosphate bath must be maintained at a sufficient level in order for successful weighting to be achieved (Carboni, 1952). The foam method of tin weighting was developed as a precaution to prevent the phosphate and silicate baths from becoming too basic (Howitt, 1946). Whether it is an alkali or an acid that may attack the silk, the central concern is pH. Peters (1963) and Robson (1985) agree that the degree of hydrolysis depends upon pH, having the least reaction between pH 4 to 8.

Oxidation

In oxidative degradation, groups containing oxygen are formed along or at the end of the polymer chains (Kamiya & Niki, 1978). According to Otterburn (1977), "oxidation of silk fibroin can take place at any of three sites: side chains, N-terminal residues, and the polypeptide backbone" (p.71). Oxidation can be initiated by such chemical agents as hydrogen peroxide and potassium permanganate, or simply by the combination of atmospheric oxygen and radiation as will be discussed in a subsequent section on the effects of light. In fact, "all organic compounds are susceptible to attack by molecular oxygen" (Kamiya & Niki, 1978, p. 80). As with chemical agents, the amorphous regions of the fibroin molecule are most accessible to oxygen, and therefore oxidation occurs first and more rapidly in those regions than in the crystalline regions (Kamiya & Niki, 1978).

Kamiya and Niki (1978) discuss factors that influence the rate of oxidation of polymers. They indicate that oxidation occurs more rapidly when double bonds are present, and that oxidation of double bonded polymers often leads to crosslinking. Furthermore, the more branching that is present in a molecule, the faster is the oxidation since hydrogens on tertiary carbons are more readily oxidized than primary and secondary hydrogens (Kamiya & Niki). For the fibroin molecule, this means that the numerous amino acid side groups and the presence of double bonds in various side groups make the fibroin susceptible to rapid oxidation.

Oxidation of fibroin appears to have two main results: colour change and crosslinking. The colour change comes about as the side groups are altered by the addition of oxygen especially at the tyrosine residues (Otterburn, 1977). The exact nature of the groups formed is not known. The most familiar discolouration of silk due to oxidation is yellowing.

Crosslinking also is believed to occur mainly at the tyrosine residues. Crosslinked fibroin becomes stiffer and eventually more brittle as the oxidation advances. This increased stiffness also may be due to chains in the amorphous regions of the molecule being broken by oxidation, causing them to rearrange and crystallize in a new configuration (Kamiya & Niki, 1978).

Catalysis by Metal Compounds

The effects of metal compounds on silk has been noted by several researchers. Mauersberger (1947) indicates that the presence of metal complexes weakens a fabric, a condition noted when metal compounds are used as mordants. The degradative effects seem to increase with exposure to sunlight (Howitt, 1946; Mauersberger) suggesting that the presence of the metals photosensitizes the silk. Kamiya and Niki (1978) explain that a metal complex initiates a "chain of auto-oxidation due to both the activation of the oxygen molecule and the decomposition of hydroperoxide" (p. 118). Hydroperoxide [R-O-O-H] is a primary product resulting from oxidation of simple hydrocarbons. Metallic impurities reduce the period of initiation and then accelerate the rate of the oxidative reactions (Kamiya & Niki). If the metal salts are acting as sensitizers, then the accelerated oxidation will become more severe with higher concentrations of the sensitizers (Schnabel & Kiwi, 1978).

Metal complexes may also cause damage by mechanical means. Gandswindt (1921) describes how "the increase in weight is accompanied by an increase in volume" (p. 19) which lowers its mechanical strength.

Environmental Factors

Light, heat, moisture, and air quality have all been identified as environmental conditions that contribute to the deterioration of textiles. Photochemical and thermal degradation produce changes in the mechanical properties of silk that are irreversible.

Light

Light is a form of energy and is composed of photons that travel as waves of varying wavelengths. In its truest definition, light is only that part of the radiation spectrum that we can see, the wavelengths between 400 and 750 nm (Thomson, 1986). Between 100 and 400 nm is the ultraviolet region, and above 750 nm is infrared radiation. Sunlight and fluorescent lamps include wavelengths below 400 nm in the ultraviolet region. (Ultraviolet filters can be used to remove those wavelengths from the light being received).

Degradation of a material requires energy, and light is a readily available form of energy that can cause photochemical deterioration (Macleod, 1978). In order for damage to occur, the material must absorb photons. Damage caused by light is related to the wavelength of the radiation, with shorter wavelengths having more energy and a greater effect (Grattan, 1978; Thomson, 1986; Zeronian, 1975). Therefore, ultraviolet radiation (100-400 nm) is more harmful than visible light. Furthermore, because radiation usually cannot penetrate below the surface of a material, only the surface is damaged. Photochemical damage often appears as fading, colour change, cracking, embrittlement, and loss of strength.

Due to their chemical composition, organic materials, including textiles, are highly susceptible to damage from radiation. Giles and McKay (1963) found that "there is no threshold light intensity below which fading does not occur" (p. 5). This same conclusion was drawn later by Crews (1987), who added that "there is no known light source that does not cause some degree of color loss" (p. 21). Silk, as one of the most sensitive natural fibres to all kinds of deterioration, is accordingly the most sensitive to light damage. Becker and Tuross (1992; 1994) indicate that exposure to light is often the primary cause of silk degradation.

While the literature indicates that the process of photochemical degradation is not fully understood, it is generally believed that light causes photochemical degradation of silk fabrics by an oxidation reaction, that often results in a noticeable yellowing of the fabric (Becker & Tuross; Harris, 1934). Ultraviolet radiation initiates photochemical reactions involving oxygen, and these reactions can cause cleavage of the polypeptide chains, crosslinking, formation of unsaturated groups, and cleavage of side groups that can result in generation of volatile products (Schnabel & Kiwi, 1978). When organic polymers absorb ultraviolet radiation in an oxygenated environment, the chemical changes that occur cause discolouration and deterioration of physical properties.

The acidity or alkalinity of silk appears to have an influence on the rate and extent of photochemical degradation. Das (1992) found silk to be most stable to light at pH 10, with its stability decreasing dramatically when the pH is above eleven or below three.

In studying the effects of light on natural protein fibres, Shäfer, Föhles, and Höcker (1993) found that there is indeed yellowing of *Bombyx mori* silk upon irradiation. Under microscopic examination, these researchers noted that the light damages the fibre's surface first. Similarly, Kuruppillai et al. (1986) investigated the effects of heat and light on unweighted silk fabrics. By artificially aging silk samples separately in heat and light, they found that the effects of heat and light were similar. Other researchers believe that light is the dominant cause of degradation (Becker & Tuross, 1994).

Robson (1985) suggests that "the sensitivity of silk to light is greatly increased by metallic weighting", and that this "sensitivity is due to the catalytic action of metallic salts used in the process" (p. 689). Roberts and Mack (1936) studied the effects of light on unweighted and tin weighted silk and found that weighted silk exhibited greater loss in strength than unweighted silk after exposure to both sunlight and an artificial light source. The loss of strength increased as time of exposure became longer. A subsequent study showed that both unweighted and tin weighted silks lost less strength when stored in the dark than in either form of light (D'Olier & Mack, 1936). This study also showed that weighted silk lost more strength than unweighted silk when both were stored in the dark, which suggests that light is not the only operative factor attacking weighted silk.

Bruner and Goehring (1935) also studied the effects of light on unweighted and weighted silk fabrics. They found that unweighted, lead weighted, and tin weighted silks all showed the greatest deterioration after exposure to the full spectrum of radiation, as measured by a decrease in breaking strength. Lead weighted silk consistently exhibited greater loss in strength than the other silks. Finally, it was found that the rate of deterioration increased as exposure time increased beyond seventy-two hours (Bruner & Goehring).

A more recent study found that silk fibroin irradiated with UV light lost strength most rapidly during the first ten hours of exposure (Tsukada & Hirabayashi, 1980). They attribute this loss of strength to a decrease in the orientation of the fibroin molecules within the fibre which creates a more disordered, and therefore weaker, structure.

Heat

High temperatures cause thermal degradation that can be equally as damaging as photochemical degradation. Gradual thermal decomposition is marked by reaction of side chains, fission of main peptide bonds, and formation of radicals (Kambe, 1978). Like ultraviolet radiation, heat accelerates oxidation reactions in the presence of oxygen.

The action of heat on silk is not as widely studied as that of light, although Kuruppillai et al. (1986) researched the deterioration of silk in both heat and light. Their results showed that heat does cause a loss of strength in silk fabrics. Their study used only unweighted silks, and so no inference can be drawn about any difference in the effect of heat on weighted silks as compared to unweighted silk fabrics.

One study found that the dry heat (95 °C) used to condition fabrics to a constant mass produced yellowing of weighted silk (Southard & Tague, 1932). This led to the conclusion that exposure of silk weighted with tin to 25% above par and 40% above par to such temperatures causes partial oxidation of the weighted fibroin. Unweighted samples exposed to the same drying conditions did not show any yellowing, even at slightly higher temperatures (Southard & Tague).

Humidity

There is little research on the effects of moisture, either alone or in combination with other factors, on silk or weighted silk. The only study that could be found examined humidity as a factor in the photochemical degradation of silk among other fibres. The researcher states that "the effect of humidity on the rate of degradation is small, there being only slightly less loss in strength in dry than in humid air" (Egerton, 1948, p. 663).

Degradation, especially oxidative degradation, is quickened by the presence of moisture (Feller, 1994). In studying the degradation of various fibres, Giles and McKay (1963) also found that moisture caused an increase in the rate of photodegradation over the rate when no moisture was present.

Air

Air is not frequently studied as an environmental condition that has an influence on silk degradation even though photo-oxidation of silk requires the presence of oxygen. However, Roberts and Mack (1936) examined the degradation of unweighted and tin weighted silk fabrics in the absence of both air and light. Both unweighted and tin weighted silks stored in the dark in an evacuated tube had a slightly higher breaking strength after a period of time than the samples stored in the dark in air (Roberts & Mack). The difference in the breaking strengths, however, are very small and may indicate that the time period was not sufficiently long to produce noticeable changes. The results of this study could have been more useful if samples of silk had also been exposed to light in the absence of air.

Many chemical agents and environmental factors have been discussed as they contribute to the degradation of silk, and especially of tin weighted silk. It is important to remember that none of these elements acts in isolation. Fibre degradation is the cumulative result of natural aging and exposure to various harmful substances and conditions.

Evaluation of Changes in Physical Properties of Silk

In order to assess the degradation of any textile, there must be well defined, systematic tests with which to measure the identified variables of degradation. Previous researchers who have studied silk have used assorted combinations of existing tests for measuring components of the deterioration of the silk. Surface morphology, tensile strength, and elongation have been used most often as practical tools for estimating the degradation of silk fabrics.

Scanning Electron Microscopy

The surface morphology of fibres can be examined with the use of a simple light microscope. However, for reliable and minute inspection of fibre features and damage, the scanning electron microscope (SEM) is more powerful, having superior depth of field at high magnifications (Needles, 1981). Researchers at the Getty Conservation Institute have found that SEM allows for higher resolution images and the advantage of compatibility with x-ray analytical methods (Stulik & Doehne, 1991). Small samples can be analyzed, and SEM is particularly useful for examining mechanical damage, such as fibre fracture (Zeronian, Alger, Ellison, & Al-Khayatt, 1986; Bresee & Goodyear, 1986).

Researchers studying the degradation of silk have used SEM to examine the appearance of fibres (Becker & Tuross, 1994; Miller & Reagan, 1989). It has been found that "SEM can be a valuable tool to assist in the diagnosis of the cause of fabric wear or fibre failure by mechanical stress" (Zeronian et al, 1986, p. 91). Examining the surface appearance of fibres before and after weighting may be useful for studying the effects of a particular tin weighting treatment on the morphology of silk fibres. The effects of light aging on the fibre's surface structure may also be observed.

Bresee and Goodyear (1986) studied the shape of naturally occurring and artificially induced fibre fractures in silk. They classified the types of fractures into ten categories based on shape and associated cause of damage which were previously established by Hearle, Lomas, Cooke, and Duerdon (1989).

Tensile Strength, Extension at Break and Energy to Rupture

Tensile strength, or breaking strength, defined as the "maximum tensile force observed during a test in which the specimen is stretched until it breaks"

(CAN/CGSB-4.2 No. 9.1, p. 2) is a common measurement in research on fibre, yarn and fabric degradation. It is especially suitable for indicating the loss of strength of a fabric after treatment or aging, when "before and after" samples are available. Weighted silk frequently has been subjected to tensile strength tests as an indication of fibre weakness. Halvorson (1991) and Becker, Hersh and Tucker (1989) have used tensile strength measurements as indicators of silk degradation.

Many of the early studies (D'Olier and Mack, 1936; Ross et al., 1936) use breaking strength as the primary test for degradation. This reliance on tensile strength may be due to the fact that instruments for measuring other properties were not readily available. However, modern researchers who can choose from a wide variety of tests to assess fibre degradation have not abandoned breaking strength as a useful measure of silk damage (Hersh, Tucker, & Becker, 1989; Kuruppillai et al., 1986; Miller & Reagan, 1989). Rather, these researchers use tensile strength in combination with other measurements to form a more rounded conception of degradation. A decrease in extension at break, for example, may suggest that cross linking has occurred. Extension at break (%) is calculated as 100(change in length at break/original length).

Energy to rupture, or work of rupture, is a measure of the "toughness" of a fabric and is calculated from the area under the curve on the breaking strength graph. It combines the properties of tensile strength and elongation and might indicate whether the weighting finish and light exposure caused changes in the toughness of the silk. These values were used by Halvorson (1991) as an indication of the effects of parylene-C on the tensile properties of silk.

Evaluation of Changes in Chemical Properties of Silk

While physical tests reveal much about micro and macro changes in the properties of silk, chemical tests can indicate what changes have occurred on the molecular level. Sensitive chemical analysis may show chain breaks and changes in bonding of the fibroin polymer and help to explain deterioration. After all, changes in physical properties are the manifestation of chemical changes which result in degradation.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a highly sophisticated tool for chemical analysis of polymers. This technique can reveal the presence and precise concentration of impurities or other foreign matter on polymers, as well as showing the "effects of irradiation, deformation, fatiguing, and weathering" (Griffiths & de Haseth, 1986, p. 426). The main principle of FTIR is that "infra-red radiation interacts with an organic compound, [and] certain frequencies of energy are absorbed while others are transmitted or reflected" (Greaves, 1992, p.11). The spectra of absorption and reflection are determined by the bonds and chemical groups of the compound, and can be measured instrumentally to produce unique spectra for each compound. By comparing the spectra of an unknown sample to the series of standards, the unknown sample can be identified.

Recent studies have shown that this instrumental technique is useful in conservation science for identifying specimens as well as determining relative degrees of degradation. Because only a tiny sample is required, FTIR is especially appropriate in the examination of historic artifacts which demand the least interference with the physical object as possible. In fact, FTIR has been used in conservation studies as a tool for identifying early semi-synthetic and synthetic plastics (Shearer & Doyal, 1991). Cardamone (1989) states that several variations on FTIR have been used to examine textiles, including transmittance FTIR and attenuated and multiple reflectance FTIR. Attenuated total reflectance FTIR may be the most promising technique for conservation scientists, since it can be used "to analyze samples with rough surfaces such as wood, paper, and polymers" (Hon, 1986, p. 353). Textiles, due to their construction, are rarely perfectly smooth, making other types of FTIR which require a sample of uniform thickness difficult to use successfully.

The use of FTIR can be applied to silk degradation studies. If the spectra for a historic silk sample showed a higher concentration of terminal amino groups than would be present in new silk, this would indicate that chemical changes had taken place in the silk molecules resulting in more end groups. An increase in the number of terminal amino groups would mean that the fibroin chains have been broken into shorter segments by some degradative process. However, quantitative results may be difficult to achieve.

Weighting of Silk

Nomenclature of Weighted Silk

The amount of weighting in a silk fabric can be expressed in many ways. The first way uses the weight of the silk before degumming ("par") as a comparison. Silk could be weighted *to par*, meaning only the weight lost in degumming is replaced; *below par*, where less weight is added than was lost; or *above par*, where weight was added in excess of the weight lost in degumming. The weighting is usually given as a percentage above or below par; for example, if one kilogram of raw silk is degummed to produce 750 grams of fibroin, there was a twenty-five percent loss of weight due to removal of the sericin. If that silk is weighted back up to one kilogram, it is weighted *to par*. If the weighting adds 500 grams, to make the silk weigh 1250 grams, it is weighted to 25% *above par*.

The second method of indicating the amount of weighting simply uses a percentage based on the weight of the fabric (Hartsuch, 1950). If a quantity of weighted silk is measured at one kilogram and through testing the weight of the pure silk is determined to be 500 grams, the remaining 500 grams represents the weighting materials. This silk would be said to have 50% weighting, since only 50% of the fabric is actually silk.

A third way of expressing the amount of weighting achieved in a silk fabric may be confused with the second. When the original mass of the degummed silk is known, weighting can be expressed as a percent increase in weight based on the degummed weight. If 100 grams of degummed silk is weighted so that it weighs 150 grams, a fifty percent increase in weight was achieved, and the silk is said to be weighted 50%. This is the terminology used to identify the amount of weighting applied to the new silk in this research since the mass before weighting was known.

Another way of expressing the amount of weighting is less common in the literature but seems to have been used in the industry. Hartsuch (1950) provides an example of how weighting can be expressed on the basis of ounces per pound of raw silk. This method is based on the assumption that there are 12.4 ounces of pure silk fibroin in one pound (16 ounces) of raw silk. (There would be 3.6 ounces of sericin boiled off in degumming). If the 12.4 ounces of silk fibroin are weighted to 31 ounces, fifteen ounces of weighting was added *above* the original one pound, or 18.6 ounces total. The silk is identified by this new weight, with a 2 ounce allowance. Thus, the silk in this example would be called 30/32 oz. silk, and sold as such.

Similarly, Chittick (1913) simply uses the weight of the weighted silk, in ounces, as the name for the silk, and assumes that the unweighted, degummed silk was approximately 12 ounces. Thus, a 26 ounce weighted silk would contain 12 ounces of silk and fourteen ounces of weighting materials.

History of Silk Weighting

Researchers believe that weighting, or *loading*, of silk has been in practice for hundreds of years, but reached the peak of its popularity in the late nineteenth and early twentieth centuries (Ballard et al., 1986; Becker, Hersh, Tucker, & Waltner, 1987; Hersh et al., 1989; Miller & Reagan, 1989; Scott, 1931a; Tyler, 1949). There is no consensus on the actual dates of various methods and uses of weighting. Marsh (1957) states that weighting by metal salts and tanning agents was known early on, but that silk weighting became commercially important around 1850. Many other researchers indicate that the extensive use of weighting developed in the 1880s and

1890s. The literature does not indicate a date which corresponds to the end of the weighting industry. Marsh (1957) describes the practice used "nowadays" (p. 305), which suggests that some form of silk weighting was practiced throughout the 1950s.

How the potential to weight silk was discovered is not known, but it has been suggested that manufacturers developed weighting as a means of fraudulently increasing the weight and volume of the silk. This meant that a fabric containing less silk could be sold at the same price but with less cost to the manufacturer, thereby increasing profits (Becker et al., 1987; Carboni, 1952). The manufacturers and dyers took advantage of this opportunity: "By artificially increasing the weight of the silk entrusted to them by others the dyers were able to cover the deficiency and to offer silk for sale at prices which counteracted the higher scale of wages paid in London" (Warner, 1920, p. 182-3). This practice was soon found to be deceptive and was subsequently legislated (Scott, 1931a; Tyler, 1949).

Another reason is more commonly cited in the literature as the main motivation for silk weighting. Removal of the sericin gum decreases the weight of silk by up to twenty-five percent (Becker et al., 1987; Bogle, 1979). When the sericin is removed the silk has less body, so artificial weighting has been used historically to replace the weight lost during the degumming process and to enhance the draping qualities of the silk (Tyler, 1949). King (1985) describes the "sound of stiff, rustling petticoats and sharply creased ruffles" (p. 173) which were the fashion of the day and could be achieved more easily with weighted rather than unweighted silk. These favourable results of weighting led the industry to develop rapidly, as:

> ...The practice of weighting the silk having once begun it would be naturally used to a greater and greater extent, being limited only by the power of the material to absorb it, the ability of the dyer to apply it, or the limitations of the strength of the fibre (Chittick, 1913, p. 33).

Strength was a limitation for both manufacturers and consumers. The poor durability of some weighted silk fabrics was noticed from the beginning. Legislation was enacted in London in 1606 restricting the amount of weighting allowed in an attempt to regulate the quality of silk for consumers (Tyler, 1949). Yet, three hundred years later, weighting methods used in the early twentieth century were still suspected of weakening the silk.

In 1932, following investigation by the Silk Association of America, the Federal Trade Commission demanded that the amount of weighting had to be specified on the label if the increase in mass after weighting was more than 10 % for all most colours. If the added weighting was less than ten per cent, the silk could be labelled *pure dye silk*. Black silk could have up to a 15 % mass increase before it had to be labelled as weighted. (Mauersberger, 1947).

Chittick (1913) discussed recommended levels of weighting for different types of silk. At that time, weighting of the woven fabric was still developing as the industry up to that point had focused on weighting silk in the yarn form. Thus, many fabrics had warp and filling yarns weighted to different amounts, with the filling usually being more heavily weighted. For coloured tin weighted fabrics of fair quality, Chittick advises that it is not safe to exceed 18 ounces for the warp yarns and 24 ounces for the filling yarn (or an average of 21 ounces). These measurements are based on the assumption that one pound of silk (454 grams) loses 25% of its weight in degumming, to weigh approximately 12 ounces. An 18 ounce weighted silk, then has twelve ounces of silk and six ounces of weighting, so the increase in weight due to weighting is fifty percent. For the recommended average of 21 ounce silk, the increase in weight would be sixty-four percent. (Methods of distinguishing the amount of weighting in a silk are discussed in a previous section of this chapter).

Weighting Agents

As mentioned, many substances have been used as weighting agents since the inception of weighting. The materials employed range from common household products to complex combinations of industrially prepared chemicals. Each method was tested and/or adapted to meet the needs of the industry, although some were almost immediately recognized as undesirable. The various developments in the use of weighting agents may have arisen since the chemical mechanism of weighting was not well understood ("Discussion at Clothworkers' Hall", 1925). Furthermore, weighting processes were usually patented, so new techniques could procure patent rights, or at the least could circumvent existing patents.

Organic Weighting Agents

Sugars, waxes, oils, and glue were some of the generic substances that were tried as weighting agents (Howitt, 1946; Robson, 1985; Scott, 1931a). Robson mentions that such organic compounds were used to decrease the cost of the weighting process as well as to reduce the damaging effects associated with metal compounds. However, none of these products was found to be satisfactory nor became widely used since any subsequent cleaning procedures removed most of the added weight. Sugar, for example, could only produce a small increase in weight (not more than 10%) because of silk's low affinity for sugar and was of little commercial benefit (Gandswindt, 1921). Traditionally, sugar was used to weight only light coloured silks, the type of sugar used depending on the intended final colour. Loading with sugar was effected after dyeing since the presence of the sugar inhibited the swelling of the fibres and absorption of dyes (Gandswindt).

A weighting agent that was used to some degree for commercial weighting was tannin, or tannic acid. Tannin is readily absorbed, up to twenty-five percent by weight of the silk, making it a more effective agent than sugar. Unlike the metal compounds that will be discussed, tannin was found to have little or no effect on the strength of the silk (Ballard et al., 1986; Howitt, 1946). Tannin weighting was done either concurrently with or after the dyeing process, as the capacity for the dye matter was somewhat diminished by the presence of the weighting compounds (Gandswindt, 1921). The use of tannic acid was restricted to darker shades of colour due to the natural colour of the substance (Robson, 1985).

Inorganic Weighting Agents

Various metal compounds were used as weighting agents, and became the most common compounds consumed for this purpose by the end of the nineteenth century. The diversity of metal complexes used was great. These metals were used alone and in combination, and were generally selected according to the intended final colour of the silk to be dyed since many of the metals also were used as dye mordants. A comprehensive list of the weighting metals (and mordants) used includes: aluminum, antimony, chromium, iron, lead, magnesium, tin, tungsten, and zinc (Ballard et al., 1986; Becker et al., 1987; Hersh et al., 1989; Kuruppillai et al., 1986; Scott, 1931a, 1934). Bogle (1979) provides a list of many of the compounds (with formulas) normally associated with inorganic weighting and a brief description of the most common types of weighting.

Most authors on the subject agree that silks weighted with metal compounds have shown weakening and degradation. The exact cause of the tendering of silk weighted with metal compounds has not been identified, and there is some debate over whether the damage is purely mechanical in nature or whether it is the result of a chemical attack.

Tin. While silk was weighted by application of any of the numerous agents mentioned, tin became preferred and was patented in 1883 (Tyler, 1949). Tin chlorides have been identified as the most important weighting agent in use by the beginning of the twentieth century (Ballard et al., 1986; Becker et al, 1987; Mauersberger, 1947; Scott, 1931a). Silk has a great capacity for the absorption of tin compounds. According to Gandswindt (1921), "the absorptive capacity of silk for liquid and saline solutions also constitutes the basis for...loading with stannic chloride and tannin solutions" (p. 34).

In 1883, the first patent for the use of stannic chloride with alkaline baths was recorded, followed by the 1897 patent of the tin-phosphate-silicate method (Howitt, 1946). Between 1900 and 1920 there were few developments in tin weighting, as the tin-phosphate-silicate process found great success (Howitt). The combined compounds allowed for increased weighting of the fabric by repeated passes through the baths. Tin-phosphate weighting was especially desirable because in addition to increasing weight, volume, and scroop, there seemed to be an improvement in the lustre of the silk (Gandswindt).

Iron. Generally, iron was used to weight silk that would be dyed black or another very dark shade. Evidence of iron weighting appears quite early (Bogle, 1979), and it was likely practiced before tin weighting. The common use of iron as a mordant for certain dyes may have prompted its introduction into weighting. Iron, like tin, however, has been found to cause damage to silk both in iron weighted and mordanted textiles. Bogle suggests that the damage stems, at least in part, from the acidity of the iron bath, that would cause immediate harm. He also states that there is likely a slow oxidation of the iron and silk over time. It is likely that iron would act as a catalyst for the photo-oxidation of the weighted silk, a reaction that is commonly seen in iron-mordanted textiles.

Methods of Application

Several historical techniques for applying the weighting agents have been identified. These traditional methods were usually best suited for particular agents or for achieving specific results. Some of these techniques will be examined briefly, with special attention to the methods used for tin weighting of silk.

Weighting in the Skein. One process called for the silk to be weighted in the hank or skein (Howitt, 1946; Scott, 1931a,b). This practice was more popular in England than in the United States (Howitt). Scott (1931a) reported that weighting in the skein (in the yarn form), which was the original method, decreased in favour during the 1920s, and piece weighting became the preferred process. In piece weighting, silk was weighted as a fabric after weaving. However, Carboni (1952) discusses the weighting procedure in reference to skeins of silk.

Chittick (1913) preferred weighting in the skein and did not approve of the rising piece weighting practices: "It is much to be regretted that weightings have at last been commercially applied to piece-dyed fabrics. At this writing (January, 1913), chiffons are being extensively adulterated, as are certain satin-faced fabrics made of raw silk..." (Chittick, p. 38). There was some concern about the quality of piece weighted goods compared to those weighted in the skein.

Weighting in the Gum. Weighting in the gum was another method occasionally used. Both Howitt (1946) and Scott (1931a) mentioned patents for this process. The silk was weighted before degumming, and the sericin gum was removed at a later point. Howitt suggested that when weighting with the gum, the sericin provides a protective coating for the silk fibres, helping to prevent damage due to alkalies encountered in the procedure. However, no research was found which compared the degree of damage in silk weighted before and after degumming.

The bath process seemed to be the most common for the metal weighting agents, as indicated by the number of authors who have written about this method and neglected to mention others. In this process, degummed silk was passed through a series of chemical baths which contributed cumulatively to weighting.

Weighting in a Foam Bath. In some cases, a foam bath was used, in which the bath was frothy. This type of bath was used to prevent high alkalinity that could damage the silk by hydrolysing the peptide bonds in the main protein chains (Howitt, 1946; Scott, 1931a). Carboni (1952) discusses the foam method for degumming, and describes it as a way to "keep the skeins immobile during the process of degumming and so avoid rumpling the thread and separation of the filaments which produces the effect of flocking in degummed silks" (p. 184). He also mentions the foam bath treatment for the sodium phosphate stage of tin weighting. The foaming was achieved through use of a foam producing material, such as a silkworm chrysalis (Carboni; Scott). This method is not widely researched.

Tin-Phosphate-Silicate Bath Weighting. Weighting with tin was done by many methods, but the most common method was through a series of chemical baths. Of the various tin weighting processes, the tin-phosphate-silicate process has been written about most frequently. Several authors discuss it as being commercially important (Ballard et al., 1986; Howitt, 1946; Mauersberger, 1947; Scott, 1931a,c; Tyler, 1949).

The main loading of the silk occurred during the tin chloride bath, but successive passes through sodium phosphate and sodium silicate helped to neutralize the chlorides, and also to increase the amount of weighting that could be attained (Ballard et al.).

Several authors have written in detail about the tin-phosphate-silicate method, including Ballard et al. (1986), Tyler (1949), Scott (1931b, 1934), and Howitt (1946). Tyler and Scott discuss the normal commercial procedure used in the silk finishing industry during the 1930s and 1940s when tin weighting was still in practice. Therefore, some of the procedures and equipment may now be out of date, although the general description of the process is useful as it reports on the method from its historic context.

Ballard et al. (1986) used a historical method in 1986 to reproduce the effects of a weighting process that is no longer executed on modern silks. The procedure they used was taken from Carboni (1952) as described below. Howitt (1946) provides only a general summary of tin-phosphate-silicate weighting, drawing from many previous studies. Many variations in the process were given, along with the original references, making Howitt a valuable source.

Carboni (1952) provides a detailed description of the procedure and equipment used in the tin-phosphate-silicate method, which he also identifies as a modification of the Neuhaus method.

1) The first bath is called the *pink* bath, although it no longer contains the tin

compound which originally gave it this name. This bath is a 25-30° Bé[1] solution of stannic chloride, usually in the hydrated from of $SnCl_4 \bullet 5H_2O$, and at 18° C. The silk is submerged in this bath, and left until the desired amount of weighting is achieved, the maximum amount of weight increase being attained in six hours. The silk is then thoroughly washed in water to hydrolyze the tin compound, producing $Sn(OH)_4$ and hydrochloric acid:

$$SnCl_4 + 3HOH \rightarrow H_2SnO_3 + 4HCl \quad \text{(Robson, 1985)} \tag{5}$$

2) After washing, the silk is immersed for one hour in a 6-7° Bé bath of sodium phosphate ($Na_2HPO_4 \bullet 12H_2O$) at approximately 60° C for degummed silk. This bath must be kept alkaline in order to achieve successful weighting, but the alkalinity must be controlled so as not to damage the silk. Robson (1985) gives the following reactions for this step:

$$H_2SnO_3 + Na_2HPO_4 \rightarrow Na_2SnO_3 + H_3PO_4 \tag{6}$$

then:

$$Na_2SnO_3 + Na_2HPO_4 + HOH \rightarrow Sn(ONa)_2HPO_4 + 2NaOH \tag{7}$$

The silk is again rinsed in water:

$$Sn(ONa)_2HPO_4 + 2HOH \rightarrow Sn(OH)_2HPO_4 + 2NaOH \tag{8}$$

Steps 1 and 2 may be repeated up to four or five times to increase the percentage of weighting. Robson (1985) indicates that repeating steps 1 and 2 will result in an increase of ten per cent each time.

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[1] ° Bé stands for "degrees Baumé", which represents the density of a solution, and can be converted to specific gravity by the equation: sp. gr. = (145 - ° Bé)/145

3) Treatment with aluminum sulphate is a modification of the original Neuhaus method. This bath is included after the last pass through the sodium phosphate bath, and helps the silk to accept a greater amount of silica. The aluminum sulphate is a weakly acidic solution with a density of 7-10° Bé. The silk is kept in this bath for one hour at around 50° C.

4) Lastly, the silk is immersed in a sodium silicate bath for up to three hours, although it usually lasts for one hour only. The density used is 3-5° Bé and the temperature is maintained below 60° C. Finally, there is rinsing and soaping, then one more rinse in water before dyeing. (No equations for the reactions at step 3 and step 4 are given in the literature).

This general procedure as outlined by Carboni (1952) is well supported by other sources. Tyler's (1949) method is similar, and he includes the aluminum sulphate bath as one that is sometimes used to increase the amount of weighting achieved. Branegan (1929) describes a method almost identical to that of Carboni, but omits the aluminum sulphate bath. Scott (1934) also omits the aluminum sulphate bath, but he does provide a brief description of other modifications to the process. Scott's earlier papers (1931a,b), however, describe a different series of baths. He mentions alternating baths of tin, phosphate, and hydrochloric acid, then dilute baths of sodium carbonate and sodium silicate. There is no explanation for this discrepancy.

Identification of Weighted Silk

The older industrial methods used to determine the presence and amount of weighting agents required large samples of the silk, approximately 45 by 15 centimetres (Ballard, 1987). Other techniques requiring much smaller pieces of silk have been developed during the twentieth century. Two of the most common procedures for identifying weighted silk (but not the amount of weighting) have been discussed in the literature. The burning test is a simple test that can be carried out in any textile laboratory. The second method, energy dispersive x-ray analysis (EDXA), involves expensive equipment which may not be available to many textile conservators and requires some training in the technique and use of the equipment.

Burning Test

The burning test uses a small sample of the silk and a flame. The sample, which can be as small as a yarn, is gripped in tweezers and held in the flame so that it will burn completely. Silk is a self-extinguishing fibre, meaning that it will not continue to burn once it is removed from the flame. The silk is observed while in the flame, and the ash is examined after removal from the flame. When *unweighted* silk burns, it leaves a crispy grey ash and has the characteristic odour of burning hair.

While *weighted* silk burns initially like unweighted silk in the flame, its characteristics when held in the flame and after removal are quite different. Hartsuch (1950) and Mease (1933) describe how the ash of weighted silk may retain the shape of the yarn or fabric after the silk has burned away, showing a "skeleton" of the original structure. When held in the flame, this skeleton becomes incandescent with the red glow of a hot metal ("Identification of textile materials", 1975). The amount of ash left usually seems abnormally great for the small piece of silk that is burned, especially in the case of heavy weighting (Hartsuch). However, the burning test may not always be conclusive, and can only indicate that the silk is weighted with a metal, but not with which metal.

Spot Tests

Spot tests have long been used in other disciplines to identify unknown substances. In chemistry, there are well-defined protocols to follow which involve progression through a series of spot tests with each step either confirming or negating the presence of a particular element or compound (ASTM, 1974). The methods used in chemistry for qualitative analysis of metal cations can be adapted to conservation work and the identification of common weighting agents. Some of these tests have already been used on textiles (Weaver, 1984). Staining tests have also been developed specifically for textile applications.

Tin. When an unknown specimen is believed to contain tin, there are several possible tests that can be performed according to the reagents and equipment on hand. In the dithiol test, the sample is first acidified with hydrochloric acid in a test tube, then one or two drops of dithiol (4-methyl-1,2-dimercaptobenzene) are added and the solution is warmed (Feigl, 1958). If tin^{IV} is expected, a couple of drops of thioglycolic acid should be added to the sample before the dithiol. A red colour or precipitate indicates tin.

Another spot test for tin uses flame colour as the indicator (Feigl, 1958). The unknown sample is placed in a beaker with excess concentrated hydrochloric acid and a small strip of zinc metal. A test tube holding cold water is used to stir the solution, then the test tube is held in a Bunsen burner flame. The test is positive for tin if the flame surrounding the test tube glows blue.

There are several other tests for identifying tin which can be found in Feigl (1958). The ones describe here are two of the simplest tests requiring the least amount of equipment. It should be noted that while spot tests may be useful for identifying metal cations, there are likely to be impurities in the unknown samples that may interfere with the results of such tests.

Iron. The most common spot test for the detection of iron uses potassium ferrocyanide. One drop of this solution is added to the unknown sample, and the formation of a blue colour or precipitate indicates the presence of iron (Feigl, 1958). Impurities may affect the results of this test by reacting with the test reagent to produce a different colour.

Energy Dispersive X-Ray Analysis

Energy dispersive x-ray analysis (EDXA), also called energy dispersive x-ray spectrometry, is performed with a scanning electron microscope (SEM) and identifies the presence of heavy metal elements in the form of weighting agents, mordants, and dye complexes on the surface of a fibre (Ballard, Koestler, Blair, & Indictor, 1989;

Ballard, Koestler, & Indictor, 1986). Weighting compounds such as tin and iron have been identified successfully. However, the identification of weighting agents is based only on the presence and abundance of an element. EDXA cannot quantify damage to the fibres; rather, it can only reveal that a certain heavy metal element is present at a particular location on the fibre's surface.

EDXA is a valuable tool for studying weighted silk. Because most studies make use of naturally aged historic silks with unknown histories, SEM can help to confirm that a fabric is indeed weighted and to identify heavy metal weighting agents. Furthermore, the sample size needed to conduct EDXA is very small, making it especially suitable for conservation work with artifacts.

Summary

The Review of the Literature has provided a brief survey of the literature on weighted silk. The history, types, and methods of silk weighting have been described, providing a context for the study of the historical process. Previous research on the degradation of unweighted and weighted silk was explored, with special attention paid to the agents and conditions which influence degradation. Qualitative and quantitative methods of analysis were discussed as they have been used in measuring components of silk degradation.

There is little disagreement among researchers regarding the influence of weighting on silk degradation. Many textile conservators and scientists have noted the more severe deterioration of weighted silks when compared to unweighted silks from the same period (Ballard et al., 1986, 1990; Becker et al., 1987; Hersh et al., 1989; Kuruppillai et al., 1986; Miller & Reagan, 1989). Similarly, Hearle et al., (1989), Howitt (1946), Mauersberger (1947), Ross et al. (1936), Scott (1931a,c, 1934), and Tyler (1949) agree that weighted silk exhibits poorer durability than unweighted silk. Many of these researchers acknowledge the need for further investigation, as the reasons for the difference in degradation of unweighted and weighted silks have not yet been identified.

CHAPTER THREE: MATERIALS AND METHODS

Overview of the Research

There were two main components of the research project. The first part consisted of the characterization of weighted silk degradation and the investigation of methods for identification of weighted silk. Several techniques for confirming the presence of weighting agents were tested on silks of unknown origin. Through the examination of naturally aged silk artifacts, the degradation of historic weighted silks was characterized. Both weighted and unweighted silks were studied in order that comparisons could be made among the ways that they deteriorate. The second component of the research involved weighting new silk with tin, accelerated aging with light, then determining the effects of light on tin weighted silk under controlled conditions of exposure.

Part I: Identification and Characterization of Historic Weighted Silk

Identification of Weighting in Donated Samples of Silk

Eighteen historic silk samples were collected from textile conservators in museums and private practice in Canada and the United States. These samples were not part of museum collections but had been deaccessioned, discarded, or slated for use in experimentation. The silk pieces came from many sources, including costumes and flags, and in many cases had only estimated dates supplied by the donating conservators.

Table 2 provides an estimated date, source, colour and donor of each of the silk

Table 2
List of Donated Silk Samples Used in Identification Tests

Sample	Estimated Date[a]	Source	Colour	Donor[b]
A	c. 1903	yardage	brown	U of A
B	c. 1912	underslip	cream	G. Niinimaa
C	n/a	yardage	pink	U of A
D	n/a	blouse	grey	U of A
E	c. 1906	flag	white	CWM
F	c. 1906	flag	red	CWM
G	c. 1906	flag	blue	CWM
H	n/a	handbag	purple	PMA
I	n/a	dress- fragment	black/white	CCI
J	n/a	dress- sleeve	cream	RBCM
K	n/a	dress- fragment	cream	RBCM
L	n/a	dress- fragment	cream	RBCM
M	c. 1865	flag	brown	PCPC
N	c. 1865	flag	red	PCPC
O	c. 1865	flag	cream	PCPC
P	c. 1865	flag	cream	PCPC
Q	c. 1865	flag	cream	PCPC
R	c. 1865	flag	blue	PCPC

[a] n/a indicates that no approximate date for the silk was supplied by the donor
[b] U of A = University of Alberta Department of Human Ecology, Edmonton, Alberta; G. Niinimaa is a private textile conservator in Calgary, Alberta; CWM = Canadian War Museum, Ottawa, Ontario; PMA = Provincial Museum of Alberta, Edmonton; CCI = Canadian Conservation Institute, Ottawa; RBCM = Royal British Columbia Museum, Victoria, BC; PCPC = Pennsylvania Capitol Preservation Committee, Harrisburg, PA.

samples. The samples were labelled alphabetically from Sample A to Sample R. Generally, the donated silk samples varied in terms of colour, weave, and source. The estimated dates of the samples ranged from 1865 to 1912, although seven of the eighteen did not have even an estimated date. All of the samples showed visible signs of deterioration.

Since the donated silk samples were not part of any museum collection and were provided for the purposes of conducting research, destructive testing could be performed. These samples were used as "unknowns" in burning tests and spot tests to identify weighted silk. The results of these tests were then compared to the results of energy dispersive x-ray analysis.

Burning Test for Identification of Weighted Silk

Unweighted silk shrivels back as it approaches a flame. Once in the flame, silk will ignite and burn until it is removed; then it self-extinguishes. Unweighted silk leaves an irregular, crispy ash of carbon. On the other hand, weighted silk does not shrivel backs only slightly as it is brought toward the flame, but does ignite and burn rapidly in the flame. However, once the silk has been burned away, some form of the metal compound weighting agent remains, retaining the shape of the yarns or fabric and glowing red when held in the flame.

The burning tests were conducted as described in the review of the literature. A few fibres were pulled from one of the unknown silk samples and held in metal forceps. The fibres were slowly moved toward the upper part of the blue flame of a Bunsen burner. (A positive result is difficult to discern if the fibres are held in the small blue cone at the bottom of the Bunsen burner flame). The fibres were held in the flame for approximately ten seconds, which was sufficient to allow the silk fibres to burn and to produce either a positive or negative result. A test was considered positive for the presence of metal weighting agents if a crisp skeleton in the shape of the yarn or fibres remained, that glowed red when held in the flame.

Flame Colour Test for Tin

To test for the presence of tin, a flame colour test (Weaver, 1984) was chosen for several reasons. Since the flame test would not produce a colour change directly on the silk sample, the results of the test would not be obscured by the colour of the silk sample. The dithiol test, a spot test used to identify tin, is deemed to be positive if a red colour is produced on the sample. This type of positive result may be difficult to distinguish on certain colours of silk. Furthermore, a source for the dithiol reagent (3,4-dimercaptobenzene, or toluene-3,4-dithiol, or 3,4-dimercaptotoluene) was difficult to find and somewhat expensive[2]. This poor availability and high cost would be a deterrent to conservators working with time constraints and decreasing budgets. The flame test uses less expensive and more readily available reagents.

To conduct the flame test, a small piece of silk (approximately 1 cm by 1 cm) was placed in small beaker with excess (10 mL) concentrated hydrochloric acid (12 *N*), then 5 to 7 small pieces of zinc metal gratings (approximately 0.005 to 0.01 grams) were added. This solution was stirred with a 15 cm long test tube filled with cold water and held in test tube clamps. (A smaller test tube could be used, but was

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[2] Aldrich Chemical Company (tel. 1-800-558-9160) sells the reagent under the last name listed, catalogue number D12920-8.

not available at the time of testing). The lower end of the test tube was then held in the upper portion of a blue Bunsen burner flame for 20 to 30 seconds. A positive result was identified by the appearance of a bright blue flame encircling the test tube where it had been swirled in the test solution. An unweighted silk specimen would not produce this blue glow around the test tube. According to Weaver (1984), "hydrogen evolved from zinc and hydrochloric acid solution containing soluble tin imparts a blue color to a nonluminous Bunsen flame" (p. 174). It is not, however, the hydrogen which produces the blue colour. The blue flash is a result of rapid evaporation of the solution containing tin ions. Metallic elements have different atomic emisssion colours that can be measured instrumentally using atomic adsorption spectroscopy.

When necessary, a glass rod may be substituted for the test tube. One end of the glass rod would be swirled in the test solution, then held in the flame as described above. The blue flame is more noticeable when a glass rod is used, perhaps because the flame is concentrated around a smaller object.

A further modification of the flame colour test for tin uses the ash of a burnt specimen rather than the usual unburned piece of silk. The ash of the silk is put into the hydrochloric acid as before, and the test conducted with either a test tube of cold water or a glass rod. This modification allows the burning test discussed above and the flame colour test for tin to be done on the same small piece of silk (the burning test first to identify metallic weighting, the second test to see if the metal is tin).

Spot Test for Iron

The potassium ferrocyanide spot test for iron was selected to identify the presence of iron (III) cations in the donated silk samples. Ferric salts react with potassium ferrocyanide to produce a distinct blue compound called Prussian blue (Feigl, 1958). While this test is normally used to identify Fe^{3+} cations in solution, it was found that it could also be used on fabrics.

The iron spot test was conducted by placing a piece of silk (5 mm by 5 mm) on a clear watch glass. (When sampling artifacts, a few fibres would be sufficient for accurate observation of results). An eyedropper was used to place one drop of 1 *N* hydrochloric acid (HCl) on the fabric to acidify it, then one drop of 5 % (weight by volume) potassium ferrocyanide was added with another eyedropper. No change in colour indicated the absence of significant quantities of iron (III) cations, while the appearance of Prussian blue is considered a positive result for the presence of Fe^{3+} cations.

Both the flame colour test for tin and this spot test for iron have identification limits and dilution limits to express the sensitivity of the tests. The limit of identification is the minimum quantity of the element to be identified that must be present in the test sample in order to observe a positive result. This limit is the *quantity* sensitivity of the test. The dilution limit is the *concentration* sensitivity of the test, or the maximum dilution at which a positive result will be obtained for an element dissolved in a solution of particular volume. A low identification limit and a high dilution limit indicate a sensitive test (Feigl, 1984).

The flame test for tin has an identification limit of 0.03 μg of tin, and a dilution limit of 1:1,660,000 (Weaver, 1984). This means that for the purposes of identifying tin weighting agents, there must be 0.03 μg of tin present on the silk fibres or fabric being tested in order to produce a positive result. This amount of tin can be diluted in no more than 49,800 mL of solution in order to be detected. The potassium ferrocyanide spot test for iron has an identification limit of 0.1 μg of iron, and a dilution limit of 1:500,000 (Feigl, 1958). Thus, the ferrocyanide spot test for iron is less sensitive than the flame test for tin.

Energy Dispersive X-ray Analysis

Energy dispersive x-ray analysis was performed on the eighteen unknown samples to identify instrumentally any elements with an atomic number greater than eleven present in the samples. A tiny piece (approximately 2 mm by 5 mm) of each sample was mounted on double sided conductive carbon tape on a metal stub. A JEOL XVision field emission scanning electron microscope, model JSM•6301 FXV, was used. Readings at 15 kV accelerating voltage were taken from several spots on each sample to ensure that the location selected was not unique in its composition. A representative spectrum for each sample was printed, with the elements present in significant amounts labelled at their respective peaks.

Characterization of Silk Artifacts from the Clothing and Textiles Collection

In addition to the donated silk samples, approximately fifty silk garments and ensembles (75 artifacts in total) from the University of Alberta' s Clothing and Textiles Collection were examined. Permission for access to and use of the Collection was received from the curator. The artifacts were selected from the Collection's computer database and limited to a manageable number using several parameters: date range, silk content, and women's dress. A list of the artifacts examined can be found in Appendix A-1.

The date range of 1880 to 1920 was selected, based on a review of the literature which indicated that tin weighting was first patented in the mid 1880s and continued with few changes until the 1920s. Of course, each artifact had to have a significant component of silk. Women's dresses were chosen because silk was frequently used in these garments, and because they are common in most historic costume collections.

The artifacts selected from the Clothing and Textiles Collection for study were examined for their condition and for particular signs of damage. The "condition" of an artifact is an assessment of its general state of preservation, or its physical stability. Conservators are concerned with the observable physical properties of artifacts and often assign a numerical code to an artifact based on their evaluation of these properties. Anecdotal information found in the literature and encountered in discussions with conservators helped to identify types of damage that traditionally have been associated with weighted silk.

A report form was developed for the assessment of the condition and damage of the selected silk artifacts (see Appendix A-2). The report form was designed so that the information would be standardized and can be translated into quantitative as well as qualitative data. Copies of the completed examination reports with recommendations for continued storage of the fifty silk artifacts have been left in the Clothing and Textiles Collection for future reference.

The deterioration rating groups used on the report form were adapted from an earlier study by Horswill (1992). Artifacts were assigned to the five rating groups based on the general description provided with each rating. A rating of 1 indicates that an artifact shows no visible deterioration, while a rating of 2 means that there is minor deterioration. A rating of 3 is ascribed when an artifact has deteriorated in areas of mechanical stress or perspiration. When an artifact shows extensive deterioration throughout the fabric, (or throughout one of the main fabrics in a composite artifact), a rating of 4 is assigned. A rating of 5 is given to an artifact when the fabric is in pieces, or no longer intact.

It was expected that the completed reports would indicate patterns of damage typical of weighted silk degradation and key features for visual identification of degraded weighted silk. Thus, once the artifacts had been examined and their condition noted, it was essential to determine which artifacts were indeed weighted. After the identification tests had been conducted on the donated silk samples, the burning test was chosen to be the means for analyzing the silk artifacts.

Testing to determine whether the artifacts were unweighted or weighted silk would require the removal of fibre samples for burning. The ethical issues involved in the removal of fibre samples from artifacts when it is not essential for treatment or preservation but rather for research purposes had to be considered. The Clothing and Textiles Collection at the University of Alberta did not have an official policy governing the use of the Collection or the sampling of artifacts for research purposes. This research project was the first one to require that fibre samples be removed from a large number of artifacts for scientific analysis.

The curator of the Clothing and Textiles Collection, Professor Anne Lambert, the curatorial technician, Suzanne McLean, and the acting conservator, Joan Marshall, were consulted in order to discuss the sampling of the artifacts and to obtain informed consent and formal approval for this use of the Collection. After discussing the goals of the research and the sampling procedure, it was decided that small fibre samples could be removed from the artifacts that had been examined previously. Since the Collection is a *study* collection, the curator and other staff acknowledge the importance of research to the Collection as well as to the broader museum and conservation communities.

Fibre samples were to be taken from areas which were least intrusive, such as from frayed seam allowances. The exception to the sampling decision was that fibre samples for testing could not be removed from a particular artifact if the removal of the fibre sample would jeopardize the physical integrity of the artifact or remove important documentary evidence that is not preserved elsewhere in the artifact. The interpretation of this unofficial policy was left to the researcher with the understanding that doubts about any artifact would be discussed with the same individuals.

The goal of this part of the research was to determine if visual examination is reliable when distinguishing between weighted and unweighted silk artifacts. Report forms from the *confirmed* weighted silk artifacts were analyzed to identify patterns of damage that appear to be characteristic of degraded weighted silk. Photographs of representative artifacts in several of the deterioration rating groups were taken. Since the terms used to describe particular types of damage vary in the literature and among conservators, photographs can help to illustrate what is meant by a specific term.

Part II: The Effect of Visible and Ultraviolet Radiation on Tin Weighted Silk

Experimental Design

The second part of the research project was designed to isolate the effects of visible radiation (approximately 400 to 750 nm wavelength) and visible-plus-ultraviolet radiation (approximately 280 to 750 nm wavelength) on tin weighted silk. The differences between unweighted and tin weighted silk when irradiated with each type of radiation were of interest. To this end, two control groups were established. One control group consisted of specimens of silk that received neither weighting nor accelerated aging treatments. The other, "weighted" control group contained silk that had been tin weighted with a selected process but likewise did not undergo accelerated aging. These control groups were the standards against which physical and chemical changes that may occur after weighting and/or artificial aging were measured.

The treatment groups (listed in Table 3) included both weighted and unweighted silk. Three independent variables were manipulated: presence or absence of tin

Table 3
Light Exposure Conditions Assigned to Treatment Groups for Accelerated Aging

EXPOSURE	UNWEIGHTED SILK	WEIGHTED SILK
0 Hours	(unweighted control)	(weighted control)
10 Hours Unfiltered[a]	U-1A	W-1A
10 Hours Filtered[b]	U-1B	W-1B
20 Hours Unfiltered	U-2A	W-2A
20 Hours Filtered	U-2B	W-2B
40 Hours Unfiltered	U-3A	W-3A
40 Hours Filtered	U-3B	W-3B
80 Hours Unfiltered	U-4A	W-4A
80 Hours Filtered	U-4B	W-4B
160 Hours Unfiltered	U-5A	W-5A
160 Hours Filtered	U-5B	W-5B

[a] Unfiltered specimens irradiated with light of wavelength 280 to 750 nm from the xenon-arc lamp

[b] Filtered specimens irradiated with light of wavelength 400 to 750 nm from the xenon-arc lamp

weighting, length of accelerated aging process, and type of radiation received during accelerated aging. All groups labelled with the letter U are unweighted; those with a W have been tin weighted. The numbers 1 to 5 represent the exposure periods: 10, 20, 40, 80, and 160 hours respectively. Unfiltered light containing both the visible and ultraviolet regions of the spectrum (280 to 750 nm) is indicated by an A, while the groups receiving filtered light (wavelengths below 400 nm excluded) have been designated as B.

Fabric Selection and Preparation

The new silk fabric used in the experiment was an undyed silk habutae (8 mommie[3], No. 609 from Testfabrics in Middlesex, New Jersey[4]). This fabric is a plain weave, degummed *Bombyx mori* silk. The count of the fabric is 122 x 108 yarns per 2.5cm (warp x filling). The washed silk has a mass of 34.3 grams per square meter. A balanced plain weave was chosen to eliminate any effect on the properties being tested of having heavier yarns or floats in one direction. All samples were cut from one bolt of fabric.

Prior to treatment, the new silk from Testfabrics was cut into two pieces, each measuring 100 cm by 150 cm. Each piece was washed in a 0.2% solution of Shurgain WA Paste anionic detergent, followed by five rinses with distilled water at 23°C. The silk was then air-dried on a flat surface covered with a smooth polyester film. This preliminary washing removed any soils, impurities, or degumming chemicals remaining on the surface of the fabric. One piece was wrapped in acid-free tissue and stored in the dark, while the other piece was weighted.

Tin Weighting Treatment

Historically, tin weighting was added to silk fabrics in varying amounts depending on the process used, the type of silk being processed, and the desired effect.

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[3] mm represents "momme" or "mommie" which is a Japanese unit of weight for silk fabric that expresses the weight of a piece of degummed silk measuring 22.8 m long by 3.8 cm wide, where 1 mm = 3.75 g (Tortora & Merkel, 1996).

[4] TestFabrics Inc., P. O. Drawer 0, 200 Blackford Avenue, Middlesex, NJ 08846

According to Chittick (1913), 64% was the recommended maximum increase in weight for a silk of fair quality. Thus, a 55% to 65% range was chosen to represent the amount of weighting that might have been applied to historic silks similar to the habutae used in this study. After many trials based on historical weighting procedures, a successful process was found.

The final weighting procedure for the new silk required the silk to pass through alternating baths of stannic chloride and sodium phosphate four times each. Although some methods described in the literature include a final bath of sodium silicate, in preliminary trials it was found that higher levels of weighting could be achieved by excluding this bath. Details of the conditions of the baths are given in Table 4. The silk was thoroughly wetted by an initial soak in distilled water at room temperature for five minutes. Excess water was squeezed from the silk, then it was placed in the first stannic chloride bath. As stated in the literature, the stannic chloride bath can be reused in continuity. The sodium phosphate bath, on the other hand, must either be made fresh for each pass or the alkalinity replenished. For this project, a new sodium phosphate bath was prepared for each pass.

The weighting was carried out in stainless steel pans fitted with spigots and hoses for disposal of the chemicals. Stainless steel could be safely used without contamination of the stannic chloride solution with iron since the highly acidic bath lasted only one hour. The silk was folded in half lengthwise, then folded accordion style to fit into the pans. The silk was agitated occasionally with glass rods to circulate the stannic chloride solution throughout the pan. A large hot plate was used

Table 4

Details of the Tin Weighting Procedure Applied to New Silk Habutae

Condition	$SnCl_4 \cdot 5H_2O$	Na_2HPO_4
density[a]	sp. gr. 1.180	sp. gr. 1.063
concentration	350g/L	70g/L
liquor ratio	1:40	1:40
pH	start: 0.20 end: 0.20	start: 9.80 end: 7.80
temperature	22°C	60°C
duration of each pass	1 hour	1 hour

[a] Densities were used to mix the solutions since the compounds are hygroscopic and mixing by weight per volume may not be accurate. Specific gravity hygrometers in the ranges 1.00 to 1.220 and 1.200 to 1.420 were obtained from Fisher Scientific, catalogue numbers 11-583D and 11-583E.

to heat the sodium phosphate bath to the required temperature.

Once the weighting was complete, the silk was rinsed thoroughly to remove any excess chemicals which may have been left in the silk. The weighted silk was then laid flat to dry on a surface covered with a smooth polyester film. Once dry, the silk was stored in acid-free tissue in the dark. Energy dispersive x-ray analysis was later performed on specimens from the unweighted and tin weighted control groups to verify the presence of weighting agents on the tin weighted silk.

Sampling Technique

The unweighted and newly weighted silk fabrics were cut into specimens measuring 7 cm by 14 cm to fit the specimen holders of the Weatherometer to be used for accelerated light aging. (The cutting diagrams may be found in Appendix A-3). Pieces of acid-free mat board were cut to the same size to back each of the silk specimens in the specimen holders. The unweighted and weighted silk specimen sets were each numbered sequentially, starting from U1 and W1 respectively, then randomly assigned to the control and light aging treatment groups. The specimens assigned to each group are listed in Table 5.

Table 5
Assignment of New Silk Specimens to Treatment and Control Groups[a]

UNWEIGHTED SILK

Exposure (hrs)	Unfiltered Light	Filtered Light
0	19, 48, 53, 61, 84.	
10	1, 11, 22, 55, 88.	4, 15, 17, 27, 33.
20	29, 35, 40, 41, 85.	12, 36, 57, 63, 83.
40	10, 52, 56, 59, 69.	5, 7, 13, 70, 76.
80	9, 20, 24, 32, 75.	30, 45, 66, 67, 72.
160	8, 16, 26, 51, 65.	3, 38, 54, 58, 68.

WEIGHTED SILK

Exposure (hrs)	Unfiltered Light	Filtered Light
0	18, 33, 48, 50, 69.	
10	4, 8, 28, 41, 78.	1, 5, 16, 45, 59.
20	15, 20, 36, 66, 85.	9, 31, 65, 68, 70.
40	7, 12, 47, 53, 72.	17, 27, 29, 40, 57.
80	21, 38, 42, 52, 89.	2, 14, 46, 61, 86.
160	6, 23, 71, 83, 84.	25, 32, 37, 56, 88.

[a] Specimen numbers are shown on cutting diagrams in Appendix A-3

Accelerated Aging with Light

Aging with light was carried out in an Atlas CW35 Weatherometer for the exposures set out in Table 5. Originally, the accelerated aging conditions in the Weatherometer were to be set at the normal temperature and relative humidity that would be encountered by an artifact in a controlled museum environment. However, these conditions (temperature of 21 ± 2°C and relative humidity of 50 % ± 5 %) could not be achieved with this lamp and filter combination (see Figure 2).

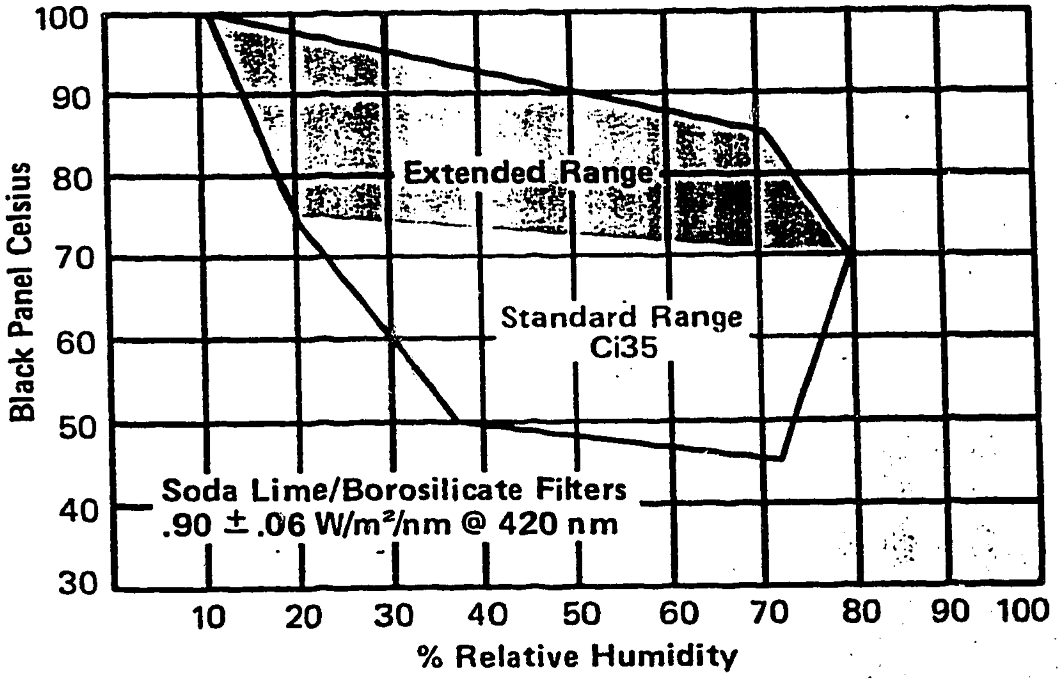

Figure 2. Temperature and relative humidity ranges that can be achieved in the Atlas CW35 Weatherometer with the borosilicate/soda lime filter combination (Atlas Bulletin No. 1360).

Since the museum environment could not be simulated, the exposure conditions were selected according to standard test method CAN/CGSB-4.2 No.18.3-M90. The silk specimens were exposed to continuous light from a xenon-arc lamp housed in a soda lime/borosilicate filter combination for the prescribed hours. The lamp irradiance was 1.10 W/m^2 measured at 420 nm. The black panel temperature in the Weatherometer was 63 ± 1°C and the ambient temperature was 38 ± 1°C. Relative humidity was maintained at 30 % ± 5 %.

Due to the limited number of specimens that could fit in the Weatherometer, several runs were required to age the specimens. Related treatment groups were aged together, so that the unweighted and weighted, filtered and unfiltered specimens exposed for a particular time period would receive exactly the same conditions. Thus, the accelerated aging was completed in five runs, one each for the 10, 20, 40, 80, and 160 hours exposure groups.

There were no unusual fluctuations in temperature or relative humidity during any of the runs that would cause a significant difference in the conditions between separate runs. The total amount of irradiance that each run received was recorded in kJ/m^2 at 420 nm. Every ten hours produced an average irradiance of 38.5 kJ/m^2, so that each group received the following amounts of irradiation: 10 hours = 38.5 kJ/m^2; 20 hours = 77.5 kJ/m^2; 40 hours = 155.0 kJ/m^2; 80 hours = 310.2 kJ/m^2; 160 hours = 620.4 kJ/m^2.

Evaluation of Changes in Selected Physical Properties of Silk

Mass of Unweighted and Weighted Silk

The masses of the unweighted and weighted silks were determined according to standard test method CAN/CGSB-4.2 No. 5.1-M90 Unit Mass of Fabrics. Five randomly selected, die-cut specimens of each fabric were conditioned at 65 % relative humidity and 21°C according to standard method CAN/CGSB-4.2 No.2-M88. The five specimens in each group were weighed together. The mass per square metre of fabric was calculated for both the unweighted and weighted silks. The increase in mass due to weighting was calculated using the following equation:

$$\% \text{ increase in mass} = \frac{(\text{mass of weighted silk} - \text{mass of unweighted silk})}{\text{mass of unweighted silk}} \times 100 \qquad (9)$$

Colour Change

Change in colour between aged and control groups of both unweighted and weighted silk was measured instrumentally using a Hunterlab D25M-9 Tristimulus Colorimeter. Standard test method AATCC 153-1985 for Color Measurement of Textiles: Instrumental was followed. The specimen was measured at the angle of least specular reflectance with a 45° circumferential incidence/ 0° viewing instrument geometry. Standard Illuminant C was used, which approximates the visible region of a daylight spectrum, as well as the 1931 2° observer. Colour measurement readings were made through a 5.1 cm specimen port.

The CIE 1976 L* a* b* equation for determining colour change was used to describe the relative lightness or darkness of the specimens, as well as to determine the components of red and green, yellow and blue in the specimens. The colour change measurements provided L*(lightness/darkness), a* (red/green), and b* (yellow/blue) colour coordinates, and ΔE which is a measure of *total* colour change (in CIELAB units). Total colour change in CIELAB units is calculated from the following equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{10}$$

where $L^* = 116\,(Y/Y_n)^{1/3} - 16$
$a^* = 500\,[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]$
$b^* = 200\,[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$

The terms X, Y, and Z represent the colour response measurements made by the Colorimeter, and X_n, Y_n , and Z_n are the corresponding tristimulus values of the standard white reference tile to which all readings are compared.

The unweighted, unexposed control group was used as the product standard for all unweighted treatment groups, as well as to measure the colour change following weighting. The weighted, unexposed control group was the standard for measuring the colour change of weighted specimens after exposure in the Weatherometer. The L*, a* and b* values for each of the five specimens in every treatment group were measured, then the ΔL*, Δa*, Δb* values were obtained as the differences between the test specimens and the relevant product standard. In addition, ΔE (CIELAB units) values were calculated for each specimen.

Because the silk was not completely opaque, the five specimens in each group were stacked on the white support tile, and the reading made on the top specimen.

This eliminated any effect of the white support tile showing through the specimen. One reading of each specimen was taken on the side which faced the xenon arc lamp in the Weatherometer, and with the warp yarns consistently in the same direction. The specimens were rotated until each one in the group had been read.

Stiffness

After the colour change measurements were completed, each 7 cm by 14 cm specimen was cut into two 2.5 cm wide x 13 cm long strips and conditioned at 65 % relative humidity and 21°C. Stiffness was tested according to ASTM D 1388-64 (Standard Test Method for Stiffness of Fabrics, Option A: Cantilever method). This method calls for strips measuring 2.5 cm by 15 cm. However, 13 cm long strips were necessary because the specimen holders for the Weatherometer had a length of 14 cm, with the top and bottom 0.5 cm of the specimen face covered by the holders. Areas that had been masked by the specimen holders would not have received the prescribed irradiation and therefore would not exhibit the same changes in properties. Ten warp specimens were tested for each control and treatment group.

To measure the stiffness of a specimen, the strip was laid on a level platform and covered with a rectangular weight of the same dimensions. The platform has a centimetre scale aligned at a 41.5° angle to the horizontal surface. The weight and specimen were slowly moved lengthwise over the edge of the platform so that the end of the strip was allowed to bend under its own weight. A reading from the centimetre scale was taken when the tip of the specimen strip touched the scale, forming an angle of 41.5° from the horizontal platform to the tip of the strip. This reading represented the length of overhang (in cm). Four measurements were made on each specimen: one for the face and reverse of the specimen at each end. These four measurements were averaged for each specimen, then flexural rigidity was calculated from the specimen averages according to the formula given in the test method (ASTM 1388-64):

$$\text{flexural rigidity, } G\ (\text{mg-cm}) = W \times (O/2)^3 = W \times c^3 \tag{11}$$

where

W = weight per unit area (mg/cm^2),

O = length of overhang as measured in centimetres (cm), and

c = bending length in centimetre (cm), which = O/2

The mass of both the unweighted and weighted silks had been previously calculated according to standard test method CAN/CGSB-4.2 No. 5.1-M90 Unit Mass of Fabrics. This mass was converted from grams per square meter to milligrams per square centimetre.

Tensile Strength, Extension at Break and Energy to Rupture

The cut strip method for breaking strength (CAN/CGSB-4.2 No. 9.1-M90 Breaking Strength of Fabrics - Strip Method - Constant-time-to-break Principle) was performed. Although a ravelled strip would normally be used for this test method, a cut strip measuring 2.5 cm wide and 13 cm long was used. It was expected that the highly degraded condition of the silk test specimens in the groups receiving the highest UV exposure might make ravelling the edges of the specimens difficult.

Furthermore, the same specimens from the stiffness tests (2.5 cm wide by 13 cm long in the warp direction) were used for the tensile tests. Again, ten specimens were tested for each control and treatment group.

The specimens were conditioned prior to testing, and the tests were performed in a conditioned atmosphere of 65 ± 2 % relative humidity and 20 ± 2°C temperature. Tensile testing was done using an Instron Universal Testing Instrument, model 4202, which operates on the constant-rate-of-extension principle. A fifty kilogram load cell was used, and the load range was adjusted so that the breaking strength was between 20% and 80% of the maximum load in the range. Gauge length (distance between upper and lower clamps) was set at 75 mm, as instructed in the test method. The clamps were 75 mm wide pneumatic grips with rubber grip faces. The speed of the crosshead was adjusted so that the specimens would break in 20 ± 3 seconds.

Extension at break and energy to rupture were calculated simultaneously with tensile strength on the Instron. Extension at break is the percent of its original length to which a fabric or yarn elongates before it breaks. Extension is calculated as follows:

$$\text{extension (\%)} = \frac{\text{change in length } (\Delta L)}{\text{original length } (L_o)} \times 100 \tag{12}$$

Energy to rupture is the area under the load-elongation curve, and indicates the "toughness" of a fabric. Energy to rupture, or total energy was calculated by the Instron machine in units of kilogram-force-millimetres (kg-f-mm). These units were converted to Newton-meters (N-m) by multiplying by a factor of 0.00981.

Surface Appearance

Scanning electron microscopy was used to examine surface features of silk fibres before and after weighting, as well as after exposure to unfiltered and filtered light. A JEOL XVision field emission scanning electron microscope, model JSM•6301 FXV, was used with a Noran Instruments light detector. Two specimens from each of the unweighted and weighted control groups and from groups U-5A, U-5B, W-5A, W-5B (unweighted, 160 hours unfiltered light; unweighted, 160 hours filtered light; weighted, 160 hours unfiltered light; and weighted, 160 hours filtered light) were selected to represent the microscopic surface characteristics of new silk as well as with high amounts of irradiation.

The specimens were cut to approximately 3 mm by 7 mm, and mounted on double-sided conductive carbon tape on the metal stubs. A layer of gold approximately 10 nm thick was applied to the specimens by sputter coating. Each pair of specimens from the six groups was examined at various magnifications. Photomicrographs at 1000X magnification were taken of one specimen of each pair. These specimens were also photographed at 25,000X to 27,000X magnification for close detail of surface structures.

Broken fibre ends sometimes reveal differences in physical properties of fibres, such as brittleness. Thus, broken fibre ends from tensile strength test specimens of the control and treatment groups listed above were examined using a Hibachi scanning electron microscope, model S-2500. (A different instrument was used due to the limited availability of the first instrument at the time it was needed). The specimens from the tensile strength tests were also mounted on double-sided, conductive carbon tape and sputter coated with gold (30 nm thickness). These specimens were examined for differences and peculiarities in the shape of the fibre breaks, then photographs of characteristic breaks were taken at 1700X magnification.

Evaluation of Changes in Selected Chemical Properties of Silk

pH

The pH values of the control and treatment groups were measured according to the standard textile test method for Determination of pH of the aqueous extract (CAN/CGSB-4.2 No.74-M91). Two specimens from each control and treatment group were tested. However, due to the size of the available specimens, a few modifications of the method were necessary.

Large specimens weighing 2.0 g were not available, so smaller specimens had to be used. The mass of the available specimen size was approximately 0.20 g. Each specimen was chopped into small pieces (approximately 5 mm by 5 mm) and placed in a 125 mL glass Erlenmeyer flask, and 50 mL of distilled water were added. (The pH of the distilled water measured 7.41). The flasks were stoppered with ground glass stoppers, swirled, then secured in the clamps of a Burrell Wrist Action Shaker, model 75, and shaken for one hour. The liquid was decanted from the flask into a small beaker and the pH reading taken using an Orion Benchtop pH/mV/Temperature meter, model 520A. Measurements were made and reported to two decimal places.

Fourier Transform Infrared Spectroscopy

Chemical analysis of the silk control and treatment groups was performed by Fourier transform infrared spectroscopy. The instrument was a Nicolet Magna 750 Fourier Transform Infrared Spectrometer. A tiny fibre sample was placed in the instrument, and the infrared beam transmitted through the fibre. A basic absorbency scan was performed on a specimen from each of the unweighted and weighted controls as well as from Groups U-5A, U-5B, W-5A, and W-5B.

The results, in the form of absorption spectra for silk specimens from each of the control and treatment groups listed above, were examined for differences in the shape and intensity of the absorption bands, with special attention to the $-NH_2$ stretch region. Changes in this region might indicate changes in the structure of the main chain of the fibroin molecule. As the peptide bonds are broken, more $-NH_2$ groups are created at the new [illegible] ends. An increase in the concentration of these primary amino groups would indicate that the fibroin chain has been hydrolyzed.

Statistical Analysis

Three factors were selected in designing the research project: silk type (unweighted or weighted), type of light (unfiltered or filtered), and length of exposure (from 0 to 160 hours). The relationships among these three factors were explored by measuring several dependent variables: total colour difference (ΔE), flexural rigidity, tensile strength, extension, and energy to rupture. The software program SPSS for Windows (release 6.0) was used to perform several types of analysis.

A three-way analysis of variance was performed for each dependent variable to identify significant main effects and significant interaction effects of the various factor levels. The independent variables were assigned codes to represent the various levels of those factors. Table 6 lists the experimental variables and their respective levels.

One-way analyses of variance on the six levels of exposure were also performed for each dependent variable using Duncan's Multiple Range Test (α = 0.05) to identify significant homogeneous subgroups. The six levels of exposure were tested in this way for each of the following four sets of data: unweighted silk aged with unfiltered light; unweighted silk aged with filtered light; weighted silk aged with unfiltered light; and weighted silk aged with filtered light. The Levene test for homogeneity of variance was run simultaneously. Any subgroups which proved not to have an equal variance were subsequently analyzed using the nonparametric Kruskal-Wallis one-way analysis of variance to verify significant differences identified in Duncan's test.

Table 6

Summary of Dependent and Independent Variables

Dependent Variables	Independent Variables Factors	 Levels
total colour change (ΔE)	Silk type:	unweighted tin weighted
flexural rigidity		
tensile strength	Light type:	unfiltered filtered
extension at break		
energy to rupture	Exposure:	0 hours 10 hours 20 hours 40 hours 80 hours 160 hours

CHAPTER FOUR: RESULTS AND DISCUSSION

Part I: Identification and Characterization of Historic Weighted Silk

In Part I of the research project, three qualitative tests to determine the presence of weighting agents on historic silk were evaluated for their validity. A burning test for metallic weighting, a flame colour test for tin, and a potassium ferrocyanide spot test for iron (III) were performed on donated samples of silk which had not been identified yet as being weighted or unweighted. In addition, forty-seven garments from the Clothing and Textiles Collection were examined using a customized report form in order to distinguish any patterns of damage due to weighting.

Identification of Weighting in Donated Samples of Silk

Burning Test

The burning tests were conducted on eighteen donated samples of unweighted and weighted silks. A positive result for the presence of metallic weighting agents was recorded when a skeleton of the yarn's shape remained and this skeleton glowed red when held in the Bunsen burner flame. Results of the burning tests on the unknown samples are shown in Table 7. The unknown samples which tested positive in the burning tests (A, B, D, H, I, J, K, and L) all showed the characteristic red glow when held in the flame beyond the initial combustion of the silk. Each of these samples also had a crisp ash that retained the shape of the yarns. The samples with negative burning test results burned rapidly in the flame and self-extinguished when

Table 7

Summary of Identification Tests for Presence of Metallic Weighting Agents on Unknown Silk Samples

Sample	Burning[a]	Tin[b]	Iron[c]	EDXA[d]
A	+	+	-	+
B	+	+	-	+
C	-	-	-	-
D	+	+	-	+
E	-	-	-	-
F	-	-	-	-
G	-	-	-	-
H	+	+	-	+
I	+	+	-	+
J	+	+	-	+
K	+	+	-	+
L	+	+	-	+
M	-	-	-	-
N	-	-	-	-
O	-	-	-	-
P	-	-	-	-
Q	-	-	-	-
R	-	-	-	-

[a] The burning test was considered positive when the ash retained the shape of the fibres and had a red glow when held in the flame

[b] The flame colour test for tin was considered positive when a blue glow was observed encircling the test tube when held in the flame

[c] The spot test for iron was considered positive when a blue colour was produced on the silk specimen

[d] EDXA considered positive for weighting when a weighting metal (especially tin or iron) was present in a significant amount

removed as expected with unweighted silk. They produced the acrid odour of burning hair, and left a crisp ash of irregular shape which did not glow red when held in the flame.

When conducting the burning tests, it was found that some experience is required for consistent results. Initially, a larger sample (approximately 10 mm by 5 mm) is required to be able to see the skeleton of the weave that is left after the silk burns away when the test is positive, and to observe the red glow of the metallic coating in the flame. However, once the researcher or conservator is familiar with the appearance of a positive result, these characteristics become easier to recognize. An experienced tester can burn a tiny sample (as small as only a yarn or two) held in fine forceps and observe the results accurately.

Flame Colour Test for Tin

The results of the flame colour test for tin were consistent with the burning test results for metallic weighting. All of the samples which tested positive for a metallic weighting agent tested positive for tin. When the burning test was negative, the tin test was also negative (see Table 7). These results mean that all of the donated silk samples which were determined to be weighted had been weighted with tin.

Initially, the hydrochloric acid, silk, and zinc filings were stirred with the cold test tube while the reaction was still bubbling, but the test was found to be more effective if the reaction of the acid and the zinc was completed before the cold test tube was swirled in it. In any case, the blue glow which indicates the presence of tin did not appear as soon as the test tube was moved into the Bunsen burner flame. After a few trials, it was found that the test tube had to be held in the flame for up to thirty seconds or more until the blue flame or flash appeared. Dipping the test tube back into the solution and returning it to the flame also helped to make the blue glow more visible. The silk eventually dissolved in the hydrochloric acid solution.

The blue flame that encircles the test tube to indicate a positive result may be missed by an unexperienced person. Once one has seen a positive test, it is easier to recognize the blue flame which sometimes appears only as a quick flash of bright blue around the edge of the test tube.

Some variation was found in the size of silk specimen that was required to achieve a positive result in the flame test. In most cases, a specimen as small as 5 mm by 10 mm was sufficient to produce the blue flame. However, for Sample A, a larger piece (10 mm by 15 mm) was needed in order to see a distinct blue flame. This variation in the size of silk specimen needed to accurately observe a positive result may be due to variations in the amount of tin weighting present in the silk samples.

Spot Test for Iron

The results of the potassium ferrocyanide spot test for iron (III) cations are shown in Table 7. When tested, none of the unknown silk samples showed the characteristic blue colour which indicates the presence of iron (III) cations. Positive results had not been expected since iron was used as a weighting agent and a mordant only on black silks, and no black samples were tested. However, the test was carried out on all samples to ensure that no false positive results would be obtained.

The iron test is less complicated than the flame test for tin in terms of both technique and recognizing a positive result. A positive result is indicated by a direct colour change to blue or the formation of a blue precipitate; such a result is easily observed. The only difficulty with this test may arise when the test is performed on very dark coloured fabrics. Since iron is present usually only as a weighting agent (or mordant) in black silks, this could pose a problem if the colour change was not visible on such a fabric. The problem was not experienced in this research since the "unknown" silk samples did not contain iron in any significant quantities and only samples H and R were dark enough to possibly obscure the results.

If the blue colour that indicates a positive result is difficult to distinguish on a dark coloured silk, modifications of the method may make the result more visible. A piece of white blotting paper placed under the silk test fibres may draw the blue colour onto the paper where it would be easily seen. Also, it may be possible to place a small piece of the silk in a test tube with the potassium ferrocyanide solution, and observe the colour change in solution. However, with both of these modifications there is the risk of bleeding dyes (which may appear blue) being mistaken for a positive result.

Energy Dispersive X-ray Analysis

Energy dispersive x-ray analysis (EDXA) was performed on the eighteen unknown samples to positively identify the elements present on the surface of the fabrics (see charts in Appendix A-3). EDXA can identify elements with atomic numbers greater than eleven. Large amounts of metals such as tin or iron would indicate that the silk had been treated with these metals. Previous researchers have found that EDXA is an accurate and efficient way to determine if a silk has been weighted (Ballard et al., 1986). The results of the EDXA are given in Table 8.

Samples A, B, D, H, I, J, K, and L were found to have large quantities of tin. These samples had been tin weighted. Of these samples, all but L also showed significant amounts of phosphorus and silicon. The presence of these three elements together indicates that the tin-phosphate-silicate (Neuhaus) method of weighting was used. The presence of aluminum in samples A and H suggests that the later modification of the Neuhaus method was employed in the weighting of these silks, where a bath of aluminum sulphate was added between the last phosphate bath and the final silicate bath. Sample L had phosphorous but not silicon, which means that this silk would have received only the tin and phosphate baths, but not a final silicate bath.

Many of the samples show trace amounts of various other elements, including sodium, magnesium, chlorine, calcium, and iron. An element was designated as being present only in trace amounts based on the magnitude of its peak. Very small peaks that barely rise above the background scatter are usually considered to be present in amounts of 1 % or less. In historic textile samples, these trace amounts may be attributed to contamination from any number of sources including perspiration, general soiling, surface contact with other fabrics and objects, or from the water used to clean the garment. Sample D, which was taken from the stained underarm area of a blouse

Table 8

Elements Present in the Unknown Silk Samples as Determined by EDXA

Sample	Elements Identified in Sample[a]
A	Sn, Si, P, Al
B	Sn, Si, P, Na
C	-
D	Sn, Si, P, Na, Mg, Cl, Ca
E	-
F	-
G	Ca
H	Sn, Si, P, Na, Mg, Al, Cl
I	Sn, Si, P, Na
J	Sn, Si, P, Na
K	Sn, Si, P, Na
L	Sn, P
M	-
N	Na, Al, Si, Cl, K, Ca
O	Na, Si, Cl
P	-
Q	Si
R	Fe, Al, Si, Sn

[a] Carbon, oxygen and sulphur, which make up the fibroin molecule and appeared in all EDXA results, are not listed in order to simplify the table. The graphs produced by EDXA are in Appendix A-4.

shows sodium and chlorine, likely due to the salts in perspiration.

Sample R is listed in Table 8 as having tin, aluminum, silicon and iron. These elements are in trace amounts and must be attributed to contamination as such small amounts could not be present as weighting agents. Such low concentrations of these elements would not serve the intended purpose of weighting. Since the history of the sample is unknown other than for the fact that it was taken from an American Civil

War flag (c. 1865), the source of the contaminants cannot be identified. The early date of this silk also precedes the general start of the tin weighting process.

Summary of Identification Tests

Table 7 provides a summary of the identification tests and EDXA results which demonstrates the strong agreement among the four types of analysis. Overall, there was excellent agreement among all the test results when elements were present in large quantity. Unfortunately, the amounts in which elements were present in each sample could not be quantified with EDXA, and *large*, when used in this context, can only be defined as being more than a trace amount.

It can be seen that in all cases where burning tests indicated the presence of a metallic weighting agent, EDXA confirmed that a metallic compound was present in large quantity. The burning test has proven to be accurate when large amounts of metal compound are present in a fabric, but it is not known at what level of weighting positive results begin to appear. Sample R, for example, was found to have a trace amount of tin that was not identified by the burning test.

Likewise, the flame test for tin indicated the presence of tin in those samples which were confirmed by EDXA to contain large amounts of tin. Again, however, sample R did not test positive for tin with the flame test but showed a trace amount when analyzed by EDXA. Results of EDXA also were consistent with the results of the iron spot tests, which showed that iron was not present *in more than a trace amount* in any of the samples.

Characterization of Silk Artifacts from the Clothing and Textiles Collection

In order to characterize the visual appearance of historic, naturally aged weighted silk, 47 unweighted and weighted silk garments from the University of Alberta's Clothing and Textiles Collection were examined. The deterioration of each garment was rated from one (no visible deterioration) to five (fabric no longer intact) on the specially designed report form. Details of damage were also noted so that patterns of damage typical of weighted silk would become apparent. (A copy of the report form used to examine the artifacts is in Appendix A-2).

Table 9 shows the distribution of ratings assigned to the forty-seven garments. While no ratings of 5 (fabric no longer intact) were assigned, nineteen of the 47 garments (40 % of the total) were given a deterioration rating of 4 because the artifacts showed extensive deterioration throughout the fabric.

Table 9

Distribution of Deterioration Ratings Assigned to Silk Artifacts[a]

Artifact Rating		# of Artifacts	% of Artifacts
1	no visible deterioration	1	2
2	minor deterioration	13	28
3	deterioration in areas of mechanical stress or perspiration	14	30
4	extensive deterioration throughout	19	40
5	fabric no longer intact	0	0
	Total	47	100

---

[a] The artifacts were women's dresses ranging in date from 1880 to 1920. Weighted silk was found in 40 % of the artifacts examined.

Burning tests were carried out on all of the artifacts previously examined to determine which ones contained weighted silk. The results of the burning tests are indicated in Appendix A-1, and summarized according to deterioration rating groups in Table 10. From these results, it can be seen that weighted silk artifacts appeared in three of the four deterioration rating groups with assigned artifacts. Of those artifacts which showed extensive deterioration throughout the fabric (rated 4), 74 % proved to be weighted. Only 20-23% of the artifacts rated 2 or 3 were weighted. Thus, although weighted silk was not restricted to the groups with the highest deterioration ratings, it was more dominant in those groups.

Table 10
Number of Weighted Silk Artifacts in Deterioration Rating Groups

Artifact Rating		# Artifacts	Burning Results	% of Group Total
1	no visible deterioration	1	0 positive	0 %
2	minor deterioration	13	3 positive	23 %
3	deterioration in areas of mechanical stress/perspiration	15	3 positive	20 %
4	extensive deterioration	19	13 positive	74 %
5	fabric no longer intact	0		

Specific types of damage were noted on the report forms, including the slits and cracks typically associated with weighting. This type of damage did not appear in any of the fourteen artifacts rated 1 or 2, and in only one of the fourteen artifacts given a rating of 3. However, seventeen of the nineteen artifacts (90 %) rated 4 showed cracks and slits throughout the fabric. This type of damage, when found, was noted to occur throughout the fabric in areas of mechanical stress as well as in areas that would not be expected to receive strain during normal wear. The artifact which did not show this type of damage was rated 4 for other reasons.

The joint occurrences of weighting *and* the pattern of geometric slits and cracks described above were calculated. One of the three weighted silks in rating group 3 showed slits throughout the fabric, while none of the unweighted silks exhibited this pattern. All thirteen of the weighted silks given a deterioration rating of 4 showed this type of damage, but so did 4 of the 7 *unweighted* silks in that group. Thus, there were weighted silks that did not show the "typical" pattern of damage, and there were unweighted silks that did show the type of damage normally associated with weighted silk. However, the pattern of slits throughout a fabric was found more often in weighted silks than in unweighted silks.

The pattern of slits and cracks that was noticed in a significant number of the artifacts rated 4 appears to be common to weighted silk. The slits may follow the grainline of the fabric, with the filling yarns having broken to form slits in the warp direction. Even when the slits do not appear to follow the grainline of the fabric, they are often nearly straight or geometric in shape. Cracks generally form along creases and folds in the silk. Plate 1 illustrates this type of damage. The photograph shows the inside of a woman's bodice (acc. # 87.69.1a) which has extensive deterioration throughout the silk lining.

Three selected silk artifacts from the Clothing and Textiles Collection illustrate the uncertainty of using visual examination as the only means of identifying weighted silk. These three bodices range in date from 1887 to 1907, all within the appropriate date range for the fabrics to have been weighted with metallic agents (especially tin and iron).

The first artifact (accession # 87.69.1a), shown in Plates 1 and 2, is a woman's bodice from a two-piece dress (c. 1904). The dress was given a deterioration rating of 4 to 5. The cream coloured satin fabric has a series of fine slits throughout the lattice-work design around the neckline and sleeve cuffs. Furthermore, the inner facings of a plain weave silk (also cream) are severely fractured throughout, with many areas breaking off altogether. Plate 1 shows this extensive damage to the silk lining. Burning tests conducted on fibre samples from both fabrics indicate that both fabrics have been weighted with a metal. The weighted satin fabric shows less severe damage, although the fine slits could easily develop into much larger tears and fractures. While both fabrics are weighted, the type and extent of damage are quite different.

The second garment (acc. # 78.13.1a) is a woman's bodice from a two-piece dress, dated 1895 to 1905. The black jacquard fabric is free from the slits and cracks of the previous artifact, and was given a deterioration rating of 2, meaning there was only minor damage. A rating of 1 would have been assigned if not for a small hole under the left sleeve. This artifact did not show any localized or scattered patterns of damage apart from the one small hole. Fibres removed for burning tests showed the silk to have been weighted with a metallic weighting agent. Although weighted, this artifact did not show the signs of damage that have traditionally been attributed to weighted silk degradation.

Another artifact (acc. # 81.13.28a) illustrates the variation in condition and appearance of historic silk artifacts. This bodice, from a woman's brown two-piece dress (c. 1887), was given a deterioration rating of 4 (extensive deterioration throughout the fabric) like the first artifact mentioned. Large areas of "shredding" on the sleeves as well as many areas of abrasion can be seen in Plates 3 and 4. In the shredded areas, the filling yarns have broken, leaving long warp threads unsecured. The poor condition of the garment has not resulted from weighting, as fibres did not show the characteristics of weighted silk in the burning test. Although given a deterioration rating of 4, the silk fabric had not been weighted.

These three examples help to clarify the ambiguities inherent in using visual examination alone to confirm the presence of metallic weighting agents in silk. The patterns of degradation in weighted silk can take many forms, as noted in the two different weighted silk fabrics in artifact #87.69.1a. However, weighted silk may show little damage, if any, in certain artifacts. Furthermore, unweighted silk may have extensive damage that is not due to weighting.

The difficulty in using only visual examination to identify weighted silk lies in the unknown histories of the artifacts. Each artifact has been exposed to a unique set of environmental conditions and physical stresses that play an important role in the way that it degrades. The lack of a consistent pattern of damage among the weighted silks at various deterioration ratings suggests that there may not be one model of weighted silk degradation. Various types of silk artifacts may show different patterns of damage that may or may not be due to weighting. Many historic silk flags, for example, show severe damage that often looks like the damage typically associated with weighting. However, researchers have found that historic silk flags generally were *not* weighted (Ballard, Koestler, Blair, Santamaria, & Indictor, 1989).

Horswill (1992) came to a similar conclusion in an earlier study. After examining and analyzing thirty-four historic silk artifacts, the researcher found that many of the heavily weighted silks were in poor condition. However, there were also weighted silks which were judged to be in good condition, indicating that degradation was the result of many interacting factors. "The condition of use, manufacture, storage and display may all have had an impact on the deterioration of these silks" (Horswill, p. 170-1).

Factors such as environmental conditions, physical/mechanical strains, chemical attack, and amount and type of weighting may all influence the way in which weighted and unweighted silks degrade. Seventy-four per cent of the artifacts given a rating of 4 (extensive deterioration throughout the fabric) were indeed weighted, and only the remaining 26 % were unweighted and had degraded as a result of some other factor. While other factors must be considered, the results of this research indicate that often visual appearance may provide clues to suggest that a silk contains metallic weighting.

Plate 1. Detail of weighted silk lining showing slits and cracks throughout (University of Alberta Clothing and Textiles Collection, acc. # 87.69.1a). Reprinted with permission. (Photograph by author).

Plate 2. Inside of woman's bodice, c. 1904, showing severe degradation in weighted silk lining (University of Alberta Clothing and Textiles Collection, acc. # 87.69.1a). Reprinted with permission. (Photograph by author).

Plate 3. Detail of damage on sleeve of unweighted silk garment (University of Alberta Clothing and Textiles Collection, acc. #81.13.28a). Reprinted with permission. (Photograph by author).

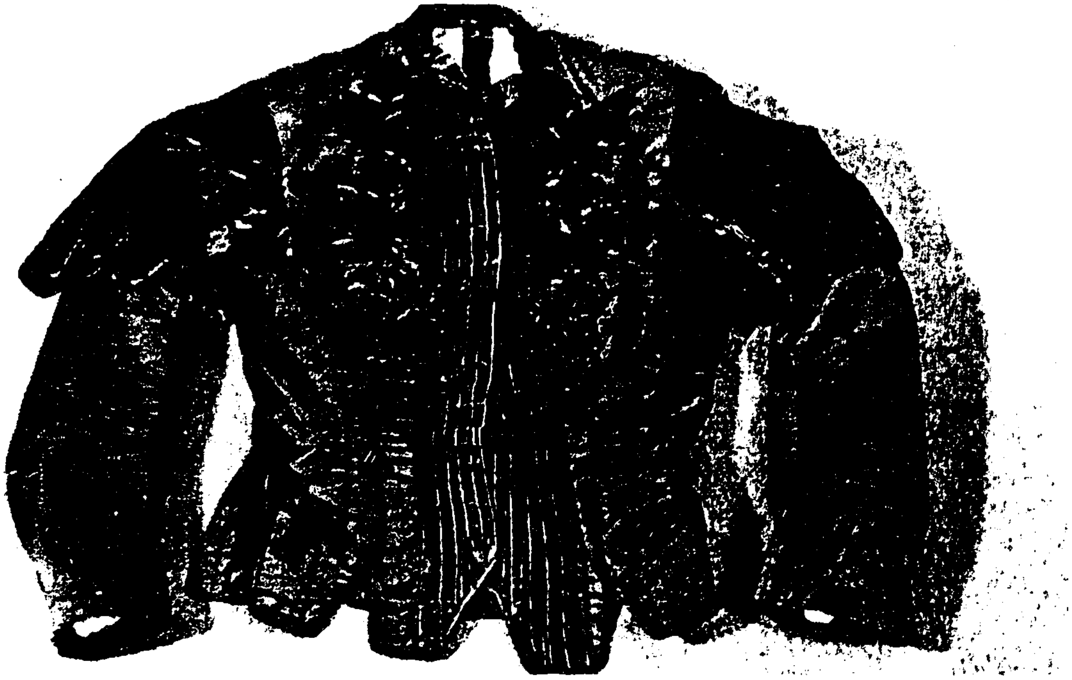

Plate 4. Front view of woman's bodice, c. 1887, showing abrasion on sleeves and near shoulders (University of Alberta Clothing and Textiles Collection, acc. # 81.13.28a). Reprinted with permission. (Photograph by author).

Summary of Part I

It has been determined that there are several simple tests that can be used to identify silks that have been weighted with metallic compounds. While some of these tests require a certain degree of skill and experience, the techniques themselves are relatively easy to perform and are inexpensive, which are important considerations for textile conservators in small laboratories. The burning test, flame test for tin, and ferrocyanide spot test for iron can be conducted on small yarn samples with accurate results. Although no positive results were obtained for iron, the spot test was tested on a control containing iron to ensure that the procedure and reagents were correct.

Contrary to anecdotal evidence, it has been found that the visual appearance of a silk artifact is not adequate proof of weighting. A highly degraded condition with extensive cracking and splitting of the fabric may not be confirmation of weighting in silk. Systematic examination and subsequent testing has shown that weighted silks, like unweighted silks, exhibit a wide range of deterioration, from very little to severe damage.

Part II: The Effects of Visible and Ultraviolet Light on Tin Weighted Silk

The effects of tin weighting and accelerated light aging using both unfiltered and filtered light on new silk were evaluated by examining changes in physical and chemical properties of the silk fabric. Control groups of both unweighted and weighted silk were not subjected to the accelerated light aging procedures and represent the original properties of unweighted and weighted silks respectively.

Changes (or lack thereof) in colour, stiffness, tensile strength, extension at break, energy to rupture, microscopic appearance, pH and chemical structure were monitored to determine the different effects of light on unweighted and weighted silk. Particular attention was paid to the differences in properties obtained after the silks were irradiated with light (ultraviolet plus visible light, and visible light only). These aging conditions represented the light a weighted silk would receive during its active life compared to the light a weighted silk would receive once it enters a museum environment as an artifact.

The results of the three-way analysis of variance on colour change (ΔE), flexural rigidity (stiffness), tensile strength, extension at break, and energy to rupture show that there were significant main effects of type of silk (unweighted/weighted), type of light (unfiltered/filtered), and length of exposure for all dependent variables. Table 11 summarizes the F-ratios from the three-way analysis of variance. For colour change, flexural rigidity, tensile strength, and extension at break, there were also significant interaction effects for all two-way interactions as well as the three-way interaction of silk type, light type, and exposure. The raw data from the physical testing of these five dependent variables are compiled in Appendix A-5.

Evaluation of Changes in Selected Physical Properties

Mass of Unweighted and Tin Weighted Silks

The mass of each of the silk fabrics was measured according to standard textile test method CAN/CGSB-4.2 No. 2 (Unit mass of fabrics). The mass of the unweighted,

Table 11

Summary of F-ratios from Three-Way Analysis of Variance on Silk Type, Light Type, and Exposure for Five Dependent Variables

Effect	ΔE	Stiffness	Tensile Strength	Extension	Energy
Main Effects:					
Silk Type	1559.90[illegible]**	976.147**	617.965**	189.170**	410.668**
Light Type	15693.630**	129.766**	2046.849**	1239.442**	986.713**
Exposure	1702.498**	42.337*	386.498**	257.034**	174.691**
2-way Interactions:					
Silk x Light	2229.913**	60.378**	89.239**	18.943**	0.016
Silk x Exposure	66.331**	27.029*	17.685*	7.246**	1.358
Light x Exposure	1400.969**	47.304**	256.980**	113.683**	74.813**
3-way Interaction:					
Silk x Light x Exposure	113.698**	33.319*	12.795**	13.921*	17.038*

* denotes an F statistic with a significance of $p < 0.01$

** denotes an F statistic with a significance of $p < 0.001$

washed silk purchased from Testfabrics was determined to be 34.3 grams per square meter. After tin weighting, the mass of the silk was measured as 57.3 grams per square meter. The increase in mass produced by weighting was thus calculated to be 67 %. In other words, the treated silk was determined to be 67 % weighted based on the original mass of the silk.

Colour Change

Colour measurements comprised the values for three coordinates in the CIELAB colour measurement system: lightness/darkness (L^*), red/green (a^*), and yellow/blue (b^*). The changes in these values were used to calculate total colour change in CIELAB units of five individual specimens for each treatment group according to the following equation: $\Delta E_{CIELAB} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The individual ΔL^*, Δa^*, and Δb^* values, as well as the individual ΔE values may be found in Appendix A-4.

The initial change in colour due to the weighting process (0.97 in CIELAB colour difference units, CDU) was calculated as the difference between the unexposed specimens of unweighted and tin weighted silk. The tin-phosphate procedure used for weighting the new silk caused a slight change in the colour of the silk, but the change was so small as to be visually imperceptible. According to Billmeyer and Saltzman (1981), colour differences of less than 1.0 CDU are not visually perceptible.

The ΔE values for the unweighted silk at various levels of exposure were calculated by using the unweighted, unexposed control as the product standard. However, due to the small colour change following tin weighting, the ***weighted,*** unexposed control was used as the product standard to determine the effect of unfiltered and filtered light on weighted silk. Thus, the mean ΔE values (in CIELAB CDU) represent the average total colour change of a particular treatment group from the appropriate original, unexposed silk (see Table 12).

Tin weighted silk showed a considerable colour change with accelerated aging

Table 12

Effect of Unfiltered and Filtered Light[†] on the Colour (ΔE_{CIELAB}) of Unweighted and Tin Weighted Silk Fabric

Exposure	Unweighted		Weighted	
	Unfiltered	Filtered	Unfiltered	Filtered
0	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}
10	2.07^{b}	0.87^{b}	4.88^{b}	0.63^{b}
20	2.59^{c}	1.04^{c}	6.04^{c}	0.72^{b,c}
40	4.54^{d}	1.14^{d}	8.89^{d}	0.80^{c}
80	6.31^{e}	0.99^{e}	10.94^{e}	0.37^{a}
160	8.12^{f}	1.05^{c}	13.32^{f}	0.59^{b}

[†] Unfiltered light = 280 to 750 nm; filtered light = 400 to 750 nm

[a,b,etc.] *in each column*, means with the same letter belong to homogeneous subsets (highest and lowest means are not significantly different) determined using Duncan's Multiple Range Test ($\alpha = 0.05$).

under the full spectrum of the xenon-arc lamp (unfiltered light), nearly twice as great as the change in unweighted silk (see Figure 3). The *weighted* silk had a rapid initial colour change of approximately 4.8 CDU in the first ten hours, then a slowing of the process so that the last 80 hours of exposure caused a change of only 2.4 CDU. The total colour difference after 160 hours exposure to unfiltered light was approximately 13 CDU. However, each interval of unfiltered light aging produced a statistically significant colour difference according to Duncan's Multiple Range Test ($\alpha = 0.05$).

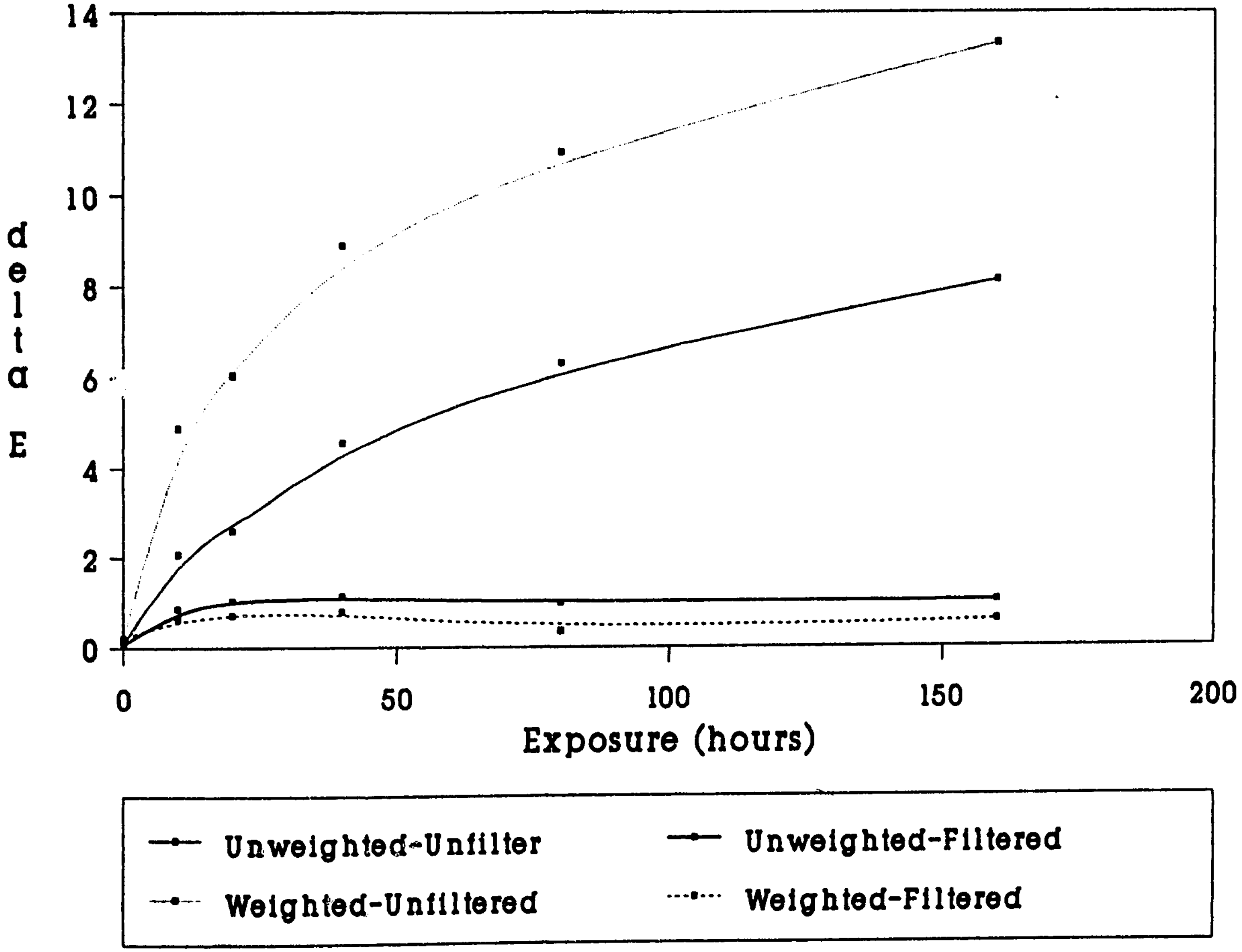

Figure 3. Total colour change of unweighted and tin weighted silk under increasing exposure to unfiltered and filtered light

The *unweighted* silk also showed noticeable colour change with exposure to unfiltered light from the xenon-arc lamp, although the change was 3.5 to 5 CDU less than the change in the *weighted* silk at each exposure. Again, the first ten hours produced the most rapid change (2 CDU). This rate slowed as exposure continued, with the last 80 hours causing an additional 1.8 CDU of change. The overall colour change of the unweighted silk after 160 hours of unfiltered exposure was 8 CDU, notably less than that of the tin weighted silk (13 CDU). As with the weighted silk, each increase in exposure time to unfiltered light caused a statistically significant colour difference according to Duncan's Multiple Range Test. The specimens which were covered with the ultraviolet filtering film received only the visible region of the radiation spectrum, as the harmful ultraviolet rays (wavelengths below 400 nm) were blocked by the filter. It was expected that the colour change, if any, of the filtered specimens would be much less than the unfiltered specimens.

Surprisingly, the changes in colour of both the unweighted and weighted silks under filtered light were statistically significant after just ten hours and increased with exposure time. The colour change after 160 hours of exposure was 1 CDU or less for both types of silk. The change in colour produced under filtered light and measured in the colorimeter was not sufficient to be visually perceptible, since colour changes of less than 1 CDU are not visible (Billmeyer & Saltzman, 1981). While statistical analysis indicates that there was a significant colour change with each increasing interval of exposure to filtered light, these changes are not of practical importance since they would not be visible.

In addition to total colour difference measurements (ΔE), the coordinates for the lightness/darkness, red/green, and yellow/blue components of colour in the CIELab* colour measurement system can indicate important components of colour change. When yellowing is the main visual colour difference, examination of the b* coordinates may be useful. The b* coordinate designates yellowness (+b*) or blueness (-b*). Increasing positive values of b* indicate that a fabric is becoming more yellow.

Although the Δb^* values of the specimens were not analyzed statistically, trends among the individual measurements within and between treatment groups indicate yellowing of both unweighted and tin weighted silks under *unfiltered* light. Examination of the changes in the coordinates for yellow/blue (the Δb^*) values shows rising *positive* Δb^* values for increasing lengths of exposure time, confirming that the colour change in the unfiltered specimens was indeed yellowing.

In an earlier study, Halvorson (1991) evaluated the total colour change (ΔE_{CIELAB}) of parylene C-coated silk fabrics with exposure to simulated daylight, filtered and unfiltered. The control groups, which were uncoated, showed similar colour change behavior as the unweighted and weighted silks in the present study. The weighted silk fabrics generally demonstrated greater colour change after exposure than did the unweighted silks. In addition, most of the specimens which received unfiltered light containing both visible and ultraviolet radiation had higher colour change values than the filtered specimens (visible light only).

Stiffness

The changes in the stiffness of the silk specimens was measured as flexural rigidity, or the resistance of the fabric to bending. Flexural rigidity is denoted in units of milligram-centimetres (mg-cm). According to ASTM D1388-64 (the standard test method for stiffness of fabrics), a change in the flexural rigidity of a fabric only becomes perceptible at 10 % percent change or greater.

The new tin weighted silk had a much higher initial flexural rigidity than the unweighted silk, as can be seen in Table 13. The untreated silk had a flexural rigidity of 21.1 mg-cm, and the tin weighted silk was 42.9 mg-cm, thus the weighted silk was twice as stiff as the unweighted silk. When handled, the weighted silk did have a noticeably crisper hand. Since the purpose of weighting was to restore body to the silk after removal of the sericin gum, the tin weighting procedure used to weight the new silk for this research was successful in achieving this increase in body and stiffness.

With exposure to *unfiltered* light, the stiffness of the tin weighted silk experienced a slight drop from 42.8 to 38.0 mg-cm (11%) after the first ten hours of exposure. The increase in stiffness of the weighted silk after 40 and 80 hours of unfiltered light was significant when compared to the stiffness at 0, 10, and 20 hours. After 160 hours, the mean flexural rigidity of weighted silk was significantly different from the control and all previous exposure groups. By the end of the full 160 hours of exposure, the stiffness had increased to 109.4 mg-cm which was 2.5 times greater than the unexposed silk.

Table 13

Effect of Unfiltered and Filtered Light[†] on the Stiffness of Unweighted and Weighted Silk Fabric

Exposure (hours)	Unweighted Unfiltered		Unweighted Filtered		Weighted Unfiltered		Weighted Filtered	
0	$21.06^{a,b}$	1.00^{N}	21.06^{a}	1.00^{N}	42.86^{a}	1.00^{N}	42.86^{a}	1.00^{N}
10	20.00^{a}	0.95	19.03^{b}	0.90	38.03^{a}	0.89	42.00^{a}	0.98
20	20.03^{a}	0.95	$17.60^{b,c}$	0.84	40.76^{a}	0.95	42.60^{a}	0.99
40	20.42^{a}	0.97	16.56^{c}	0.79	53.11^{b}	1.24	33.14^{b}	0.77
80	23.06^{b}	1.09	$17.96^{b,c}$	0.85	59.67^{b}	1.39	$39.85^{a,b}$	0.93
160	26.79^{c}	1.27	$19.41^{a,b}$	0.92	109.44^{c}	2.55	$39.04^{a,b}$	0.91

[†] Unfiltered light = 280 to 750 nm; Filtered light = 400 to 750 nm

[N] Data from previous column normalized by dividing by unexposed mean (unweighted or weighted as appropriate)

[a,b,etc.] *in each column*, means with the same letter belong to homogeneous subsets (highest and lowest means are not significantly different) determined using Duncan's Multiple Range Test ($\alpha = 0.05$).

Compared to tin weighted silk, the *unweighted* silk had a slower and less extreme increase in stiffness, rising from 21.05 mg-cm to 26.79 mg-cm (27 %) after 160 hours (see Figure 4). In the unweighted silk, only the specimens irradiated for 160 hours had a mean flexural rigidity that was significantly different from the unweighted, unexposed control. However, the group exposed for 80 hours increased significantly (9.5 %) from the lower exposure groups, but not from the control, as

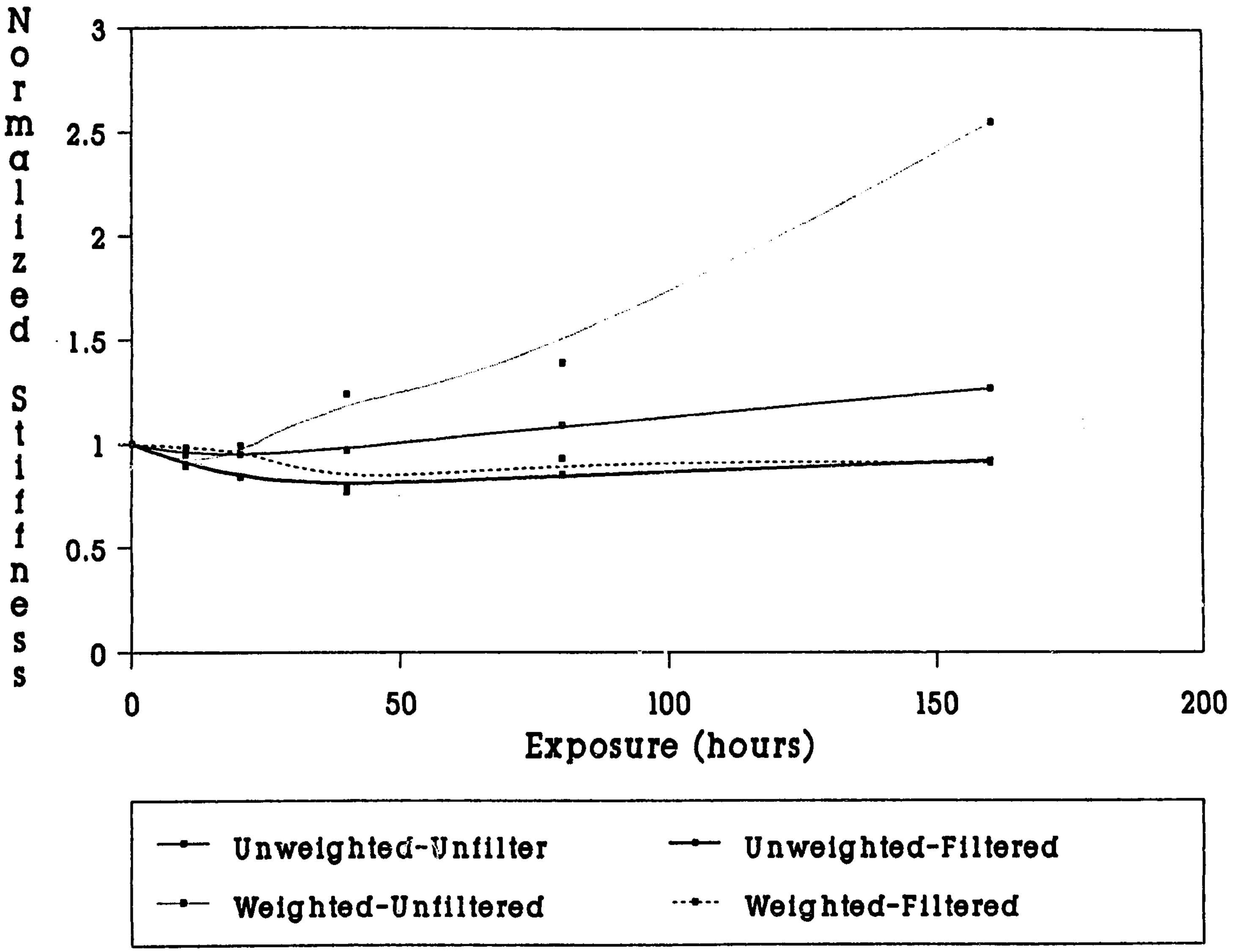

Figure 4. Changes in stiffness of unweighted and tin weighted silk under increasing exposure to unfiltered and filtered light

determined by Duncan's Multiple Range Test.

Under *filtered* light, there was virtually no change in stiffness for either the unweighted or the weighted silk. According to the standard test method, a 10 % change in flexural rigidity is just noticeable (ASTM D1388-64). The slight fluctuations in the stiffness of the silks under filtered lights would be imperceptible.

Changes in flexural rigidity of unweighted and weighted silks exposed to light also were evaluated by Halvorson (1991). After exposure to simulated daylight, the *weighted* silks showed only slightly higher increases in stiffness than the *unweighted* silks. The greatest changes in stiffness were observed for those specimens which received both visible and ultraviolet radiation, with very little change in the specimens which received *filtered* light

Tensile Strength

The initial change in tensile strength following tin weighting was calculatedas it was not known whether the weighting process itself had caused damage to the silk. The tensile strength decreased from 176 N to 163 N, thus the loss in strength associated with the tin weighting procedure was 7 %. While not a big change, this 7 % loss in strength means that the weighted silk had been degraded somewhat during the weighting process, which may have made the weighted silk more susceptible to light damage. In contrast to these results, are those of Roberts and Mack (1936), who found that the strength of silk decreased considerably after weighting with tin, and that increasing the amount of weighting applied produced even greater losses. Forbes and

Mack (1935) also described a significant loss of tensile strength after weighting. Details of the weighting processes used in these studies were not given.

The mean tensile strengths of unweighted and tin weighted silks measured after exposure to unfiltered and filtered light are shown in Table 14. The main effects of silk type, light type, and length of exposure were all significant for tensile strength, as determined by a three-way analysis of variance. Furthermore, the two-way interactions between silk type and light type, silk type and exposure, and light type and exposure were all significant. Duncan's Multiple Range Test ($\alpha = 0.05$) identified significant differences between the means of treatment groups and the appropriate controls.

New tin weighted silk exposed to *unfiltered* light underwent rapid and severe loss of strength. After only ten hours under the xenon-arc lamp, the weighted silk had lost 14 % of its original tensile strength. Another ten hours caused a further 16 % decline in strength. By the end of eighty hours of unfiltered light exposure, the tensile strength of the weighted silk was only 31 % of its original value. The final strength after the full 160 hours was 21.1 N, an 87 % decrease from the weighted, unexposed control.

Each prescribed increase in exposure time produced a statistically significant change in tensile strength of the tin weighted silk according to Duncan's Multiple Range Test. After each increase in exposure to unfiltered light, the mean of the treated specimens was significantly different from the control as well as from the previous exposure groups.

Unweighted silk showed a similar pattern of strength loss when aged under

Table 14

Effect of Unfiltered and Filtered Light[†] on the Tensile Strength (N) of Unweighted and Weighted Silk Fabric

Exposure (hours)	Unweighted				Weighted			
	Unfiltered		Filtered		Unfiltered		Filtered	
0	176.0^{a}	1.00^{N}	176.0^{a}	1.00^{N}	163.4^{a}	1.00^{N}	163.4^{a}	1.00^{N}
10	165.4^{b}	0.94	$172.7^{a,b}$	0.98	140.5^{b}	0.86	$157.0^{a,b}$	0.96
20	155.3^{c}	0.88	168.1^{b}	0.96	115.1^{c}	0.70	167.0^{a}	1.02
40	133.9^{d}	0.76	173.8^{a}	0.98	71.3^{d}	0.44	$157.8^{a,b}$	0.97
80	105.1^{e}	0.60	$173.3^{a,b}$	0.98	50.1^{e}	0.31	$148.0^{b,c}$	0.91
160	57.6^{f}	0.33	$171.2^{a,b}$	0.97	21.1^{f}	0.13	$137.9^{b,c}$	0.84

[†] Unfiltered light = 280 to 750 nm; Filtered light = 400 to 750 nm

^{N} Data from previous column normalized by dividing by unexposed mean (unweighted of weighted as appropriate)

$^{a,b,etc.}$ *in each column*, means with the same letter belong to homogeneous subsets (highest and lowest means are not significantly different) determined using Duncan's Multiple Range Test ($\alpha = 0.05$).

unfiltered light; however, the rate was much slower (see Figure 5). After ten hours, the mean tensile strength had decreased by only 6 %, as compared to the 14 % in weighted silk. A fifty per cent loss was not reached until somewhere between 80 and 160 hours. After the maximum 160 hours of exposure, the tensile strength of the unweighted silk had been reduced by 67 %. As with the weighted silk, each exposure group was significantly different from the unweighted control as well as from the other exposure groups.

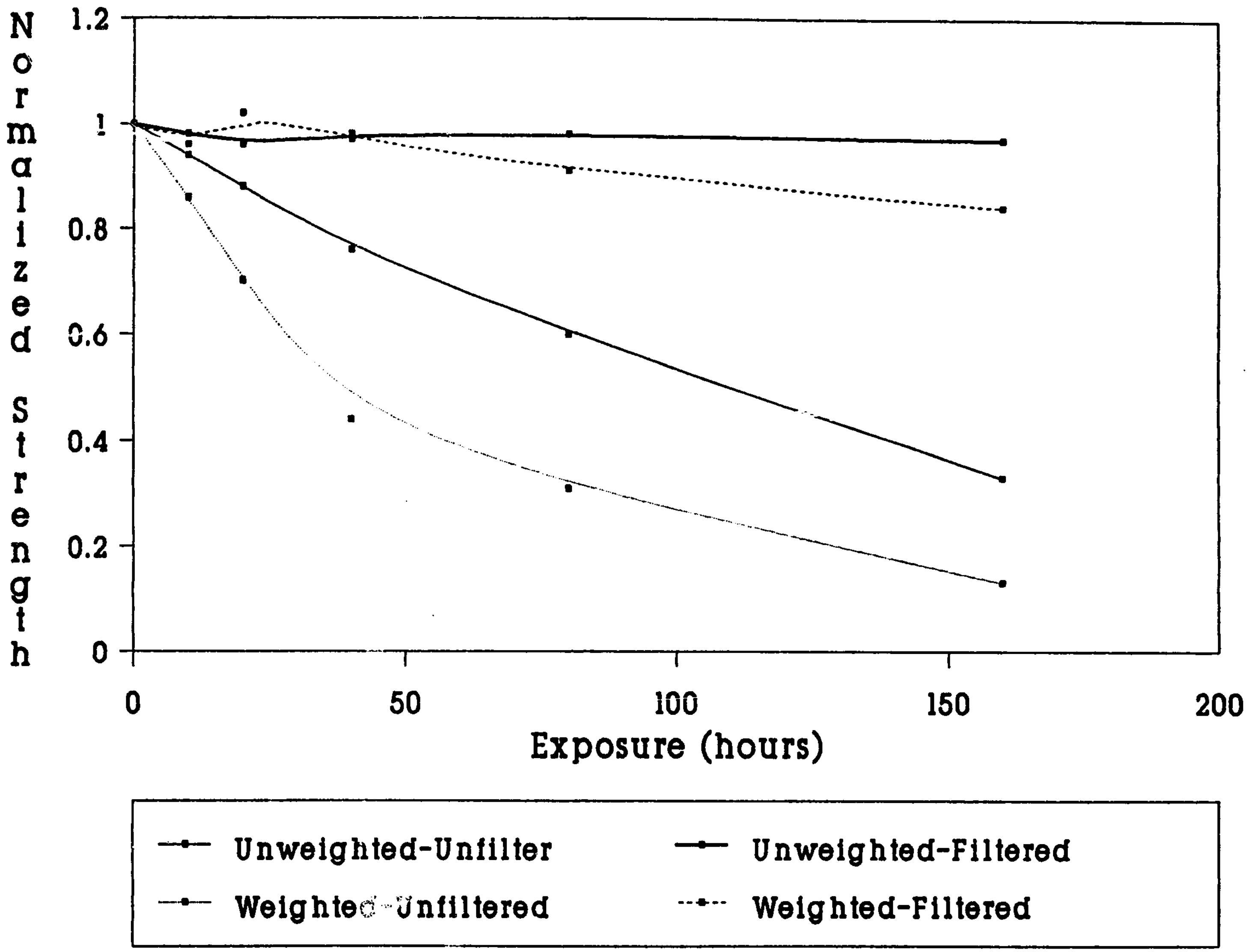

Figure 5. Changes in tensile strength of unweighted and tin weighted silk under increasing exposure to unfiltered and filtered light

In older studies on the effects of light on tin weighted silk, researchers observed similar results. Egerton (1948a) found that "tin-weighted silk loses strength at a much greater rate than unweighted silk on exposure to light" and that the "photochemical degradation of tin-weighted silk is due to oxidative attack on the silk fibroin" (p. 663). The researcher observed that tin weighted silk lost 70 to 80 % of its tensile strength when exposed to sunlight for one month, whereas pure undyed silk lost only 20 to 30 % of its original strength (Egerton, 1948b). Similarly, Roberts and Mack (1936) found that silk weighted 40 % to 50 % showed great losses in both tensile strength and tear resistance after exposure to indoor lights for four months.

More recently, Tsukada and Hirabayashi (1980) found that silk fibroin irradiated with ultraviolet radiation showed a rapid decrease in strength during the first ten hours of exposure. After measuring the degree of crystallinity as well as the orientation, these authors suggested that "the highly oriented β structure of the silk fibroin could be transformed into disordered β structure by the radiation of ultraviolet waves on the fibroin molecules" (p. 509).

The effect of *filtered* light on tensile strength was less dramatic than the effect of unfiltered light. Both unweighted and weighted silk showed small decreases in tensile strength as exposure time under filtered light increased, although the decrease for weighted silk was greater than that of the unweighted silk. After 160 hours, the *unweighted* silk lost only 3 %, while the tin weighted silk lost 16 % of its original tensile strength. For the tin weighted silk, only the mean tensile strengths after 80 and 160 hours were significantly different from the weighted control.

In a study by Halvorson (1991), weighted silks consistently suffered greater losses in tensile strength than unweighted silks after exposure to simulated daylight. When the ultraviolet region of the light spectrum was filtered out, the loss of strength was significantly reduced in both unweighted and weighted silks.

Extension at Break

Extension represents the percentage of its original length that a fabric specimen will stretch before it breaks. The mean values of the extension at break of the unweighted and weighted silk fabrics after exposure to light are listed in Table 15.

The extension at break of the new tin weighted silk was compared to that of the unweighted silk to determine the effect of the weighting process on extension. It was found that the extension at break changed very little, decreasing only 2 % after weighting. A large decrease in extension at break would indicate that the weighting had coated the fibres and "welded" them together. When such bonding between adjacent fibres occurs, the fabric becomes more rigid and loses extensibility similar to the effect of molecular crosslinking.

The effects of *unfiltered* light exposure on the extension of tin weighted silk were profound. After the first twenty hours of exposure, the breaking extension of the new weighted silk showed a linear decrease of 39 %. Continued exposure beyond 20 hours caused further decline, but less quickly, as a levelling of the slope of the extension curve can be seen in Figure 6. After a maximum 160 hours of exposure, the mean extension at break for the tin weighted silk was reduced to 22 % of the weighted,

Table 15

Mean Extension at Break (%) of Unweighted and Weighted Silks after Exposure to Unfiltered and Filtered Light[†]

Exposure (hours)	Unweighted Unfiltered		Unweighted Filtered		Weighted Unfiltered		Weighted Filtered	
0	25.2^{a}	1.00^{N}	25.2^{a}	1.00^{N}	24.5^{a}	1.00^{N}	24.5^{a}	1.00^{N}
10	22.8^{b}	0.91	24.6^{a,b}	0.98	19.5^{b}	0.79	23.3^{a}	0.95
20	20.7^{c}	0.82	23.2^{b}	0.92	14.9^{c}	0.61	23.9^{a}	0.97
40	17.4^{d}	0.69	24.6^{a,b}	0.98	9.9^{d}	0.40	23.2^{a}	0.95
80	12.1^{e}	0.48	23.9^{a,b}	0.95	8.1^{e}	0.33	19.8^{b}	0.81
160	7.3^{f}	0.29	23.5^{b}	0.93	5.5^{f}	0.22	18.1^{b}	0.74

[†] Unfiltered light = 280 to 750 nm; Filtered light = 400 to 750 nm

[N] Data from previous column normalized by dividing by unexposed mean (unweighted or weighted as appropriate)

[a,b,etc.] *in each column*, means with the same letter belong to homogeneous subsets (highest and lowest means are not significantly different) determined using Duncan's Multiple Range Test ($\alpha = 0.05$).

unexposed control.

Each period of exposure to *unfiltered* light produced a significant decrease in extension at break from the weighted control as determined by Duncan's Multiple Range Test; in addition, the breaking extension of the silk fabrics after each successive exposure period changed significantly from the previous extension.

Unweighted silk was similarly affected by unfiltered light, although the extension decreased more slowly. The mean extension at break of the silk after ten hours of

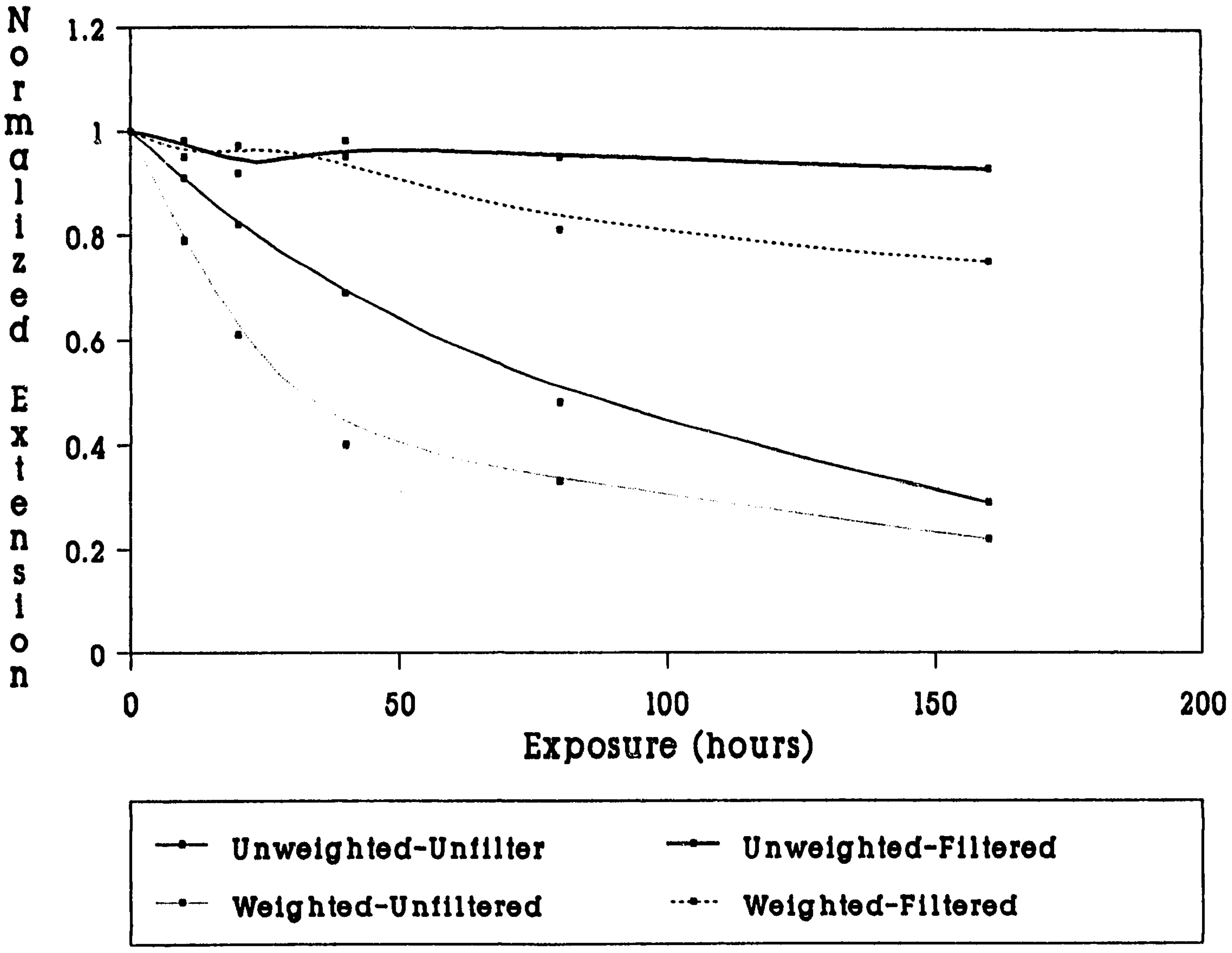

Figure 6. Changes in extension at break of unweighted and tin weighted silk after exposure to unfiltered and filtered light

exposure dropped only 9 %, but the decline continued more steadily. A comparison of the curves in Figure 6 for unweighted and weighted silk exposed to unfiltered light shows that the curve for the *unweighted* silk is nearly linear up to 40 hours, while the slope of the *weighted* silk line changes around 20 hours. It is interesting to note, however, how similar the breaking extensions of the unweighted and weighted silk are after 160 hours of exposure. The unweighted silk lost 71 % and the tin weighted silk lost 78 % of their original extensibilities.

As with the weighted silk, the values for extension at break of the *unweighted* silk subjected to *unfiltered* light were significantly different. Duncan's test showed that each treatment group was significantly different from the unweighted, unexposed control as well as from the other treatment groups.

Filtered light was less damaging to the extension properties of both unweighted and tin weighted silks. The tin weighted silk showed significant differences in extension at break only after 80 and 160 hours of filtered light (19 % and 26 %, respectively, of the unexposed fabric's extensibility). The unweighted silk showed less change, with a maximum decrease of 8 %. Significant changes in the unweighted silks were identified after 20 hours and 160 hours. (The low extension measured after 20 hours is unusual but does not indicate any particular trend). Halvorson (1991) also observed a greater decrease in extension at break of both unweighted and weighted silk fabrics when the ultraviolet region was included in the radiation than when the ultraviolet rays were eliminated.

These decreases in breaking extension are likely the result of molecular crosslinking. Crosslinking occurs when bonds form between adjacent molecules, and leads to increased stiffness and, eventually, brittleness. The decrease in extension at break (and increase in stiffness) of the unweighted and weighted silk fabrics after exposure to ultraviolet plus visible light indicates that crosslinking has occured in the silk fabrics.

Energy to Rupture

Energy to rupture, or work of rupture, is an indication of the toughness of a fabric, and combines tensile and extension properties into one value. Although not as common as these other two properties, it can be particularly useful when describing the overall durability of a fabric or the response of the fabric to a sudden load. The mean values for energy to rupture of the unweighted and weighted silk fabrics after exposure to light are listed in Table 16.

The energy to rupture of the new unweighted silk was 1.97 N-m. After weighting, this number dropped to 1.57 N-m, meaning that the conditions of weighting caused an approximate 20 % decline in the silk's energy to rupture. While the tensile strength and extension measurements showed little change, energy to rupture indicates that the silk has indeed become significantly less "tough". This discrepancy shows how energy to rupture might be a meaningful measure of a fabric's physical stability.

The energy to rupture of the *weighted* silk was greatly reduced after exposure to *unfiltered* light containing both visible and ultraviolet radiation. The first 20 hours reduced the work of rupture by 63 %, at which point the rate stabilized (see Figure 7).

Table 16

Energy to Rupture (N-m) of Unweighted and Weighted Silks Exposed to Unfiltered and Filtered Light

Exposure	Unweighted				Weighted			
(hours)	Unfiltered		Filtered		Unfiltered		Filtered	
0	1.97[a]	1.00[N]	1.97[a]	1.00[N]	1.57[a]	1.00[N]	1.57[a]	1.00[N]
10	1.68[b]	0.85	1.92[a,b]	0.97	1.03[a]	0.65	1.46[a]	0.93
20	1.39[c]	0.71	1.78[b]	0.90	0.58[a]	0.37	1.61[a]	1.02
40	0.93[d]	0.47	1.90[a,b]	0.96	0.18[b]	0.12	1.46[a]	0.93
80	0.43[e]	0.22	1.85[a,b]	0.94	0.09[b,c]	0.06	1.15[b]	0.73
160	0.10[f]	0.05	1.75[b]	0.89	0.03[c]	0.02	0.92[b]	0.59

[a] Unfiltered light = 280 to 750 nm; Filtered light = 400 to 750 nm

[N] Data from previous column normalized by dividing by unexposed mean (unweighted or weighted as appropriate)

[a,b,etc.] *in each column*, means with the same letter belong to homogeneous subsets (highest and lowest means are not significantly different) determined using Duncan's Multiple Range Test ($\alpha = 0.05$).

Every exposure period caused a significant change in the energy to rupture of the weighted silk relative to the unexposed weighted silk. However, the changes between 40 and 80 hours (0.18 to 0.09 N-m), and between 80 and 160 hours (0.09 to 0.02 N-m) were not statistically significant. The lack of statistical significance between the means of these last groups reflect the levelling off of the curve, where the rate had slowed to a point where additional exposure time caused little additional damage. The silk was very weak and brittle at this point.

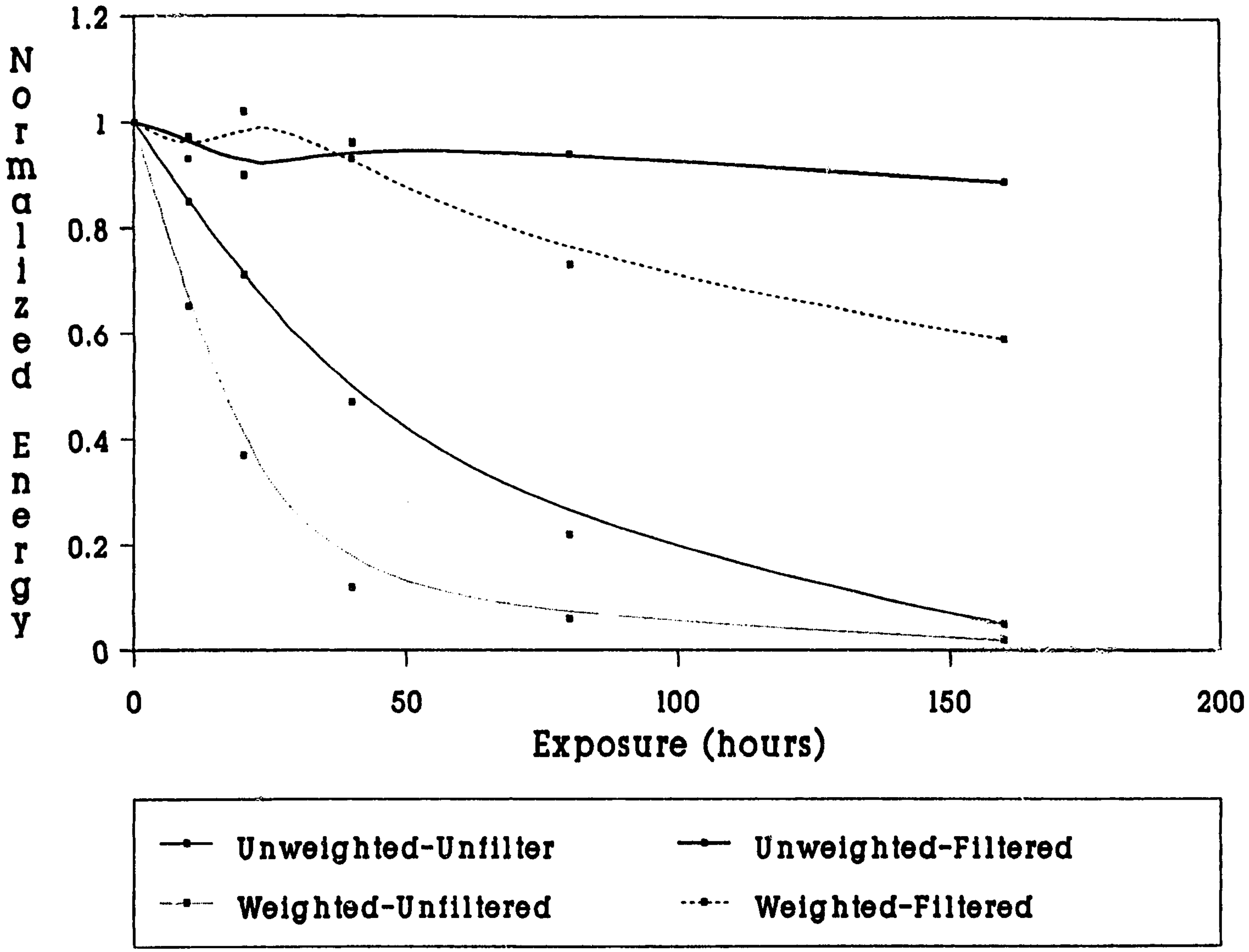

Figure 7. Changes in energy to rupture of unweighted and tin weighted silk after exposure to unfiltered and filtered light

The *unweighted* silk also suffered great losses in energy to rupture under unfiltered light from the xenon-arc lamp. Although the decline was not as steep during the first twenty hours as for the tin weighted silk, the reduction was consistent over time resulting in a large net decrease in energy to rupture. In fact, the mean energy to rupture of the *unweighted* silk after 160 hours of unfiltered light was 0.10 N-m, which was only slightly higher than that of the tin weighted silk (0.03 N-m) after the same exposure.

Duncan's Multiple Range Test again confirmed that each increase in exposure produced a statistically significant change in energy to rupture of unweighted silk. In the unweighted silk, the rate of decline in energy to rupture did not level off as early as it did in the tin weighted silk. Until at least 160 hours increasing the length of exposure to unfiltered light caused a significant change in energy to rupture.

Filtering out the ultraviolet component of the light reduced the loss in energy to rupture of the unweighted and weighted silks. However, the changes in energy to rupture after 160 hours of exposure to only visible light were notable, especially in the tin weighted silk. The *unweighted* silk lost only 11 % of its original energy to rupture, compared to the 41 % loss in the *weighted* silk. The latter figure represents a significant reduction in the toughness of the silk, meaning that even under filtered light the weighted silk became weak and brittle. In an earlier study, Halvorson (1991) also found that the energy to rupture of weighted silk experienced a noticeable decrease when exposed to visible radiation, while the change in unweighted silk was negligible.

Scanning Electron Microscopy

Fibre specimens from both unweighted and weighted silk fabrics exposed to 0 hours and 160 hours unfiltered and filtered light were examined with a scanning electron microscope. The fibres were inspected for differences in the surface appearance and shapes of fibre breaks (fracture morphology) after tensile testing. Plate 5 shows fibres from the unweighted, unexposed control group. These fibres are typical of normal silk fibres, most of which have a smooth, flat appearance and slightly uneven diameter. The surface debris visible on the fibres is often found in most fibres, and is usually due to salt and mineral deposits.

Plate 6 shows the new silk after being weighted with tin. These fibres are also relatively smooth, with few surface flaws. A few flaws such as fibrils peeling up from the surface are common and are not always indicative of damage from some external source such as weighting. However, the fibres in Plate 6 do show an unusual feature. Between the two central fibres, a coating has broken where it bridged the gap between the two fibres. While the coating did not appear on every fibre, it was found in many places in the small mounted fabric specimen. The coating may be the weighting agent which "spot welded" adjacent fibres where they were close together. No evidence of the coating was seen in the exposed, weighted fibres which were examined, nor in any of the unweighted specimens examined.

The unweighted and weighted silks that had been exposed to 160 hours of unfiltered and filtered light were also examined under SEM. Plates 7 through 10 show these fibres. To compare the ***unweighted*** silks, the fibres in Plate 7 exposed to unfiltered light have smooth surfaces with some surface debris, but no sign of fibrillation or damage. The fibres in Plate 8, which received only visible radiation, are similarly unblemished by cracking or fibrillation. It is difficult to attribute damage to specific treatment conditions based on microscopic appearance because it is difficult to select representative fibres for viewing. When specimens were examined, fibres from two mounted specimens of each silk and light type combination were examined under various magnifications, and a representative photograph was taken.

In the *weighted* specimens, the surfaces of the fibres exposed to ultraviolet plus visible light (unfiltered), show many irregularities (Plate 9). Many of the fibres have small fibrils peeling off, as well as deep grooves and blemishes. The weighted silk fibres shown in Plate 10 are typical of those exposed to filtered light for 160 hours. Few fibres showed damage like the fibrillation on the central fibre.

From the photographs shown in Plates 5 to 10, it is difficult to assess the effects of weighting on the surface appearance of silk. There are some indications that weighting left a visible coating on the fibres, and that the tin weighting agent enhanced the deterioration of fibre surfaces, especially fibrillation, under unfiltered light (see Plate 9). Contrary to this evidence, Ballard et al. (1986) concluded that weighted silk could not be distinguished from unweighted silk by its surface appearance using a scanning electron microscope.

Under high magnification (27,000X), particles were found on the silk specimens (unweighted and weighted) exposed to unfiltered light for 160 hours (see Plate 11). The largest of these particles was only 0.1 microns, which was too small to identify with energy dispersive x-ray analysis. (A typical silk fibre is approximately 10 microns). The particles are likely mineral deposits picked up during accelerated aging in the Weatherometer. None of the unexposed specimens nor those which were aged with filtered light appeared to contain this debris when examined. Plate 12 shows the surface of a weighted, *filtered* specimen under high magnification, with no visible debris. Halvorson (1991) also observed that surface debris appeared on clean silk fibres after accelerated aging (without a filter) in the Atlas Weatherometer which she attributed to mineral deposits.

The shapes of the fibre fractures among the specimens shown in Plates 5 through 10 were also examined. (These breaks resulted from tensile testing). The appearance of broken fibre ends may indicate differences in fibre structure (Hearle et al, 1989). Bresee and Goodyear (1986) used the classification system developed by Hearle et al. specifically to study the fractography of historic silk fibres. Plates 13 and 14 show representative tensile and brittle fractures. As with the earlier photos, many fibres were examined before a typical break was selected.

The unweighted, unexposed fibre in Plate 13 shows the typical shape of a tensile break according to the classification of breaks developed by Hearle et al. (1989). In contrast, the break in Plate 14 is more consistent with a *brittle* tensile fracture, with a relatively flat, broken end. This fibre was tin weighted which increased the stiffness of the fabric, and also decreased its energy to rupture, which together can translate into brittleness of the fibres.

Brittle tensile fractures, similar to the one shown in Plate 14, also were noted in the *unweighted* specimens that had received 160 hours of exposure. Since the stiffness of this fabric was significantly higher than the unexposed control, the fibres likely were crosslinked during exposure to unfiltered light. High levels of crosslinking decrease extensibility which results in embrittlement of the fibres (Bresee, 1986; Grattan, 1978). The *weighted* specimen irradiated with unfiltered light showed brittle fractures at its fibre ends similar to the one in Plate 14. When unweighted and weighted silks were exposed to *filtered* light, however, more irregularly shaped breaks were typical and there was more variation from fibre to fibre.

Selected Chemical Properties

Changes in physical properties often are the observable manifestations of changes that have occurred at the molecular level. To determine the chemical changes that occurred in new silk after weighting and after various levels of light exposure, two chemical properties were investigated. The pH of the aqueous extract of the silk after each treatment was measured. The pH of a fabric's extract may indicate that the fabric, or an additive on the fabric, is acidic or alkaline. Fourier transform infrared spectroscopy (FTIR) was performed on fibre samples from the unweighted and weighted controls, as well as on specimens exposed to unfiltered and filtered light.

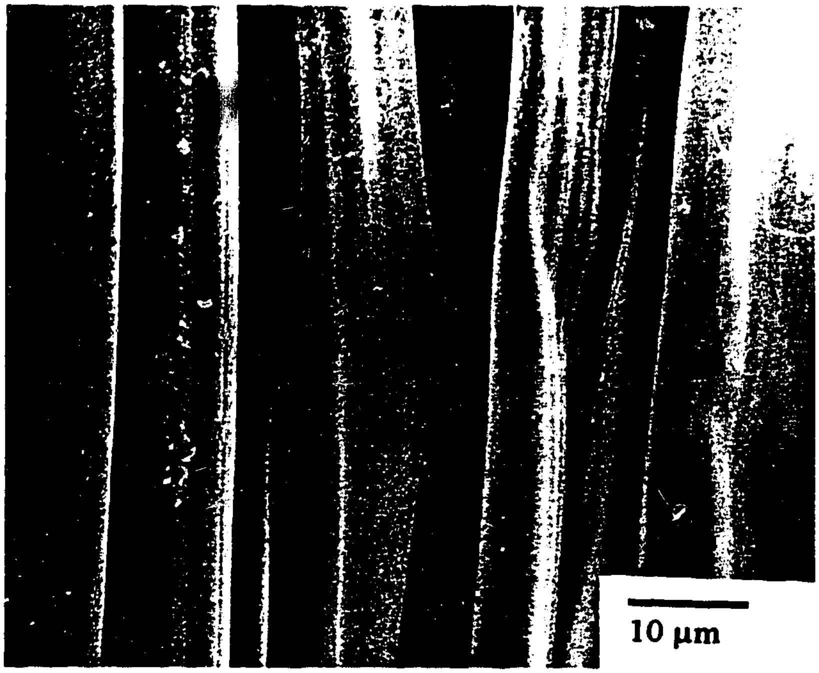

Plate 5. Unexposed, unweighted silk fibres, with smooth surface and slightly uneven diameter.

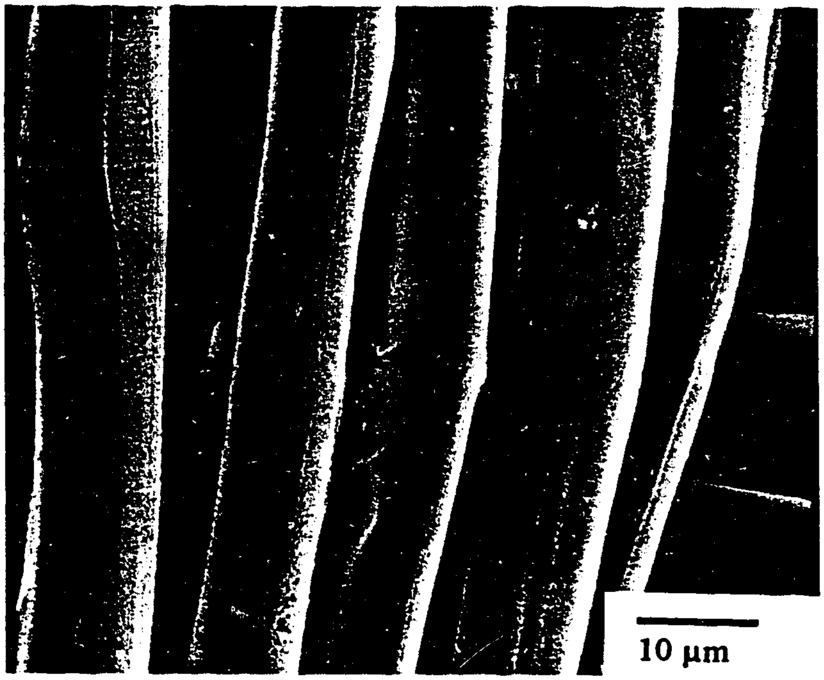

Plate 6. Unexposed, tin weighted silk fibres, showing break in coating which joins two central fibres.

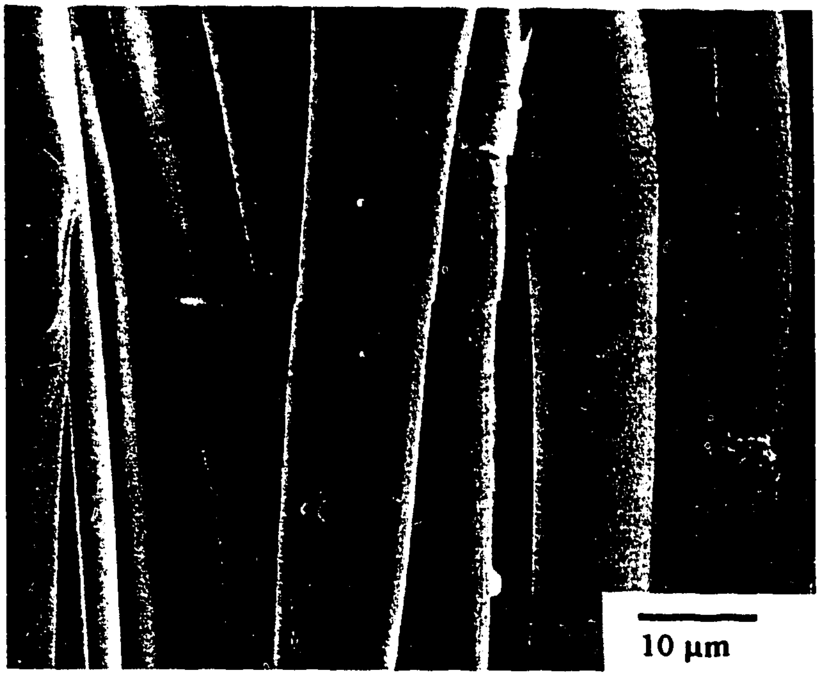

Plate 7. Unweighted silk fibres exposed to 160 hours of visible plus ultraviolet radiation, with little damage.

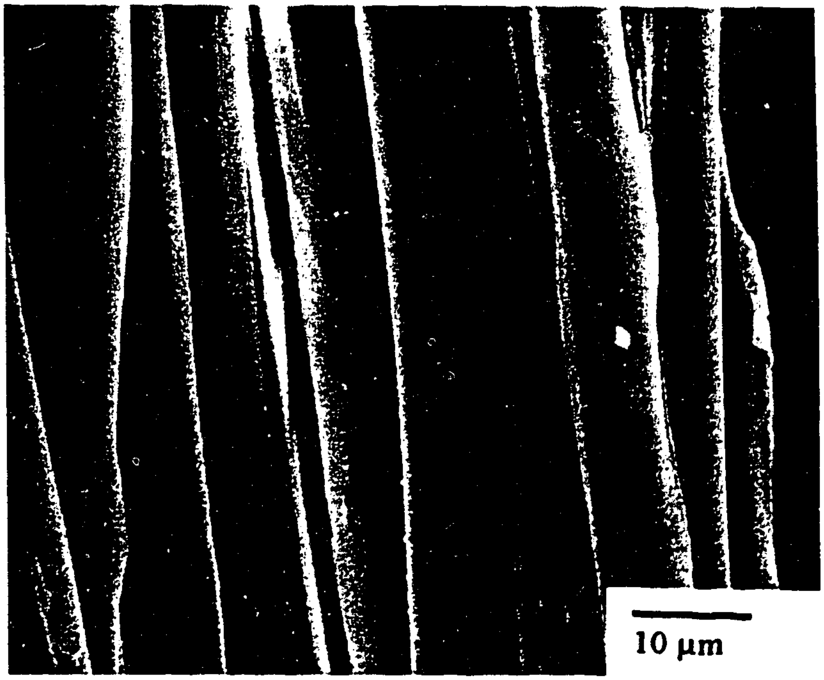

Plate 8. Unweighted silk fibres exposed to 160 hours of visible radiation only, with smooth, undamaged surfaces.

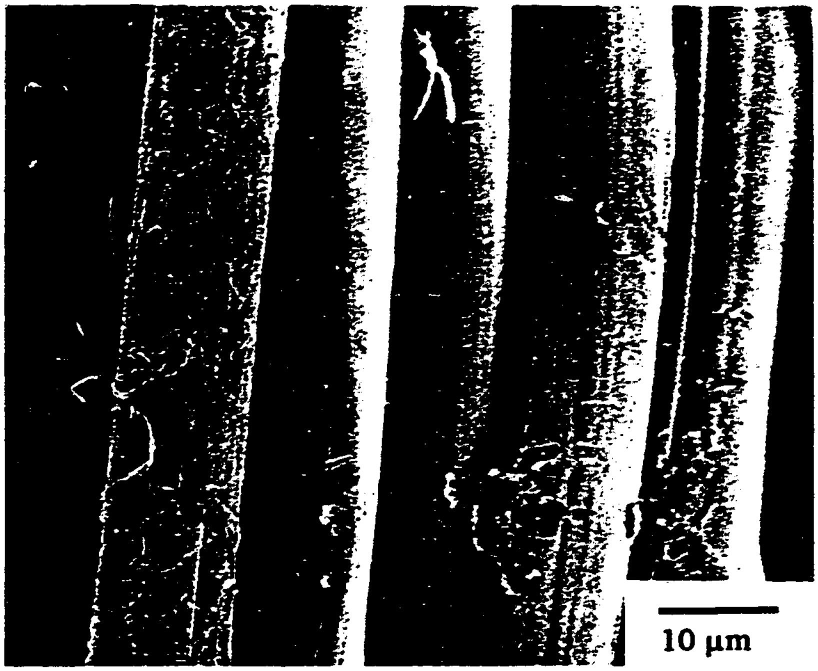

Plate 9. Tin weighted silk fibres exposed to visible plus ultraviolet radiation, showing fibrillation and surface debris.

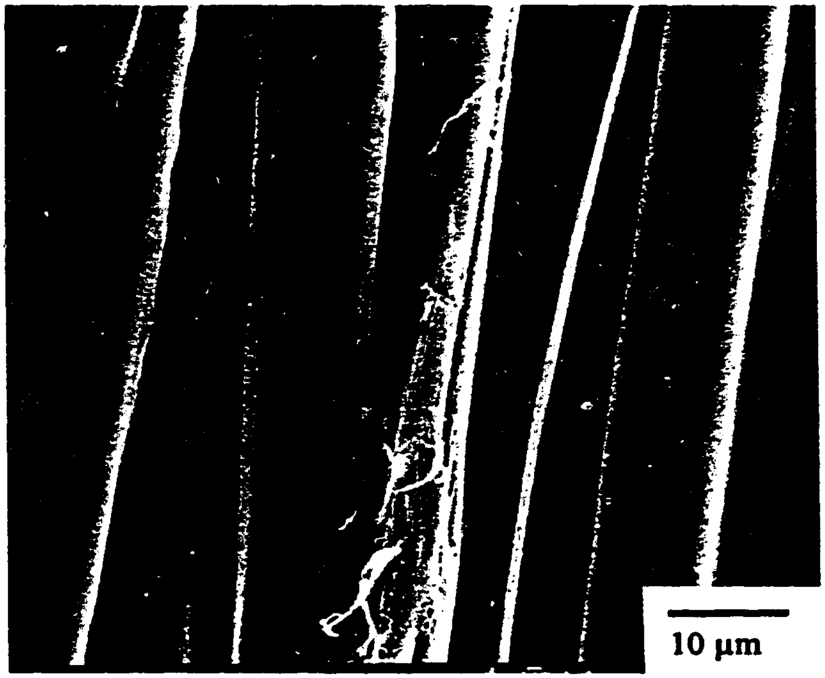

Plate 10. Tin weighted silk fibres exposed to 160 hours of visible radiation only, showing occasional fibrillation.

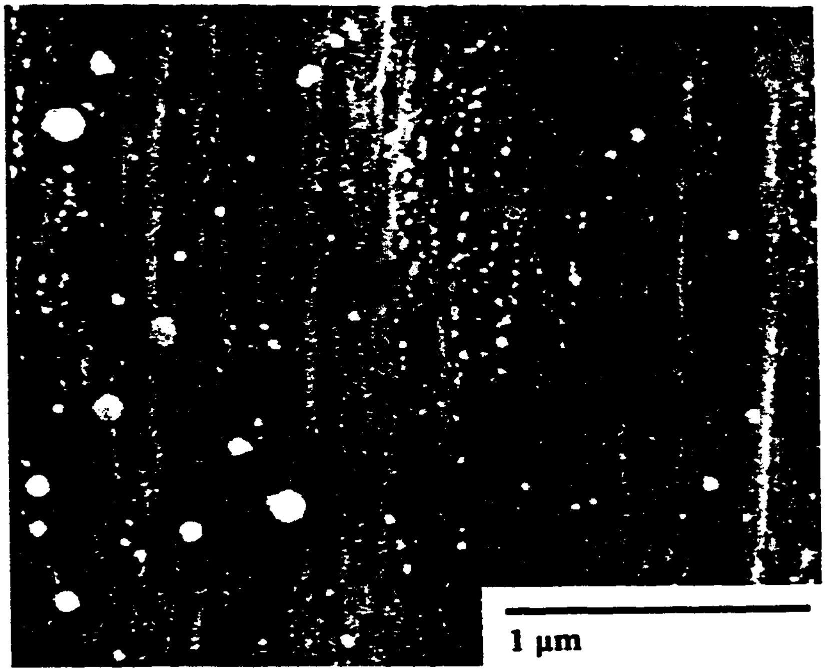

Plate 11. Surface of tin weighted silk exposed to 160 hours of unfiltered radiation, showing surface debris deposited during accelerated aging.

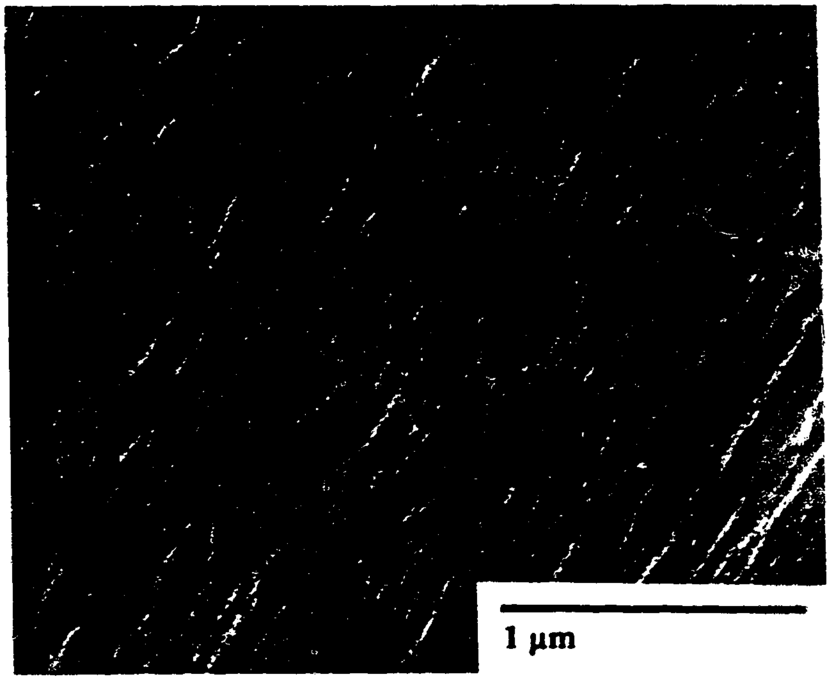

Plate 12. Surface of unexposed, tin weighted silk, showing absence of surface debris.

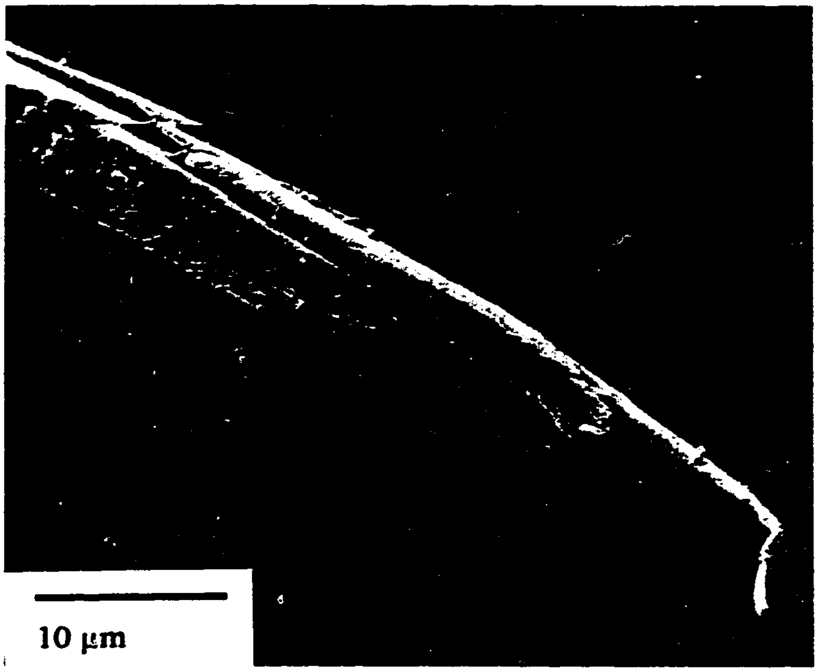

Plate 13. Unexposed, unweighted silk fibre end, showing tensile fracture due to tensile testing.

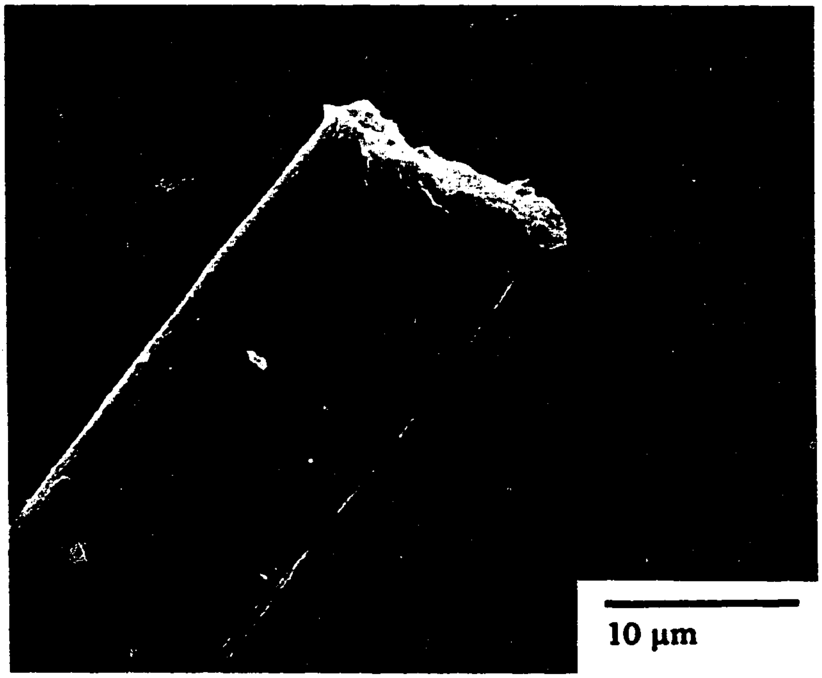

Plate 14. Unexposed, tin weighted silk fibre end, showing brittle fracture due to tensile testing.

pH

The pH values of the aqueous extract of silk specimens exposed to unfiltered and filtered light are given in Table 17. Measurements could not be made on sufficient a number of specimens to allow for statistical analysis, but the values themselves may indicate trends in pH changes.

From the table, it is clear that the weighting process had a great impact on the pH of the new silk. After the selected tin weighting procedure was applied, the pH of the washed silk, which was fairly neutral (6.83), became quite alkaline (9.46). This change in pH is likely due to the high alkalinity of the last sodium phosphate bath (9.80). The high initial alkalinity of the tin weighted silk likely affected its degradation by ultraviolet and visible light.

Accelerated aging with unfiltered light had a small effect on the pH of the unweighted silk, as it dropped only from 6.8 to 6.3 after 160 hours. However, when the tin weighted silk was exposed to unfiltered light, the initial pH of 9.5 decreased noticeably to 8.4 after 160 hours. (This change represents a tenfold decrease in alkalinity because the scale of pH is a logarithmic scale). Increasing exposure to filtered light had little effect on the pH of either unweighted or tin weighted silks.

The weighted silks exposed to unfiltered light were the only specimens with pH measurements that consistently decreased. Since the *unweighted* silk did not decrease in pH as much as the *weighted* silk, the greater decrease must be due to the tin weighting compound. The action of ultraviolet light on tin weighted silk created a source of acidity that worked to neutralize the alkalinity somewhat.

Table 17

pH of the Aqueous Extract of New Silk After Weighting and Accelerated Aging with Unfiltered and Filtered Light[†]

Exposure	Unweighted				Weighted			
(hours)	Unfiltered		Filtered		Unfiltered		Filtered	
	pH	$[H_3O^+]$[•]	pH	$[H_3O^+]$	pH	$[H_3O^+]$	pH	$[H_3O^+]$
0	6.83	1.5×10^{-7}	6.83	1.5×10^{-7}	9.46	3.5×10^{-10}	9.46	3.5×10^{-10}
10	7.26	5.4×10^{-8}	7.20	6.3×10^{-8}	9.35	4.5×10^{-10}	9.60	2.5×10^{-10}
20	6.63	2.3×10^{-7}	6.62	2.4×10^{-7}	9.23	5.9×10^{-10}	9.58	2.6×10^{-10}
40	6.71	1.9×10^{-7}	7.15	7.0×10^{-8}	9.19	6.5×10^{-10}	9.41	3.9×10^{-10}
80	6.49	3.2×10^{-7}	6.63	2.3×10^{-7}	8.87	1.0×10^{-9}	9.36	4.1×10^{-10}
160	6.26	5.5×10^{-7}	7.30	5.0×10^{-8}	8.37	4.0×10^{-9}	9.49	3.2×10^{-10}

[†] Unfiltered light = 280 to 750 nm; Filtered light = 400 to 750 nm

[•] concentrations of H_3O^+ in mol/L

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy was performed on specimens from the unweighted and tin weighted control groups and 160 hour exposure groups. Differences in the absorption spectra were expected to indicate chemical changes that took place after weighting and/or after exposure to unfiltered and filtered light. Of particular interest were the changes in the concentration of terminal amino groups ($-NH_2$), since an increase in these groups would indicate that the peptide bonds along the main fibroin chain had been broken.

The spectra for the six specimens analyzed are shown in Figure 8. The $-NH_2$ stretch region falls approximately between wavenumbers 3000 cm^{-1} and 3600 cm^{-1}. While there appeared to be a change in this region, visible as a levelling off of the peaks for the three weighted silk specimens, this region overlaps the absorption region for water. Further analysis showed that this change was indeed the result of higher water content in the weighted specimens.

Other changes were noticed between the spectra for unweighted and tin weighted specimens, but the differences could not be explained conclusively. A subtraction spectrum was produced by subtracting the spectrum for the unweighted control from spectrum for the weighted control at a 1:1 ratio. In this new graph, there was in fact a peak for water that would have caused the levelling off in the region of 3000 - 3600 cm^{-1}. Another significant peak occurred around wavenumber 1700 to 1800 cm^{-1}. This peak could not be definitively matched to the standard spectra for any functional group, but falls in the region of both phosphate and carbonyl groups. There was another important peak at 1100 to 1200 cm^{-1}, in the region of certain tin compounds as well as some of the phosphates.

Unfortunately, the results of the FTIR analysis were not conclusive. Differences in the infrared absorbency of the unweighted and weighted silk fibres were observed, but without knowing the exact composition of the weighting compound that remained in the fibres, the groups causing these differences cannot be positively identified.

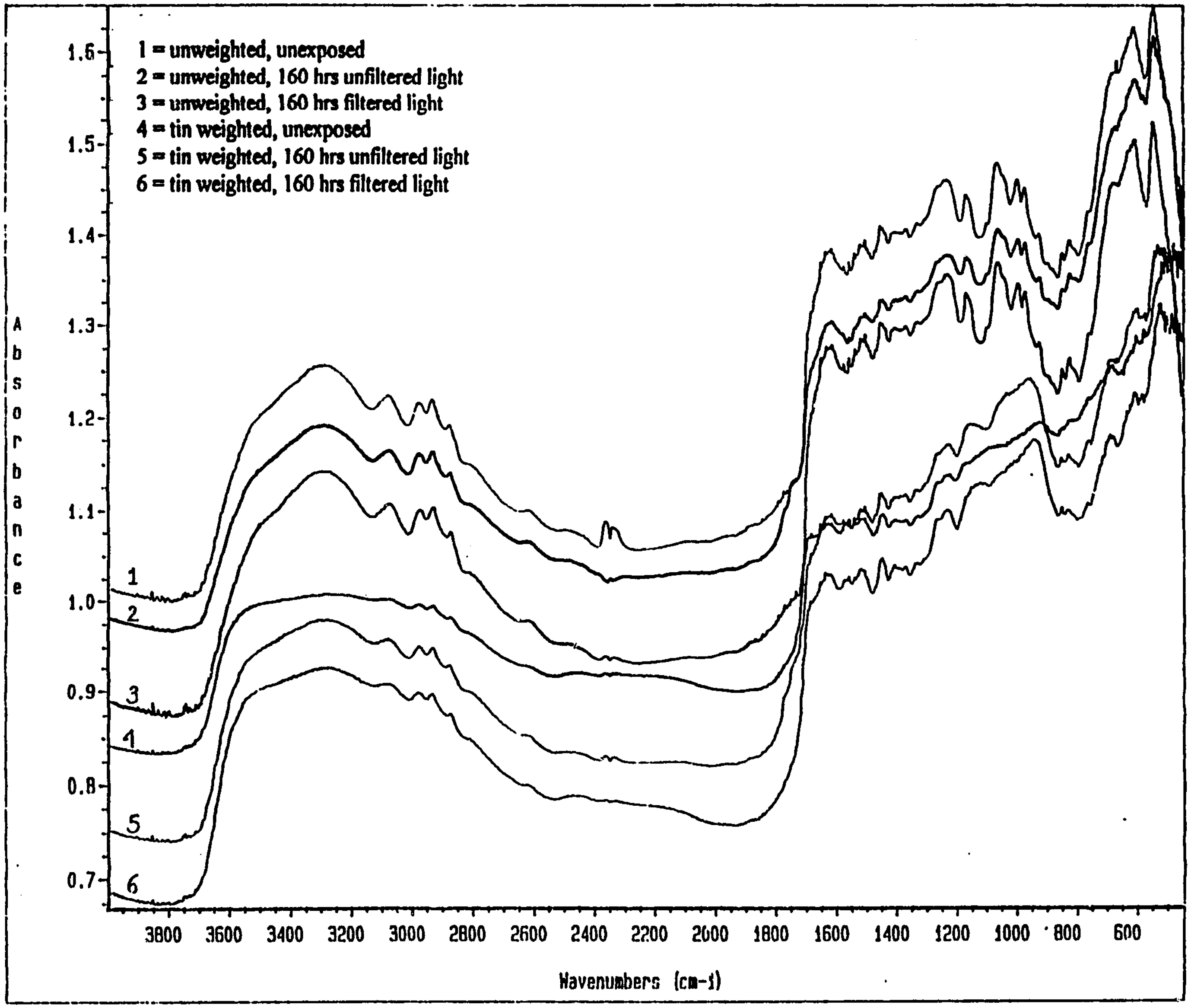

Figure 8. Infrared absorption spectra for unweighted and tin weighted silk produced by Fourier transform infrared spectroscopy

Discussion of Results from Part II

In this part of the research, the effects of tin weighting and of increasing exposure to visible and ultraviolet radiation on selected physical and chemical properties of unweighted and tin weighted silk were studied. Changes in colour, stiffness, tensile strength, extension at break, energy to rupture, and pH were measured, and changes in microscopic appearance and chemical properties were analyzed. Statistical analysis of the results was performed where possible to define significant differences among the various treatment groups. Increasing exposure to unfiltered light produced significant deterioration of both unweighted and tin weighted silk, but the reaction of the weighted silk was consistently more extreme. When ultraviolet radiation was eliminated, the deterioration of both types of silk by light was greatly reduced.

The mechanism of the photodegradation of silk is complex. It is known, however, that ultraviolet radiation is more harmful than visible radiation (Howard & McCord, 1960; Robson, 1985; Thomson, 1986). The shorter wavelengths of ultraviolet rays have more energy than radiation from the visible region, and therefore are capable of causing significant changes in the physical and chemical properties of silk (Feller, 1994). Exposure to ultraviolet and visible radiation has been observed to produce colour change (yellowing), fading of dyes, embrittlement, and loss of strength.

Tin weighted silk suffers these same effects, but to greater extremes than unweighted silk. While the initial changes in the properties of silk after weighting were small, the differences after exposure to ultraviolet and visible radiation were amplified. This phenomenon suggests that tin compound deposited in the silk during weighting acts as a *photosensitizer*. A photosensitizer catalyzes the degradation of a material under light by absorbing additional high energy radiation and then passing the energy on to the material (Feller, 1994). The absorbed energy that is passed on to the primary material (in this case silk) may be dissipated through the breaking of bonds, resulting in degradation of the material.

Metallic elements are known to catalyze the degradation of polymers, including fibres. "A metal complex is expected to initiate the chain of autoxidation due to both the activation of the oxygen molecule and the decomposition of hydroperoxide" (Kamiya & Niki, 1978, p.118). The weighting of silk, which leaves a metallic compound in the fibres (in this case a tin compound), acts as an initiator in the degradation process.

The direct breaking of chemical bonds by absorbed energy (photons) is called *photolysis* (Feller, 1994; Kambe, 1978). In photolysis, chemical changes are caused by the absoprtion of light rays of "sufficiently high energy content to change the molecular structure of the irradiated material" (Howard & McCord, 1960). Tensile strength, extension and energy to rupture are affected when a sufficient number of peptide bonds along the main polymer chain are broken to cause break down of the molecule.

After 160 hours of irradiation with ultraviolet and visible light, tin weighted silk lost 87 % of its tensile strength, the breaking extension decreased by 78 %, and energy to rupture decreased by 98 %. The unweighted silk showed a 67 % loss of tensile strength, 71 % decrease in extension at break, and 95 % decrease in energy to rupture.

These results indicate that photolysis of the fibroin in both unweighted and tin weighted silk occurred with exposure to ultraviolet radiation.

When bonds in the fibroin molecule are broken and reformed, the structure of the fibroin changes, as does its absorption of visible light, and a colour change results. Colour change and yellowing are also associated with oxidation of the functional groups on the amino acid side groups of the fibroin polymer (Kamiya & Niki, 1978).

Embrittlement of fabrics is related to crosslinking, whereby " previously unconnected segments of polymer are connected by formation of new covalent bonds between them" (Bresee, 1986, p. 42). If broken bonds (often free radicals) reform between adjacent molecules, the new crosslinks lead to increased stiffness or brittleness, and a decrease in extensibility. Exposure to light often leads to this effect, as "crosslinking is an important type of reaction in photo- and high energy radiation degradation" (Mita, 1978, p. 249). The increase in stiffness and decrease in extension at break of the unweighted and weighted silk fabrics after exposure to ultraviolet radiation indicates that crosslinking occured in the silk fabrics.

Crosslinking and main chain scission by photolysis may occur simulaneously, to produce loss of strength, a loss of extensibility, and increased stiffness (Jellinek, 1978). However, Schabel and Kiwi (1978) indicate that crosslinking occurs only in the absence of oxygen, and that when oxygen is present, the primary result is main chain scission due to autoxidation.

Examination of the results from Part II indicate significant changes in the physical properties of both unweighted and weighted silk under unfiltered light. Unfortunately, the results of FTIR did not show how the structure of the silk had changed as a result of tin weighting or irradiation. Other analytical techniques, such as amino acid analysis, may have shown changes in the silk at the molecular level better.

The results of the specimens exposed to filtered light (visible radiation only) show smaller changes, if any, in the physical properties of the silk. There is no known level of light which does not cause some damage to organic materials (Giles & McKay, 1963). Thus, these results simply indicate that the exposure periods to visible radiation alone were not long enough to produce noticeable changes in the physical properties of the silk specimens.

Museum conservators have long been aware of the effects of ultraviolet radiation on organic materials and the use of ultraviolet filters has become standard practice. The results of this research emphasize the importance of filtering all museum light sources in order to reduce damage to artifacts. However, prolonged exposure even to *filtered* light does cause some deterioration of the physical properties of silk, with tin weighted silk being more susceptible to light damage than unweighted silk.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

Summary

Weighted silk has long been recognized as a particular challenge to textile conservators. While silk artifacts from much earlier periods have remained in fair condition, many weighted silks from the late nineteenth and early twentieth centuries have not fared as well. The presence of weighting in a silk artifact must be identified not only because it is an important consideration in treatment and storage decisions, but also because weighted silk contains documentary evidence of historical developments in the silk industry.

Identification tests must meet certain criteria to be useful to conservators. First and foremost, the test must be either non-destructive, reversible, or require that only a minute sample be removed, so that the physical integrity of the artifact is not jeopardized. Secondly, the test must be quick to produce results and easy to perform. The demanding schedule in many conservation laboratories often precludes prolonged testing. Furthermore, the test should be inexpensive in terms of equipment and reagents. Three tests which fit these criteria were evaluated in the first part of this research project.

Once identified, the care of weighted silk is the next concern. Even if satisfactory treatments for the consolidation of highly degraded silk are developed, preservation efforts will continue to include preventive conservation. Further damage to weighted silk artifacts can only be prevented, or at least delayed, if the effects of such factors as light are well understood.

When studying the effects of light on a class of artifacts, it is important to consider the type of light to which the artifacts would have been or are exposed. Artifacts in a museum usually are displayed under controlled conditions of exposure with filters to eliminate the ultraviolet portion of natural and artificial light sources. This precaution generally prolongs the life of the artifact. However, the conditions to which an artifact was exposed before entering the museum are varied and seldom controlled or known. By including both filtered and unfiltered light (containing the ultraviolet region), the effects of light on a class of artifacts can be represented as experienced within and outside of the museum.

Part I: Identification and Characterization of Historic Weighted Silks

Identification of Weighting in Donated Samples of Silk

The first objective for this research was to test the validity of three simple, non-instrumental techniques for identifying the presence of metallic weighting agents in historic silk artifacts. In order to meet that objective, three identification tests for weighted silk were evaluated for their validity when used on historic silks. The results of the burning test, flame colour test for tin, and potassium ferrocyanide spot test for iron were compared to the results of energy dispersive x-ray analysis (EDXA). All three tests were found to be valid when more than a trace amount of the weighting agent was present.

In the burning test, a yarn is burned so that its characteristics in a Bunsen flame can be observed. When weighted silk is burned, the silk fibres burn away, leaving the metal coating as a skeleton of the original shape of the weave or yarn. The metallic skeleton glows red when held in the flame. The flame colour test for tin produces a blue glow around a cold test tube when the test tube is swirled in a solution of hydrochloric acid, zinc metal, and a small piece of the weighted silk fabric, then held in a Bunsen burner flame. In the spot test for iron, a blue colour is produced on the iron (III) coated silk fabric when the potassium ferrocyanide test solution is applied.

Characterization of Silk Artifacts from the Clothing and Textiles Collection

The second objective in conducting the research was to characterize the visual appearance of weighted silk degradation and to identify patterns of damage that are common to historic weighted silk artifacts. Thus, forty-seven artifacts (womens' dresses, c. 1880 to 1920) from the Clothing and Textiles Collection at the University of Alberta were examined in order to identify patterns of degradation that are common to historic weighted silks. The results of this survey of artifacts showed that all weighted silks do not fit into one particular category based on overall condition, but that many weighted silks do show similar forms of damage. Visual features such as extensive splitting throughout the fabric may be indicative of weighting. However, further analysis or testing is necessary to be able to conclude decisively that a silk is weighted.

Part II: Effects of Visible and Ultraviolet Light on Tin Weighted Silk

Initial Effect of Tin Weighting

The third objective of the research was to examine a selected tin weighting procedure for its immediate effect on silk, so a tin-phosphate weighting procedure, based on a historic method, was applied to new silk and several physical and chemical properties were evaluated. The weighting process had a significant effect on stiffness, tensile strength, extension, and energy to rupture before the silk was subjected to any accelerated aging.

Weighting the silk caused an imperceptible, yet measurable colour change, but nearly doubled the stiffness of the silk. Tensile strength and extension at break showed negligible changes, with only a 7 % loss of tensile strength and a 2 % decrease in extension at break. However, there was a significant decrease in the energy to rupture of the silk after weighting (20 %). Changes in the surface appearance of the new tin weighted silk, if any, were difficult to distinguish under the scanning electron microscope.

The pH of the silk after tin weighting was alkaline (9.5) compared to the neutral pH of the unweighted silk (6.8). Chemical changes due to the presence of the weighting agent were observed with Fourier transform infrared spectroscopy. Changes in the infrared absorbencies of the silks in the regions of 1100 to 1200 cm^{-1} and 1700 to 1800 cm^{-1} were evident but could not be defined. These changes in infrared absorbance indicate that the fibroin molecule had undergone chemical changes, but the nature of the changes could not be determined.

Effect of Visible and Ultraviolet Light

The last objective of the research was to determine the different effects of visible and ultraviolet light on selected physical and chemical properties of unweighted and tin weighted silk. New unweighted and tin weighted silks were exposed to visible and visible plus ultraviolet radiation and changes in several physical and chemical properties were evaluated.

Although the tin weighted silk had already degraded somewhat before exposure to aging treatments, the differences between the unweighted and weighted silks were amplified with accelerated aging under ***unfiltered*** light. (Unfiltered light contained both visible and ultraviolet radiation). The magnitude of the changes in physical properties such as colour, stiffness and tensile strength that occurred in tin weighted silk with exposure to unfiltered light were consistently greater than the changes in the unweighted silk.

The results of the aging process invariably showed that the tin weighted silk underwent more drastic changes than the unweighted silk after the full 160 hours of exposure to unfiltered light. The colour change of the weighted silk (13.3 CDU) was much greater than the colour change of the unweighted silk (8.1) after exposure. The same conditions caused an increase in the stiffness of unweighted silk of 1.3 times its original stiffness, but the weighted silk became 2.5 times stiffer than the unexposed weighted silk. The tensile strength of the unweighted and weighted silks after 160 hours of unfiltered light dropped by 67 % and 87 % respectively.

In extension at break and energy to rupture, the overall decreases were only slightly greater for the tin weighted silk than for the unweighted silk after 160 hours of exposure. The tin weighted silk lost 78 % and the unweighted silk lost 71 % of their original extensions. The losses in energy to rupture of the unweighted and weighted silks were 95 % and 98 % respectively, for a difference of only 3 %.

The pH of the unweighted and weighted silks changed slightly after exposure to 160 hours of unfiltered light. A decrease in pH of only 0.60 units was observed in the unweighted silk, with a decrease of 1.1 units in the pH of the weighted silk. Chemical changes in the fibroin molecule due to visible plus ultraviolet radiation could not be identified with Fourier transform infrared spectroscopy.

Effect of Visible Light Only

When the effects of unfiltered and filtered light were compared, differences were immediately apparent. When the ultraviolet region of the spectrum was filtered out, the damage inflicted on both unweighted and weighted silk was reduced considerably. The differences in fabric properties produced by filtered and unfiltered light became more exaggerated as length of exposure increased. When the light was filtered, there was either little change in the properties or a much smaller change than when the light was unfiltered.

Neither unweighted silk nor weighted silk showed visible colour change after 160 hours of exposure to visible radiation, having total colour change measurements of less than 1 Colour Difference Unit. Similarly, neither unweighted nor weighted silk changed in stiffness by more than 10 % under the same exposure, the point at which changes in stiffness become barely perceptible.

The tensile properties did show significant differences in the effect of visible radiation between unweighted and weighted silk after 160 hours of exposure to filtered light. The ***weighted*** silk lost 16 % of its original tensile strength, 26% of its breaking extension, and 41 % of its energy to rupture. The ***unweighted*** silk showed losses of 3 %, 7 %, and 11 % respectively.

Scanning electron microscopy did not reveal any differences in either unweighted or weighted silk after exposure to filtered light. Furthermore, no changes in the chemical composition of either unweighted or weighted silk due to exposure to filtered light were identified. There were no significant changes in pH, and the results of Fourier transform infrared spectroscopy did not indicate changes in infrared absorbance due to visible radiation.

Conclusions

The highly degraded condition of many weighted silks from the late nineteenth and early twentieth centuries has been one of the primary means by which weighted silk was identified. The diverse and generally unknown histories of artifacts before they enter a museum play a large role in the deterioration of the artifacts and may produce an unlimited array of different forms of damage. Because of the unknown factors of an artifact's previous life and the diversity in the appearance of silk degradation, visual examination alone is not sufficient evidence to decide that a silk is weighted, although there are visual clues that might *indicate* that a silk has been weighted.

Severe deterioration throughout the fabric, especially in the form of fine slits and rather geometric cracking, is a strong indication of weighting. This type of damage, when due to metallic weighting, occurs throughout the fabric including areas that would not receive mechanical strain, perspiration damage, or prolonged light exposure. However, this association of condition, type of damage, and weighting was studied only in women's dresses from 1880 to 1920. The degradation of other classes of artifacts (flags, for example) from earlier or later dates may not follow the same patterns, or may show the pattern of damage but not be weighted.

Further analysis in the form of identification tests can be used to confirm the presence of metallic weighting in a silk artifact. The burning test conducted on a small yarn sample can indicate that a metallic weighting agent is present. If the identity of the specific metal must be determined, the date of manufacture (if known) and the colour of the silk can provide clues as to which metal may have been used. When tin is suspected, the flame colour test for tin can be used for confirmation in historic silk artifacts. Further analysis may be needed to determine how effective the potassium ferrocyanide spot test for iron is for identifying iron (III) in silk artifacts.

Before conducting any test, the ethics of removing a sample for analysis should be considered and the reasons for identifying the weighting agent must be evaluated. In some instances, it may be sufficient to determine simply that the silk was weighted with a metal and that only a few fibres must be removed for the burning test. The flame test for tin requires a larger sample of fabric, but removal of a larger sample may not be warranted. These decisions are made for individual artifacts as the circumstances demand, and in consultation with all of the people who are charged with the care of the artifact.

When a weighted silk has been identified, decisions on treatment and long term care are made. These decisions are made only after careful examination and condition reporting of the artifact, and consideration of the individual weaknesses and needs of the artifact. Some weighted silks have been shown to be in surprisingly good condition, and appear able to withstand the handling and exposure to light that come with exhibition. Other weighted silk artifacts may have extensive deterioration that becomes worse each time they are handled. Because of this diversity, it is difficult to establish specific guidelines that might apply to *all* weighted silk artifacts.

In this study, ultraviolet light caused severe damage to new tin weighted silk that had no previous degradation. Increasing exposure led to significant changes in colour and stiffness, with dramatic losses in tensile strength, extension, and energy to rupture. While the intensity of the light used for accelerated aging was higher than what would normally be encountered in a museum exhibit, a similar pattern of damage would occur, only at a slower rate under the lower light intensity. When the ultraviolet light was filtered out, the damage was greatly reduced but not eliminated. Exposure to visible radiation only produced small but statistically significant changes in the tensile properties of the tin weighted silk.

One of the guiding questions of this research was whether the effect of light on tin weighted silk was truly much greater than its effect on unweighted silk. In other words, does tin weighting make silk more susceptible to photodegradation? From the results obtained in this research, the answer is a resounding "yes". For all levels of exposure, the deterioration of the tin weighted silk was measurably greater than that of the unweighted silk.

The results of this research must not, however, be taken to mean that light is the only factor degrading tin weighted silk. In the examination of the historic silk artifacts from the Clothing and Textiles Collection, garments were found which had extensive damage to weighted silk linings and facings which would not receive much light exposure. Other factors are operating in weighted silks to cause such degradation. Without knowing the specific conditions to which the artifact has been exposed, it is impossible to say what those other factors might be. Abrasion, mechanical stress, perspiration, and other chemical contaminants are likely candidates.

The influence of other factors may mask the effects of weighting agents on silk degradation. When metal ions are present in natural fibres such as silk, the metal acts as a catalyst in oxidative degradation. Even without exposure to light or other harmful factors, weighted silks continue to degrade because of the inherently damaging nature of metallic weighting.

Recommendations for Further Research

Throughout the course of this research, many avenues for further research were encountered. The present study had to be limited in scope due to limits of time and resources, but could easily be continued and expanded in many directions.

Part I, which dealt with identification and characterization of historic weighted silks, could be further developed. Additional tests for other metals used as weighting agents could be adapted for use on textile artifacts. For characterization, a survey of a larger number of artifacts from a wider range of dates could be conducted to determine if the condition or patterns of damage are related to a specific date range. Other classes of silk artifacts, such as men's clothing, flags, or upholstery could be examined and tested to determine if a significant number of such artifacts are weighted and if they show patterns of deterioration.

As Part II progressed, many areas for expansion and investigation were identified. In terms of the initial effects of weighting, other methods and various levels of weighting could be explored. Perhaps metallic weighting is not detrimental if it does not exceed a certain level, beyond which the damaging effects escalate. A relationship between the level (or type) of weighting and the extent of degradation may be revealed. Chemical analysis could be conducted to determine whether the weighting compound chemically bonds with silk fibres or is mechanically trapped by the fibres. A more detailed study on the fractography of weighted silk fibres compared to unweighted silk fibres, especially in historic, naturally aged silks might reveal important differences.

The effects of light in an oxygen-free atmosphere, such as in a nitrogen case, could be researched to determine the role of oxygen in the degradation of weighted silk. Also, the effects of dark storage in both oxygenated and oxygen-free environments could be studied to confirm whether there is an inherent vice in weighted silk that will cause it to self-destruct regardless of environmental conditions.

Recommendations for Conservation Practice

The results of part I of the research showed that visual examination alone is not sufficient to determine whether a historic silk fabric has been weighted. Although the conservator may find much useful information in the appearance of the artifact, when the presence of weighting must be known it is recommended that a more definitive test be done. The burning test is valuable when the presence of metallic weighting only must be identified. If the conservator must know *which* metal was used for weighting, then a more specific test can be done. The flame colour test for tin or the potassium ferrocyanide spot test for iron should be used for these common weighting metals.

In the second part of the research, the effects of tin weighting and the effects of visible and ultraviolet light on tin weighted silk were investigated. Although tin weighting did cause slight degradation of the silk, the changes became more exaggerated with exposure to light. Visible *plus* ultraviolet light caused the most damage, a fact well known among conservators. Thus, the ultraviolet radiation must be filtered out of all light sources illuminating weighting silk artifacts. Filtering out the ultraviolet rays, however, does not protect the artifacts from light damage entirely. Visible radiation does cause changes in physical and chemical properties of silk, but at a slower rate. Conservators should use caution when it is necessary to expose weighted silk artifacts even to *filtered* light for a prolonged period. The intensity of the light and the period of exposure should be as low and as short as possible.

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APPENDIX A-1

LIST OF ARTIFACTS FROM THE UNIVERSITY OF ALBERTA CLOTHING AND TEXTILES COLLECTION

DETERIORATION RATINGS OF ARTIFACTS EXAMINED:

Rating: 1

90.22.14

Rating: 2

78.13.01 a,b*
77.09.02 a
82.18.01*
75.05.06 a,b
77.07.05*
72.15.02 a,b
85.54.01
82.22.01 a,b
83.18.01 a,b
86.10.01
84.41.01
81.18.01 a,b
71.05.03 a,b

Rating: 3

71.08.01
83.15.01*
75.05.05 a,b
81.13.12
81.13.75 a,b
84.40.01 a,b
75.13.22*
84.19.01
86.40.02 a*
85.75.01
71.05.01 a,b,c
81.14.01 a,b
72.11.01 a,b
71.04.01

Rating: 4

89.23.01 a,b
81.23.11*
71.05.17
87.41.01 a,b,c*
89.13.03*
84.20.01*
87.27.01 a,b,c
71.09.01*
85.38.01 a,b*
81.13.28 a,b
73.08.12*
72.06.02 a,b,c*
87.69.01 a*
79.08.15 a*
78.11.01 a,b,c,d*
85.38.02 a,b
77.07.10*
81.13.14
87.44.24 a,b*

* indicates artifacts with a silk component that tested positive for metallic weighting in burning test

APPENDIX A-2

SAMPLE OF REPORT FORM FOR SILK ARTIFACT EXAMINATION

EVALUATION OF SILK DEGRADATION
CLOTHING AND TEXTILES COLLECTION
UNIVERSITY OF ALBERTA

Acc. #:____________
Location:____________

ARTIFACT INFORMATION:

Category:__________________ Colour:______________ Date:____________

ARTIFACT CONDITION:

DETERIORATION RATING SCALE *

1	2	3	4	5
No visible deterioration.	Minor deterioration.	Deterioration in areas of mechanical stress or perspiration.	Extensive deterioration throughout fabric.	Fabric in pieces, no longer intact.

(* DRS adapted from: Horswill, M. T. (1992). Characterization and preservation of weighted silk. PhD dissertation, University of Wisconsin, Madison.)

DETAILS OF CONDITION (check all that apply)

all-over soiling ________
stains ________
discolouration ________
distortions ________
abrasion ________
fraying ________

holes/loss ________
tears ________
slits/cracks ________
creases ________
powdering ________
previous repair ________

Comments:

MICROSCOPE OBSERVATIONS

BURNING OBSERVATIONS

RECOMMENDATIONS:

REPORT BY:____________________________ DATE:________________

APPENDIX A-3

CUTTING DIAGRAMS OF NEW SILK FABRIC FOR UNWEIGHTED AND WEIGHTED SPECIMENS

UNWEIGHTED SILK

1	2	3	4	5	6	7	8	9	flaw	10	11
12	13	14	15	16	17	18	19	20	21	22	23
24	25	26	27	28	29	30	31	32	33	34	35
36	37	38	39	40	41	42	43	44	45	46	47
48	49	50	51	52	53	54	55	56	57	58	59
60	61	62	63	64	65	66	67	68	69	70	71
72	73	74	75	76	77	78	79	80	81	82	83
84	85	86	87	88	89	90					

98 cm

84 cm

WEIGHTED SILK

1	2	3	4	5	6		7	8	9	10	11	12
13	14	15	16	17	18		19	20	21	22	23	24
25	26	27	28	29	30		31	32	33	34	35	36
37	38	39	40	41	42		43	44	45	46	47	48
49	50	51	52	53	54		55	56	57	58	flaw	59
60	61	62	63	64	65		66	67	68	69	flaw	70
71	72	73	74	75	76		77	78	79	80	flaw	81
82	83	84	85	86	87		88	89	90			

98 cm

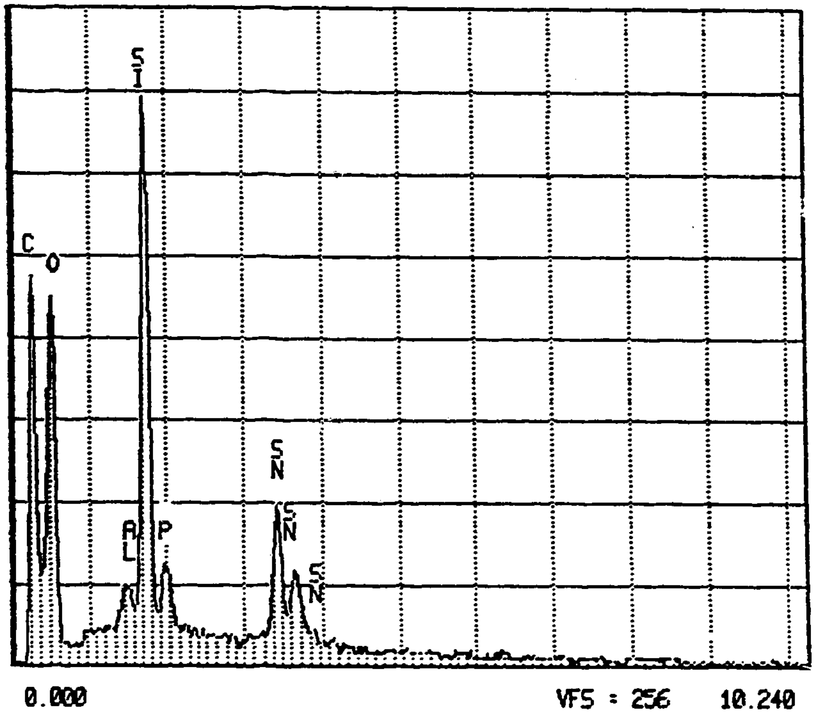
84 cm

APPENDIX A-4

GRAPHS OF ENERGY DISPERSIVE X-RAY ANALYSIS FOR DONATED SILK SAMPLES

GEOLOGY SEM FACILITY THU 16-NOV-95 10:27

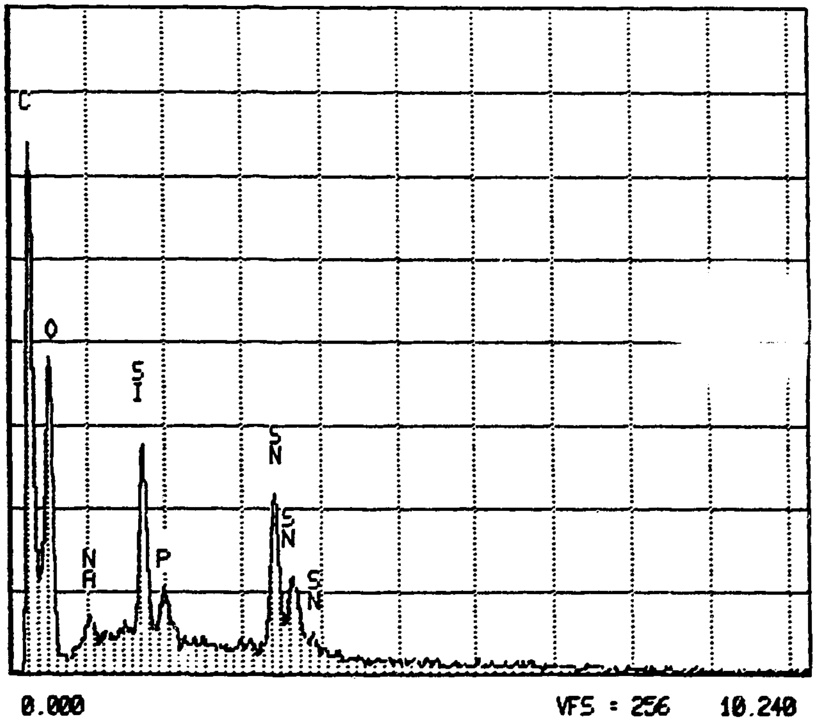
Cursor: 0.000keV = 0



42 SAMPLE A

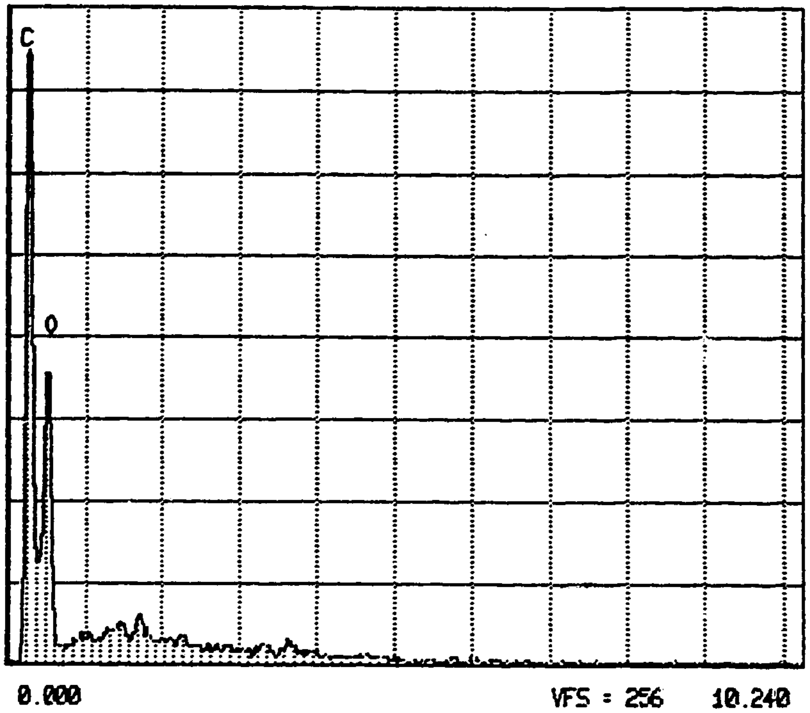
GEOLOGY SEM FACILITY THU 16-NOV-95 10:30

Cursor: 0.000keV = 0



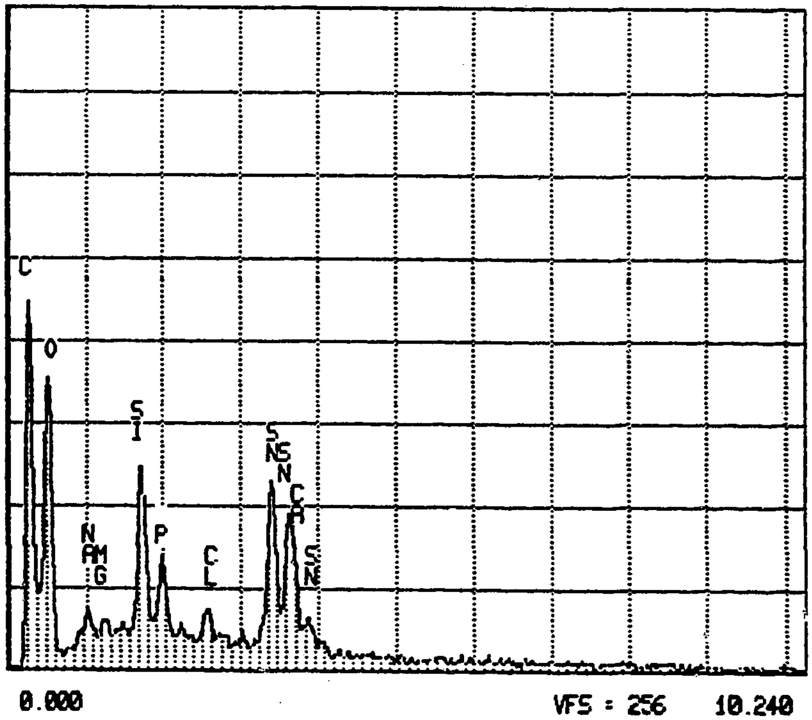
SAMPLE B 55

GEOLOGY SEM FACILITY THU 16-NOV-95 10:33
Cursor: 0.000keV = 0

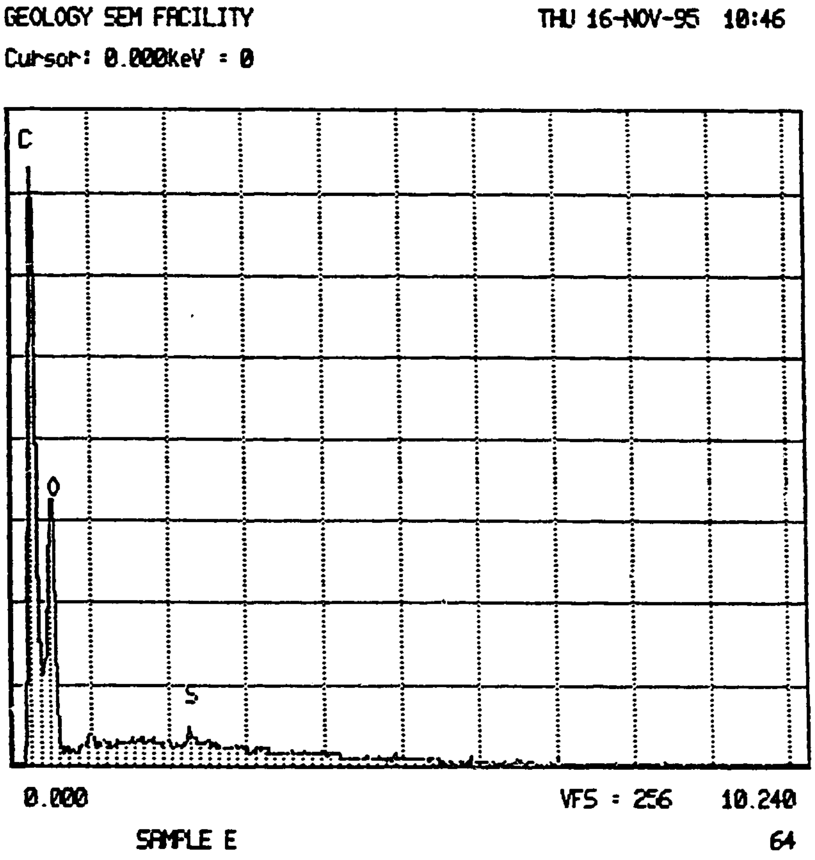


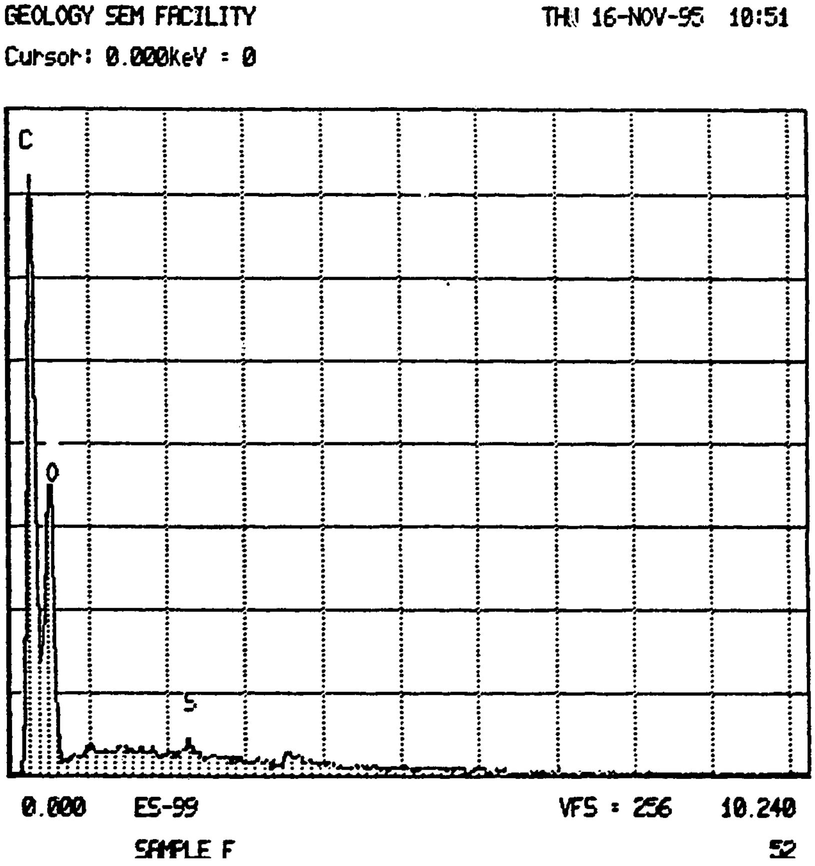
SAMPLE C
45

GEOLOGY SEM FACILITY THU 16-NOV-95 10:43
Cursor: 0.000keV = 0

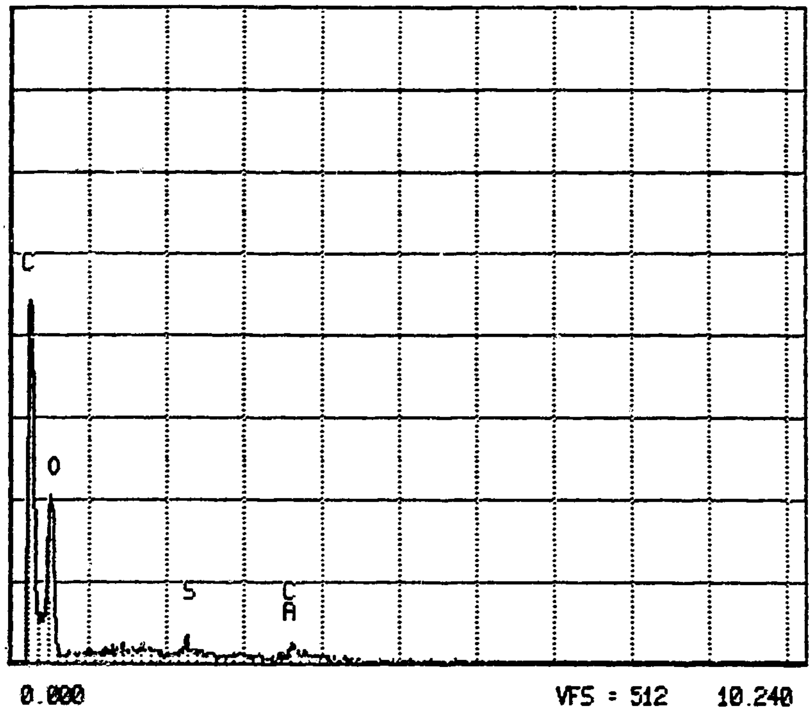


SAMPLE D
52


GEOLOGY SEM FACILITY
THU 16-NOV-95 10:46
Cursor: 0.000KeV = 0
C
O
S
0.000
VFS = 256
10.240
SAMPLE E
64

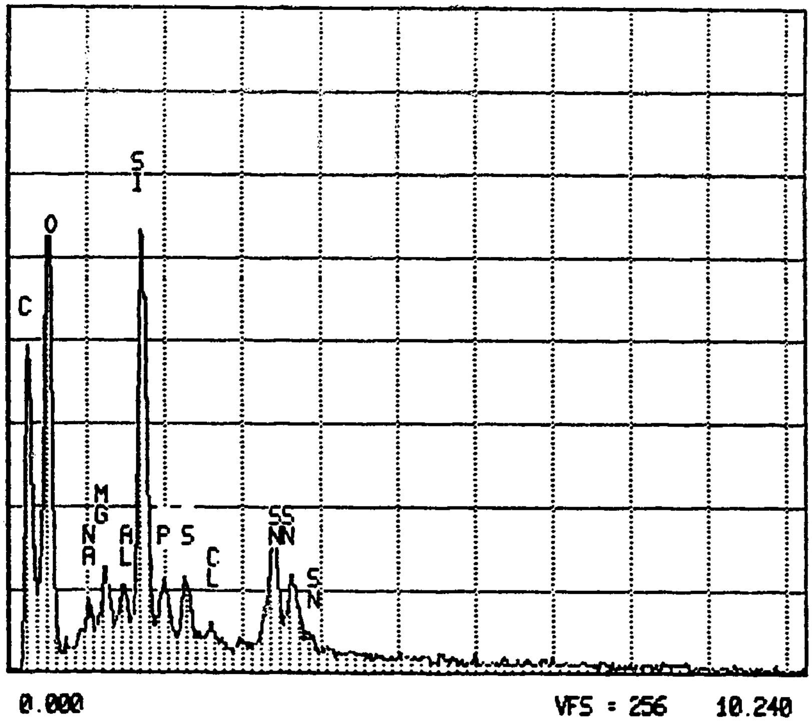

GEOLOGY SEM FACILITY
THU 16-NOV-95 10:51
Cursor: 0.000KeV = 0
C
O
S
0.000
ES-99
VFS = 256
10.240
SAMPLE F
52

GEOLOGY SEM FACILITY THU 16-NOV-95 10:59
Cursor: 0.000KeV = 0



SAMPLE G 56

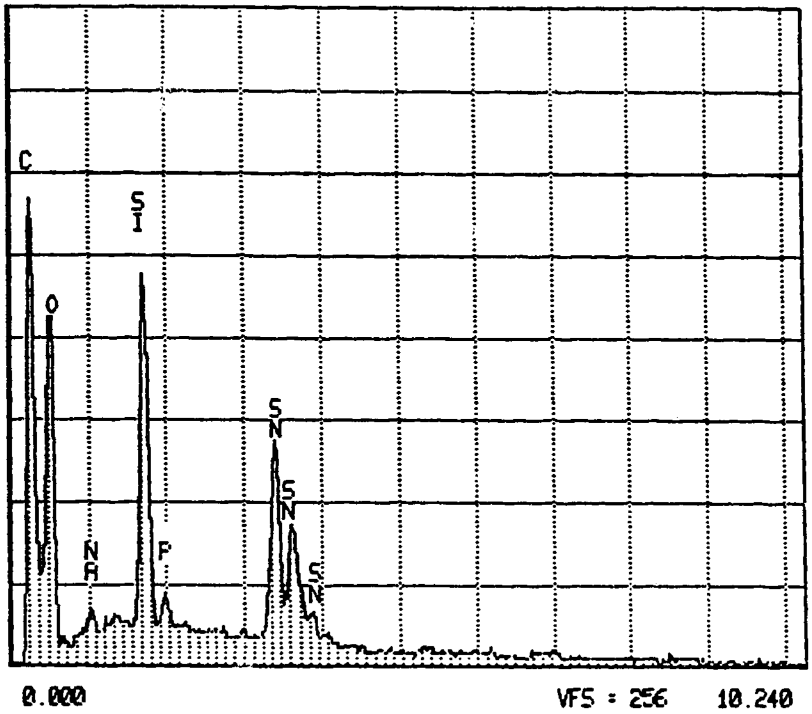
GEOLOGY SEM FACILITY THU 16-NOV-95 11:05
Cursor: 0.000KeV = 0



SAMPLE H 64

GEOLOGY SEM FACILITY THU 16-NOV-95 11:08

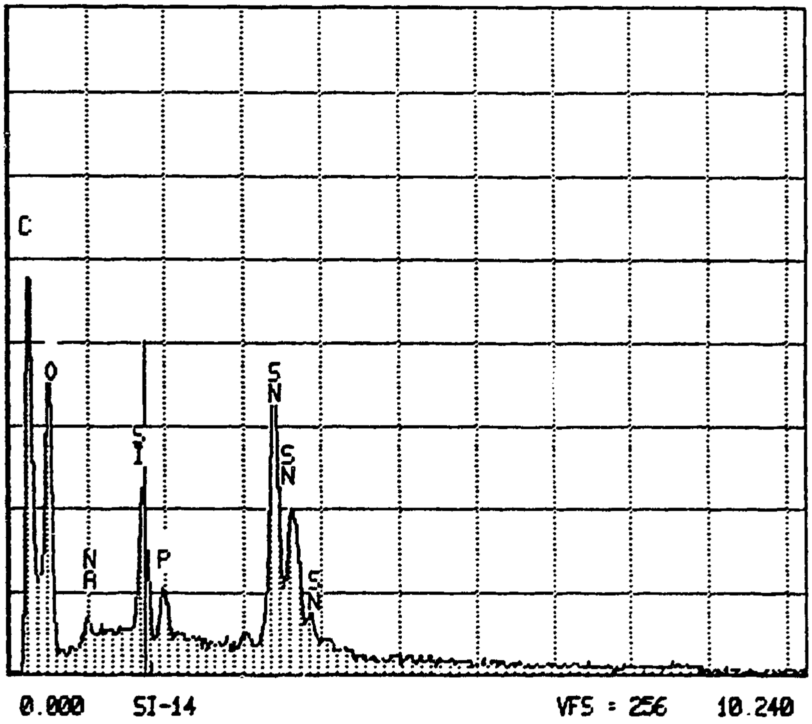
Cursor: 0.000keV = 0



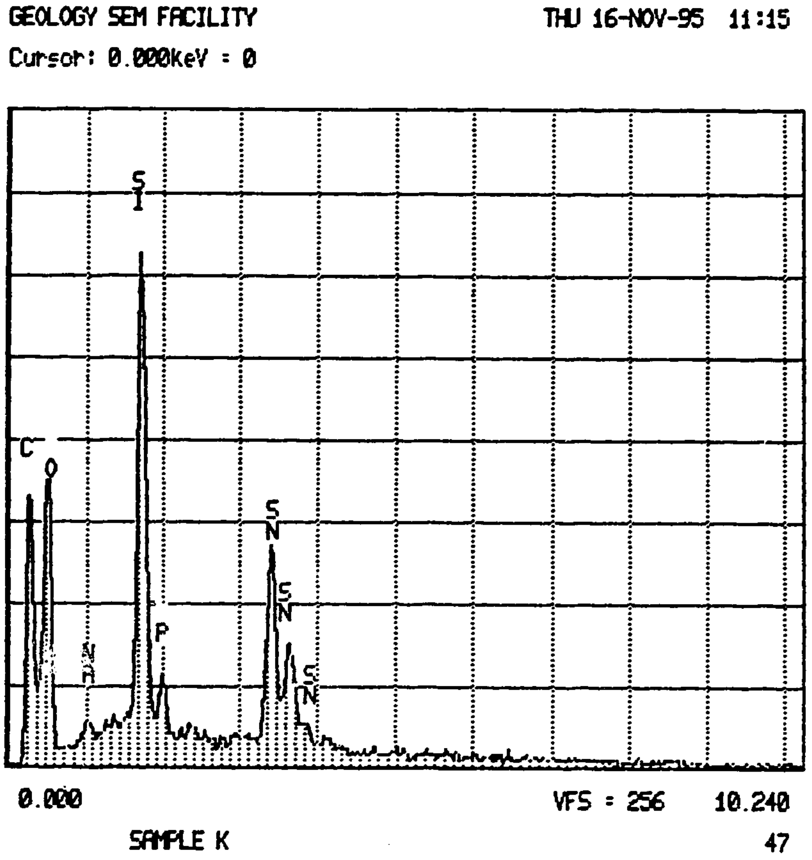
SAMPLE I 60

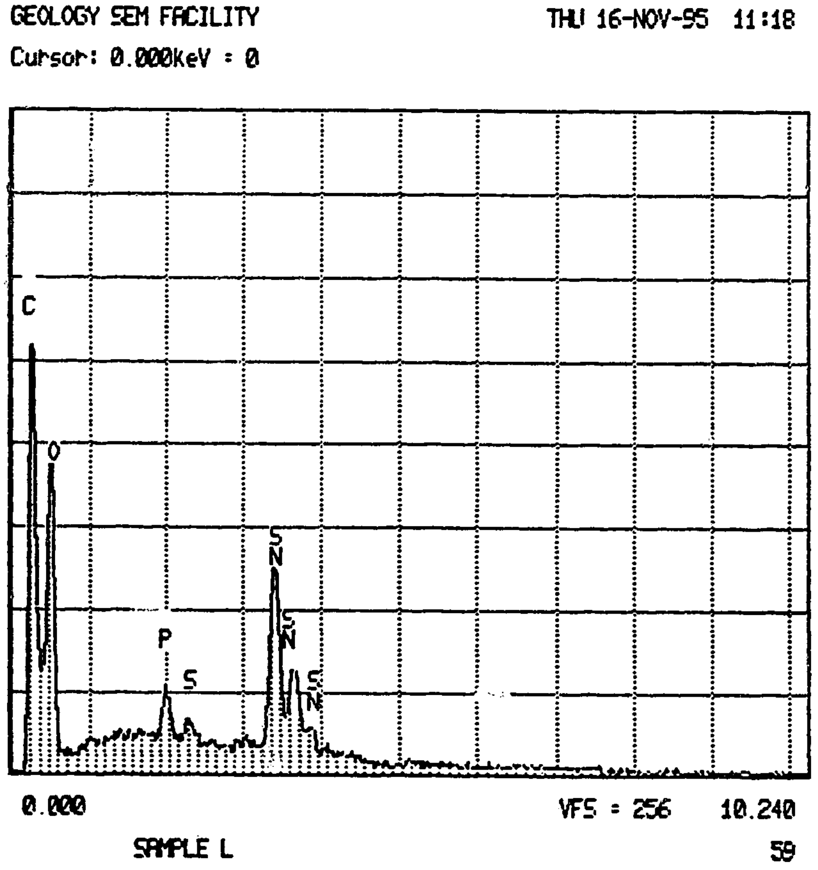
GEOLOGY SEM FACILITY THU 16-NOV-95 11:13

Cursor: 0.000keV = 0



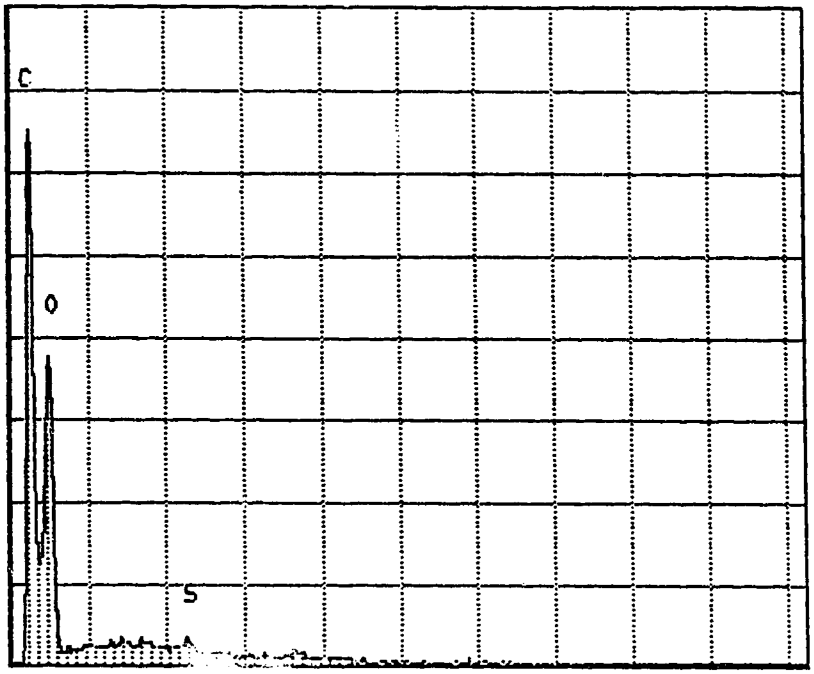
SAMPLE J 50


GEOLOGY SEM FACILITY
THU 16-NOV-95 11:15
Cursor: 0.000KeV = 0
C
O
NA
SI
P
SN
SN
SN
0.000
VFS = 256
10.240
SAMPLE K
47


GEOLOGY SEM FACILITY
THU 16-NOV-95 11:18
Cursor: 0.000KeV = 0
C
O
P
S
SN
SN
SN
0.000
VFS = 256
10.240
SAMPLE L
59

GEOLOGY SEM FACILITY THU 16-NOV-95 11:31

Cursor: 0.000keV = 0

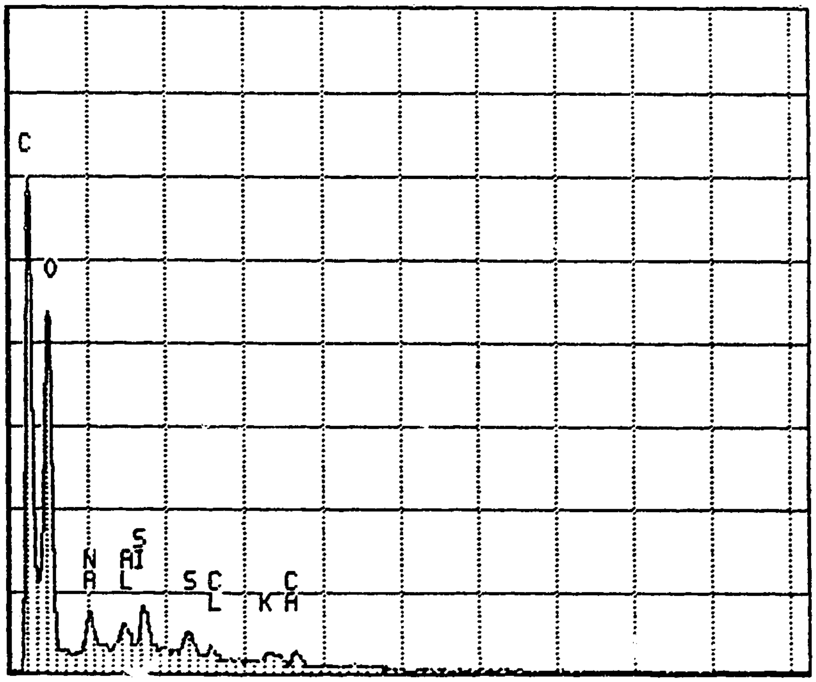


0.000 VFS = 512 10.240

SAMPLE N 15

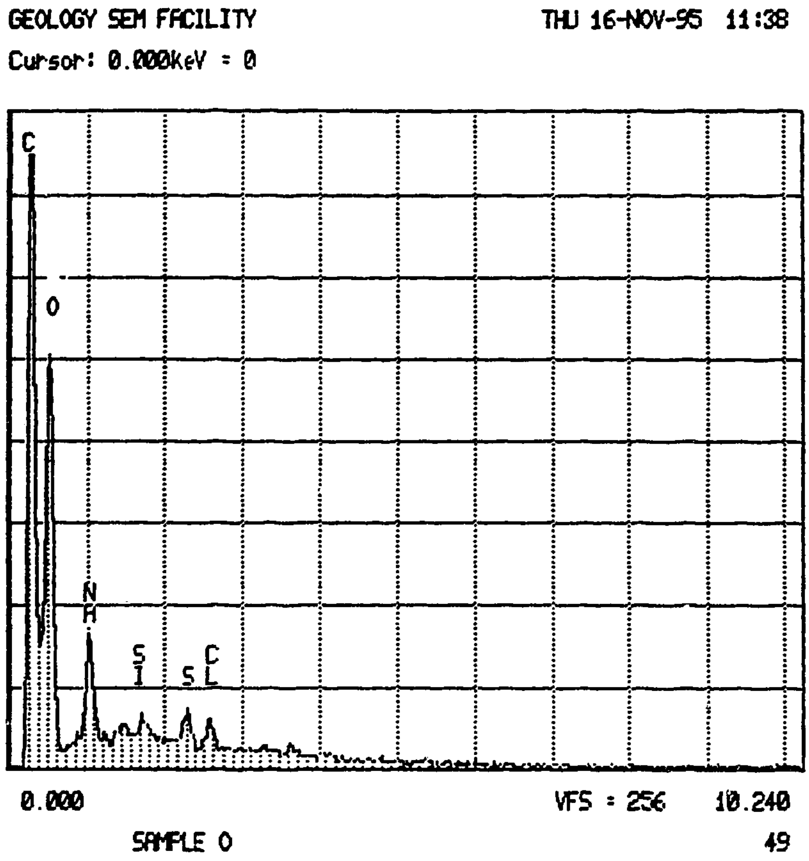
GEOLOGY SEM FACILITY THU 16-NOV-95 11:35

Cursor: 0.000keV = 0



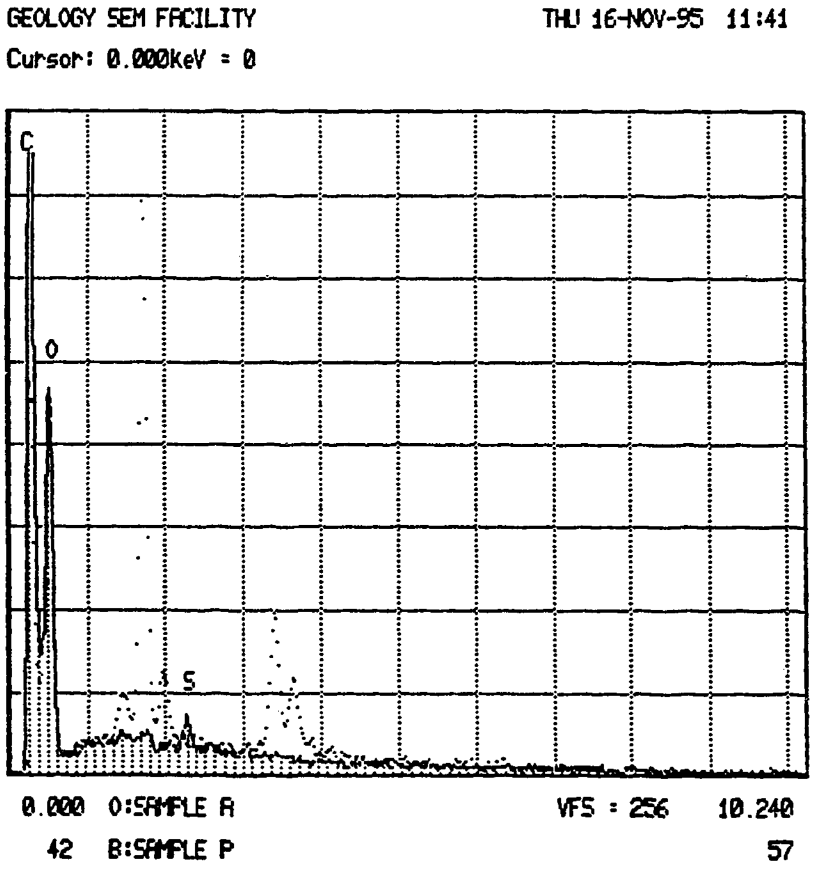
0.000 VFS = 512 10.240

SAMPLE N 13



```
GEOLOGY SEM FACILITY                    THU 16-NOV-95  11:38
Cursor: 0.000KeV = 0

0.000                                   VFS = 256    10.240
         SAMPLE O                                        49
```

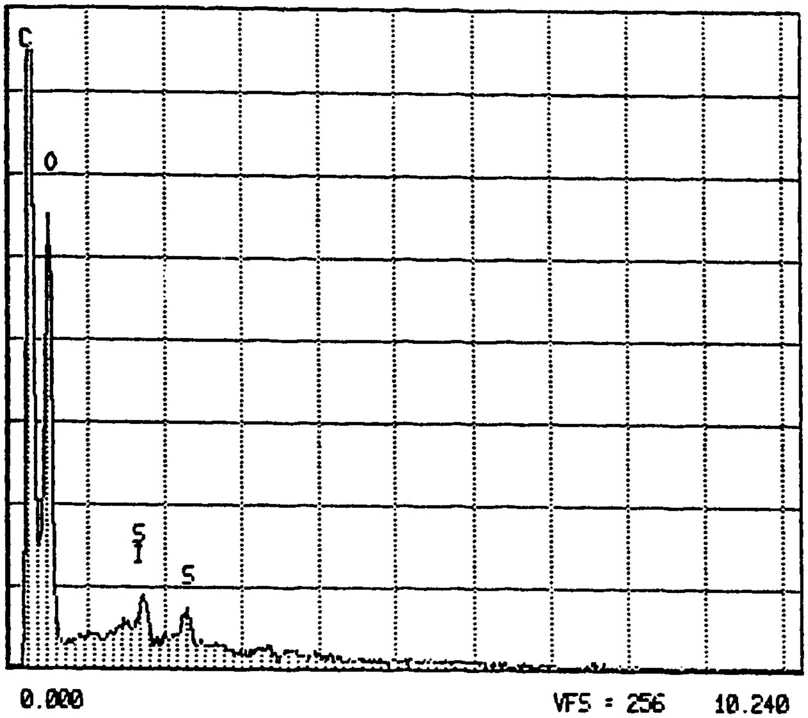


```
GEOLOGY SEM FACILITY                    THU 16-NOV-95  11:41
Cursor: 0.000KeV = 0

0.000  O:SAMPLE A                       VFS = 256    10.240
  42   B:SAMPLE P                                        57
```

GEOLOGY SEM FACILITY THU 16-NOV-95 11:44

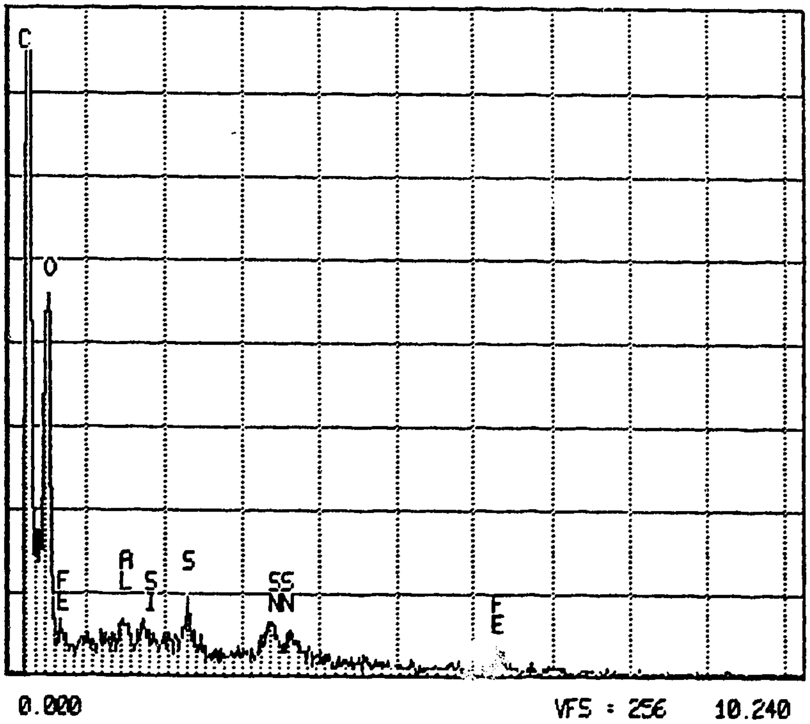
Cursor: 0.000keV = 0



SAMPLE Q 48

FIIII)’EEEEE9DB??DB??66’EEEEE9DB??

Cursor: 0.000keV = 0



0 SAMPLE R

APPENDIX A-5

RAW DATA FROM MEASUREMENT OF PHYSICAL PROPERTIES

(DEPENDENT VARIABLES)

	group	specimen	dl	da	db	de	overhang	flexrig
1	control	u53a	.04	-.02	.04	.06	3.525	18.78
2		u53b	.	.	.	.	3.775	23.07
3		u61a	.01	.02	-.07	.07	3.750	22.61
4		u61b	.	.	.	.	3.625	20.42
5		u84a	-.12	-.01	.05	.13	3.700	21.72
6		u84b	.	.	.	.	3.625	20.42
7		u19a	.05	.01	.00	.05	3.650	20.85
8		u19b	.	.	.	.	3.800	23.53
9		u48a	.03	.00	-.02	.04	3.550	19.18
10		u48b	.	.	.	.	3.600	20.00
11	U-1A	u1a	-.79	-.36	1.92	2.11	3.375	16.48
12		u1b	.	.	.	.	3.550	19.18
13		u88a	-.57	-.36	1.92	2.03	3.500	18.38
14		u88b	.	.	.	.	3.475	17.99
15		u11a	-.61	-.34	1.94	2.06	3.500	18.38
16		u11b	.	.	.	.	3.575	19.59
17		u55a	-.78	-.35	1.92	2.10	3.675	21.28
18		u55b	.	.	.	.	3.550	19.18
19		u22a	-.70	-.33	1.90	2.05	3.775	23.07
20		u22b	.	.	.	.	3.950	26.42
21	U-1B	u17a	-.07	.10	-.87	.88	3.450	17.61
22		u17b	.	.	.	.	3.550	13.18
23		u4a	.02	.07	-.85	.85	3.550	19.18
24		u4b	.	.	.	.	3.450	17.61
25		u15a	.01	.08	-.88	.88	3.575	19.59
26		u15b	.	.	.	.	3.575	19.59
27		u27a	-.07	.02	-.84	.84	3.525	18.78
28		u27b	.	.	.	.	3.600	20.00
29		u33a	-.13	.06	-.86	.87	3.550	19.18
30		u33b	.	.	.	.	3.575	19.59
31	U-2A	u41a	-.96	-.15	2.30	2.50	3.525	18.78
32		u41b	.	.	.	.	3.575	19.59
33		u85a	-.96	-.24	2.54	2.73	3.575	19.59
34		u85b	.	.	.	.	3.500	18.38
35		u29a	-.93	-.22	2.56	2.73	3.500	18.38
36		u29b	.	.	.	.	3.525	18.78
37		u40a	-1.28	-.24	2.75	3.04	3.925	25.93

	group	specimen	dl	da	db	de	overhang	flexrig
38		u40b	.	.	.	.	3.650	20.85
39		u35a	-.67	-.05	1.83	1.95	3.575	19.59
40		u35b	.	.	.	.	3.625	20.44
41	U-2B	u63a	-.02	.01	-1.02	1.02	3.400	16.85
42		u63b	.	.	.	.	3.400	16.85
43		u36a	-.07	.04	-1.06	1.06	3.475	17.99
44		u36b	.	.	.	.	3.525	18.78
45		u83a	-.07	.04	-1.04	1.04	3.650	20.85
46		u83b	.	.	.	.	3.475	17.99
47		u57a	-.17	.03	-1.03	1.04	3.625	20.42
48		u57b	.	.	.	.	3.400	16.85
49		u12a	-.16	.01	-1.02	1.03	3.225	14.38
50		u12b	.	.	.	.	3.275	15.06
51	U-3A	u10a	-1.58	-.09	4.06	4.36	3.475	17.99
52		u10b	.	.	.	.	3.500	18.38
53		u69a	-1.62	-.18	4.27	4.57	3.475	17.99
54		u69b	.	.	.	.	3.575	19.59
55		u59a	-1.62	-.16	4.41	4.70	3.800	23.53
56		u59b	.	.	.	.	3.850	24.47
57		u52a	-2.16	-.15	4.20	4.73	3.600	20.00
58		u52b	.	.	.	.	3.750	22.61
59		u56a	-1.58	-.09	4.06	4.36	3.625	20.42
60		u56b	.	.	.	.	3.550	19.18
61	U-3B	u70a	.11	.13	-1.12	1.13	3.300	15.41
62		u70b	.	.	.	.	3.250	14.72
63		u7a	.21	.16	-1.19	1.22	3.300	15.41
64		u7b	.	.	.	.	3.400	16.85
65		u13a	-.01	.13	-1.10	1.11	3.425	17.23
66		u13b	.	.	.	.	3.400	16.85
67		u76a	-.13	.18	-1.13	1.15	3.550	19.18
68		u76b	.	.	.	.	3.500	18.38
69		u5a	.13	.11	-1.10	1.11	3.350	16.12
70		u5b	.	.	.	.	3.300	15.41
71	U-4A	u9a	-2.38	-.44	5.80	6.28	3.650	20.85
72		u9b	.	.	.	.	3.775	23.07
73		u32a	-2.21	-.39	5.71	6.14	4.050	28.48
74		u32b	.	.	.	.	3.750	22.60

	group	specimen	dl	da	db	de	overhang	flexrig
75		u75a	-2.24	-.50	6.03	6.45	3.925	25.93
76		u75b	.	.	.	.	3.800	23.53
77		u24a	-2.15	-.48	5.98	6.37	3.600	20.00
78		u24b	.	.	.	.	3.725	22.16
79		u20a	-2.39	-.36	5.81	6.29	3.800	23.53
80		u20b	.	.	.	.	3.625	20.42
81	U-4B	u45a	.08	.07	-.96	.97	3.700	21.71
82		u45b	.	.	.	.	3.700	21.71
83		u66a	.13	.05	-.97	.98	3.375	16.48
84		u66b	.	.	.	.	3.475	17.99
85		u30a	.34	.05	-.99	1.05	3.300	15.41
86		u30b	.	.	.	.	3.400	16.85
87		u72a	.10	.06	-1.00	1.01	3.575	19.59
88		u72b	.	.	.	.	3.350	16.12
89		u67a	.08	.07	-.96	.97	3.350	16.12
90		u67b	.	.	.	.	3.450	17.61
91	U-5A	u16a	-3.43	-.01	7.34	8.10	3.900	25.43
92		u16b	.	.	.	.	4.050	28.48
93		u51a	-3.70	.11	7.13	8.03	4.100	29.55
94		u51b	.	.	.	.	4.150	30.64
95		u65a	-4.09	.11	7.10	8.19	3.775	23.07
96		u65b	.	.	.	.	4.025	27.96
97		u8a	-3.72	.06	7.26	8.16	3.725	22.16
98		u8b	.	.	.	.	3.950	26.42
99		u26a	-3.43	-.01	7.34	8.10	4.150	30.64
100		u26b	.	.	.	.	3.800	23.53
101	U-5B	u54a	.05	.04	-1.03	1.03	3.625	20.42
102		u54b	.	.	.	.	3.625	20.42
103		u38a	.06	.03	-1.01	1.01	3.675	21.28
104		u38b	.	.	.	.	3.800	23.53
105		u58a	.21	.10	-1.07	1.09	3.725	22.16
106		u58b	.	.	.	.	3.500	18.38
107		u68a	.13	.04	-1.03	1.04	3.550	19.18
108		u68b	.	.	.	.	3.425	17.23
109		u3a	.05	.05	-1.05	1.05	3.350	16.12
110		u3b	.	.	.	.	3.300	15.41
111	wcontrol	w48a	-.15	.05	.05	.17	4.175	52.12

	group	specimen	dl	da	db	de	overhang	flexrig
112		w48b	.	.	.	.	4.100	49.36
113		w69a	.40	-.01	-.08	.41	4.150	51.19
114		w69b	.	.	.	.	3.675	35.55
115		w50a	-.34	.02	.04	.34	3.925	43.31
116		w50b	.	.	.	.	3.950	44.14
117		w18a	-.01	-.05	-.05	.07	3.875	41.68
118		w18b	.	.	.	.	3.675	35.55
119		w33a	.09	.01	.07	.11	3.500	30.71
120		w33b	.	.	.	.	3.975	44.99
121	W-1A	w4a	-2.01	.17	4.29	4.74	3.675	35.55
122		w4b	.	.	.	.	3.700	36.28
123		w8a	-1.81	.09	4.44	4.80	3.400	28.15
124		w8b	.	.	.	.	3.375	27.54
125		w41a	-2.05	.12	4.49	4.94	3.950	44.14
126		w41b	.	.	.	.	3.875	41.68
127		w73a	-1.87	.13	4.36	4.75	3.800	39.30
128		w73b	.	.	.	.	3.975	44.99
129		w28a	-2.39	.12	4.61	5.19	3.950	44.14
130		w28b	.	.	.	.	3.775	38.53
131	W-1B	w45a	-.52	.28	-.36	.69	4.050	47.58
132		w45b	.	.	.	.	4.075	48.47
133		w16a	-.33	.24	-.36	.54	3.525	31.37
134		w16b	.	.	.	.	3.575	32.73
135		w59a	-.61	.25	-.28	.72	3.800	39.30
136		w59b	.	.	.	.	3.775	38.53
137		w5a	.02	.25	-.47	.53	3.850	40.87
138		w5b	.	.	.	.	3.925	43.31
139		w1a	-.39	.29	-.45	.66	4.075	48.47
140		w1b	.	.	.	.	4.100	49.36
141	W-2A	w15a	-3.10	.47	5.33	6.18	3.600	33.42
142		w15b	.	.	.	.	3.650	34.83
143		w85a	-3.17	.51	5.62	6.47	3.725	37.02
144		w85b	.	.	.	.	3.575	32.73
145		w20a	-3.04	.51	5.26	6.10	3.650	34.83
146		w20b	.	.	.	.	3.725	37.02
147		w36a	-3.02	.61	4.74	5.65	4.250	54.98
148		w36b	.	.	.	.	4.125	50.27

	group	specimen	dl	da	db	de	overhang	flexrig
149		w66a	-2.85	.51	4.99	5.77	4.000	45.84
150		w66b	.	.	.	.	4.025	46.70
151	W-2B	w65a	.24	.23	-.69	.77	3.975	44.99
152		w65b	.	.	.	.	3.700	36.28
153		w68a	-.02	.28	-.63	.69	3.600	33.42
154		w68b	.	.	.	.	3.725	37.02
155		w70a	-.07	.25	-.60	.65	4.225	54.02
156		w70b	.	.	.	.	3.925	43.31
157		w9a	-.08	.28	-.65	.71	3.475	30.06
158		w9b	.	.	.	.	3.550	32.04
159		w31a	.27	.22	-.68	.76	4.075	48.47
160		w31b	.	.	.	.	4.525	66.36
161	W-3A	w12a	-4.57	.93	7.62	8.93	3.825	40.08
162		w12b	.	.	.	.	3.850	40.87
163		w47a	-4.63	.96	7.70	9.04	4.375	59.98
164		w47b	.	.	.	.	4.575	68.59
165		w7a	-4.45	.96	7.33	8.63	4.600	69.72
166		w7b	.	.	.	.	4.250	54.98
167		w77a	-4.64	1.04	7.87	9.20	4.175	52.12
168		w77b	.	.	.	.	3.975	44.99
169		w53a	-4.51	.99	7.32	8.65	4.200	53.07
170		w53b	.	.	.	.	4.025	46.70
171	W-3B	w17a	-.02	.33	-.82	.88	3.275	25.16
172		w17b	.	.	.	.	3.400	28.15
173		w27a	-.58	.34	-.62	.91	3.475	30.06
174		w27b	.	.	.	.	3.375	27.54
175		w40a	-.15	.28	-.67	.74	3.750	37.77
176		w40b	.	.	.	.	3.825	40.08
177		w57a	-.11	.32	-.67	.75	3.650	34.83
178		w57b	.	.	.	.	3.575	32.73
179		w29a	.05	.27	-.66	.71	3.875	41.68
180		w29b	.	.	.	.	3.600	33.42
181	W-4A	w89a	-5.13	.72	10.07	11.32	4.150	51.19
182		w89b	.	.	.	.	4.125	50.27
183		w38a	-4.62	.77	10.02	11.06	4.725	75.56
184		w38b	.	.	.	.	4.725	75.56
185		w21a	-4.61	.76	9.36	10.46	4.350	58.96

	group	specimen	di	da	db	de	overhang	flexrig
186		w21b	.	.	.	.	4.175	52.12
187		w42a	-4.92	.70	10.48	11.60	4.475	64.19
188		w42b	.	.	.	.	4.300	56.95
189		w52a	-5.11	.90	8.87	10.28	4.300	56.95
190		w52b	.	.	.	.	4.250	54.98
191	W-4B	w61a	-.42	.18	.16	.48	4.025	46.70
192		w61b	.	.	.	.	4.000	45.84
193		w46a	-.24	.29	-.17	.41	4.300	56.95
194		w46b	.	.	.	.	4.025	46.70
195		w14a	-.08	.23	-.20	.32	3.300	25.74
196		w14b	.	.	.	.	3.400	28.15
197		w86a	-.01	.16	-.10	.19	3.975	44.99
198		w86b	.	.	.	.	3.800	39.30
199		w2a	-.40	.15	.03	.43	3.500	30.71
200		w2b	.	.	.	.	3.600	33.42
201	W-5A	w23a	-6.10	.91	11.62	13.16	5.425	114.36
202		w23b	.	.	.	.	5.275	105.13
203		w71a	-6.28	.96	11.64	13.26	5.675	130.91
204		w71b	.	.	.	.	5.625	127.48
205		w84a	-6.40	.96	11.25	12.98	5.125	96.42
206		w84b	.	.	.	.	4.950	86.87
207		w6a	-6.50	.84	12.65	14.25	5.100	95.01
208		w6b	.	.	.	.	4.900	84.27
209		w83a	-6.09	.95	11.41	12.97	5.775	137.95
210		w83b	.	.	.	.	5.450	115.95
211	W-5B	w56a	-.44	.39	-.02	.59	3.475	30.06
212		w56b	.	.	.	.	3.575	32.62
213		w37a	-.32	.40	-.13	.53	3.800	39.30
214		w37b	.	.	.	.	3.725	37.02
215		w88a	-.12	.34	-.21	.42	4.325	57.95
216		w88b	.	.	.	.	4.050	47.58
217		w25a	-.42	.38	.08	.57	3.725	37.02
218		w25b	.	.	.	.	3.675	35.55
219		w32a	-.73	.34	.28	.85	3.700	36.28
220		w32b	.	.	.	.	3.725	37.02

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
1	control	u53a	17.93	175.89	19.42	25.89	208.6	2.0464
2		u53b	18.41	180.60	19.39	25.85	214.3	2.1023
3		u61a	16.88	165.59	18.79	25.05	190.2	1.8659
4		u61b	18.27	179.23	18.88	25.17	202.3	1.9846
5		u84a	18.29	179.42	18.95	25.27	204.8	2.0091
6		u84b	18.24	178.93	18.99	25.32	207.7	2.0375
7		u19a	18.16	178.15	19.44	25.92	205.0	2.0111
8		u19b	18.29	179.42	18.67	24.89	197.7	1.9394
9		u48a	17.09	167.65	18.03	24.04	181.5	1.7805
10		u48b	17.85	175.11	18.13	24.17	197.1	1.9336
11	U-1A	u1a	16.88	165.59	16.75	22.33	169.4	1.6618
12		u1b	16.76	164.42	17.00	22.67	167.8	1.6461
13		u88a	17.39	170.60	18.17	24.23	194.6	1.9090
14		u88b	17.11	167.85	17.88	23.84	184.6	1.8109
15		u11a	15.91	156.08	15.69	20.92	150.4	1.4754
16		u11b	16.19	158.82	16.42	21.89	156.7	1.5372
17		u55a	16.95	166.28	17.63	23.51	180.6	1.7717
18		u55b	17.12	167.95	16.41	21.88	157.0	1.5402
19		u22a	16.59	162.75	17.26	23.01	169.8	1.6657
20		u22b	17.70	173.64	18.00	24.00	184.1	1.8060
21	U-1B	u17a	18.10	177.56	19.77	26.36	217.1	2.1298
22		u17b	18.28	179.33	19.39	25.85	210.0	2.0601
23		u4a	17.44	171.09	18.52	24.69	192.9	1.8923
24		u4b	17.41	170.79	18.45	24.60	192.5	1.8884
25		u15a	17.62	172.85	19.26	25.68	204.2	2.0032
26		u15b	18.05	177.07	18.50	24.67	192.2	1.8855
27		u27a	17.83	174.91	17.98	23.97	198.4	1.9463
28		u27b	16.68	163.63	18.12	24.16	190.8	1.8717
29		u33a	16.70	163.83	17.40	23.20	177.0	1.7364
30		u33b	17.90	175.60	17.13	22.84	177.1	1.7374
31	U-2A	u41a	16.13	158.24	15.44	20.59	144.3	1.4156
32		u41b	16.73	164.12	15.43	20.57	148.9	1.4607
33		u85a	15.65	153.53	15.48	20.84	134.4	1.3185
34		u85b	15.86	155.59	16.54	22.05	150.7	1.4784
35		u29a	16.22	159.12	16.55	22.07	158.9	1.5588
36		u29b	16.48	161.67	16.27	21.69	155.5	1.5255
37		u40a	15.80	155.00	15.02	20.03	138.1	1.3548

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
38		u40b	15.46	151.66	15.38	20.51	139.6	1.3695
39		u35a	14.80	145.19	14.45	19.27	123.9	1.2155
40		u35b	15.20	149.11	14.32	19.09	122.2	1.1988
41	U-2B	u63a	17.34	170.11	19.20	25.60	206.2	2.0228
42		u63b	18.53	181.78	19.33	25.77	214.4	2.1033
43		u36a	17.18	168.54	16.30	21.73	170.0	1.6677
44		u36b	16.84	165.20	16.09	21.45	161.6	1.5853
45		u83a	16.40	160.88	16.86	22.48	169.6	1.6638
46		u83b	15.68	153.82	13.72	18.29	127.0	1.2459
47		u57a	17.40	170.69	18.32	24.43	195.9	1.9218
48		u57b	17.64	173.05	17.99	23.99	196.4	1.9267
49		u12a	17.21	168.33	18.03	24.04	189.7	1.8610
50		u12b	17.13	168.05	18.04	24.05	179.7	1.7629
51	U-3A	u10a	13.99	137.24	13.71	18.28	104.7	1.0271
52		u10b	13.93	136.65	13.50	18.00	104.9	1.0291
53		u69a	12.68	124.39	13.33	17.77	81.5	.7995
54		u69b	14.09	138.22	13.17	17.56	94.7	.9290
55		u59a	13.03	127.82	12.34	16.45	86.4	.8476
56		u59b	14.23	139.60	13.61	18.15	104.4	1.0242
57		u52a	13.59	133.32	13.56	18.08	103.1	1.0114
58		u52b	13.32	130.67	12.49	16.65	89.5	.8777
59		u56a	14.01	137.44	12.43	16.57	91.2	.8949
60		u56b	13.58	133.22	12.57	16.76	89.0	.8731
61	U-3B	u70a	17.95	176.09	18.27	24.36	193.7	1.9002
62		u70b	17.21	168.83	18.69	24.92	188.6	1.8502
63		u7a	17.79	174.52	18.40	24.53	187.5	1.8394
64		u7b	18.77	184.13	18.91	25.21	216.9	2.1278
65		u13a	16.94	166.18	18.18	24.24	185.8	1.8227
66		u13b	17.27	169.42	17.97	23.96	182.0	1.7854
67		u76a	18.08	177.36	18.24	24.32	198.7	1.9492
68		u76b	17.87	175.30	18.51	24.68	195.5	1.9179
69		u5a	17.64	173.05	18.44	24.59	188.6	1.8502
70		u5b	17.69	173.54	18.70	24.93	196.4	1.9267
71	U-4A	u9a	10.44	102.42	8.90	11.87	42.1	.4130
72		u9b	10.76	105.56	9.09	12.12	42.0	.4124
73		u32a	10.84	106.34	9.36	12.48	48.1	.4723
74		u32b	11.18	109.68	9.37	12.49	49.8	.4880

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
75		u75a	9.55	93.69	7.84	10.45	32.7	.3205
76		u75b	10.79	105.85	9.05	12.07	44.3	.4344
77		u24a	10.85	106.44	8.84	11.79	44.3	.4343
78		u24b	11.70	114.78	9.93	13.24	54.9	.5382
79		u20a	10.26	100.65	8.97	11.96	40.0	.3928
80		u20b	10.76	105.56	9.52	12.69	44.9	.4405
81	U-4B	u45a	16.23	159.22	15.32	20.43	142.2	1.3950
82		u45b	18.09	177.46	16.82	22.43	187.8	1.8423
83		u66a	17.44	171.09	18.56	24.75	183.8	1.8031
84		u66b	18.55	181.98	19.05	25.40	208.0	2.0405
85		u30a	17.64	173.05	18.41	24.55	199.3	1.9551
86		u30b	18.50	181.49	18.43	24.57	206.9	2.0297
87		u72a	17.19	168.63	17.40	23.20	179.1	1.7570
88		u72b	17.26	169.32	16.84	22.45	165.6	1.6245
89		u67a	17.68	173.44	19.01	25.35	204.4	2.0052
90		u67b	18.07	177.27	19.24	25.65	208.5	2.0454
91	U-5A	u16a	5.79	56.80	5.55	7.40	9.6	.0942
92		u16b	6.50	63.77	6.67	8.89	13.2	.1295
93		u51a	5.20	51.01	4.73	6.31	7.9	.0777
94		u51b	5.97	58.57	5.29	7.05	10.0	.0978
95		u65a	6.52	63.96	5.86	7.81	12.2	.1198
96		u65b	7.11	69.75	6.42	8.56	16.1	.1577
97		u8a	6.30	61.80	5.72	7.63	11.1	.1088
98		u8b	6.72	65.92	5.71	7.61	12.4	.1216
99		u26a	3.29	32.27	4.05	5.40	4.9	.0479
100		u26b	5.33	52.29	5.22	6.96	8.3	.0813
101	U-5B	u54a	17.65	173.15	18.58	24.77	178.1	1.7472
102		u54b	17.40	170.69	18.26	24.35	190.7	1.8708
103		u38a	17.39	170.60	16.07	21.43	167.4	1.6422
104		u38b	16.85	165.30	16.30	21.73	162.1	1.5902
105		u58a	17.16	168.34	15.85	21.13	152.4	1.4950
106		u58b	17.20	168.73	17.31	23.08	174.2	1.7089
107		u68a	18.08	177.36	19.24	25.65	197.4	1.9365
108		u68b	17.83	174.91	18.90	25.20	198.5	1.9473
109		u3a	17.76	174.23	17.90	23.87	191.7	1.8806
110		u3b	17.19	168.63	17.62	23.49	172.1	1.6883
111	wcontrol	w48a	15.74	154.41	15.34	20.45	119.0	1.1674

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
112		w48b	15.16	148.72	15.68	20.91	116.3	1.1466
113		w69a	16.89	165.69	20.16	26.88	183.4	1.7992
114		w69b	17.36	170.30	18.44	24.59	166.6	1.6343
115		w50a	15.85	155.49	18.02	24.03	138.7	1.3606
116		w50b	17.91	175.70	22.40	29.87	207.2	2.0326
117		w18a	17.09	167.65	18.22	24.29	171.9	1.6863
118		w18b	17.20	168.73	18.53	24.71	175.6	1.7226
119		w33a	16.57	162.55	17.90	23.87	152.0	1.4911
120		w33b	16.78	164.61	19.30	25.73	171.4	1.6814
121	W-1A	w4a	13.01	127.63	13.43	17.91	82.8	.8127
122		w4b	14.89	146.07	16.33	21.77	123.7	1.2135
123		w8a	12.30	120.66	13.14	17.52	77.1	.7560
124		w8b	15.25	149.60	15.29	20.39	120.6	1.1831
125		w41a	14.46	141.85	13.24	17.65	95.7	.9391
126		w41b	14.07	138.03	15.47	20.63	111.2	1.0909
127		w73a	14.73	144.50	14.19	18.92	102.4	1.0045
128		w73b	14.70	144.21	14.75	19.67	106.6	1.0457
129		w28a	15.18	148.92	14.47	19.29	108.1	1.0605
130		w28b	14.60	143.23	15.94	21.25	117.6	1.1537
131	W-1B	w45a	13.36	131.06	13.51	18.01	86.5	.8487
132		w45b	15.03	147.44	15.22	20.29	108.3	1.0624
133		w16a	15.81	155.10	17.80	23.73	156.6	1.5362
134		w16b	16.97	166.48	18.68	24.91	183.1	1.7962
135		w59a	14.40	141.26	15.61	20.81	101.3	.9938
136		w59b	15.80	155.00	17.87	23.83	136.2	1.3361
137		w5a	18.60	182.47	19.97	26.63	206.9	2.0297
138		w5b	17.76	174.23	20.51	27.35	207.2	2.0326
139		w1a	16.36	160.49	17.83	23.77	151.8	1.4892
140		w1b	15.95	156.47	17.80	23.73	149.6	1.4676
141	W-2A	w15a	11.45	112.32	10.98	14.64	53.6	.5261
142		w15b	12.99	127.43	12.91	17.21	79.0	.7747
143		w85a	11.85	116.25	11.33	15.11	63.6	.6242
144		w85b	10.94	107.32	9.63	12.84	47.9	.4703
145		w20a	12.00	117.72	10.84	14.45	58.2	.5706
146		w20b	12.21	119.78	11.65	15.53	67.4	.6611
147		w36a	10.67	104.67	10.22	13.63	44.1	.4328
148		w36b	10.45	102.51	10.26	13.68	43.9	.4304

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
149		w66a	12.34	121.06	11.96	15.95	66.6	.6531
150		w66b	12.46	122.23	12.22	16.29	66.2	.6498
151	W-2B	w65a	18.75	183.94	19.36	25.81	201.1	1.9728
152		w65b	16.68	163.63	16.79	22.39	149.0	1.4617
153		w68a	17.46	171.28	18.91	25.21	178.8	1.7540
154		w68b	17.85	175.11	19.73	26.31	189.7	1.8610
155		w70a	17.32	169.91	19.27	25.69	181.6	1.7815
156		w70b	16.48	161.67	19.35	25.80	169.5	1.6628
157		w9a	15.55	152.55	16.55	22.07	133.5	1.3096
158		w9b	16.29	159.80	16.72	22.29	141.8	1.3911
159		w31a	17.15	168.24	17.10	22.80	156.7	1.5372
160		w31b	16.66	163.43	15.49	20.65	138.5	1.3587
161	W-3A	w12a	7.69	75.44	7.32	9.76	18.6	.1822
162		w12b	8.21	80.54	8.02	10.69	23.9	.2341
163		w47a	8.02	78.68	7.99	10.65	21.7	.2126
164		w47b	4.48	43.95	6.14	8.19	8.6	.0841
165		w7a	8.25	80.93	7.92	10.56	23.5	.2304
166		w7b	8.11	79.56	8.20	10.93	24.1	.2365
167		w77a	7.17	70.34	6.88	9.17	16.5	.1618
168		w77b	7.42	72.79	7.47	9.96	18.4	.1805
169		w53a	6.60	64.75	7.20	9.60	15.7	.1542
170		w53b	6.73	66.02	7.36	9.81	15.6	.1534
171	W-3B	w17a	15.52	152.25	17.01	22.68	144.8	1.4205
172		w17b	16.08	157.74	17.22	22.96	150.8	1.4793
173		w27a	17.70	173.64	18.52	24.69	175.2	1.7187
174		w27b	16.07	157.65	17.55	23.40	149.1	1.4627
175		w40a	16.17	158.63	19.20	25.60	166.2	1.6304
176		w40b	17.19	168.63	17.80	23.73	161.6	1.5853
177		w57a	14.20	139.30	15.55	20.73	102.2	1.0026
178		w57b	13.31	130.57	14.37	19.16	84.7	.8305
179		w29a	17.19	168.63	18.61	24.81	181.1	1.7766
180		w29b	17.38	170.50	18.43	24.57	172.2	1.6893
181	W-4A	w89a	5.70	55.92	5.87	7.83	10.4	.1016
182		w89b	6.67	65.43	6.14	8.19	13.8	.1353
183		w38a	4.75	46.60	6.63	8.84	9.3	.0909
184		w38b	4.51	44.24	6.24	8.32	8.1	.0792
185		w21a	5.71	56.02	6.30	8.40	10.5	.1031

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
186		w21b	5.70	55.92	5.99	7.99	10.3	.1014
187		w42a	3.94	38.65	4.67	6.23	5.9	.0578
188		w42b	4.65	45.62	5.36	7.15	7.7	.0751
189		w52a	4.64	45.52	6.70	8.93	9.3	.0916
190		w52b	4.85	47.58	6.70	8.93	9.2	.0902
191	W-4B	w61a	16.22	159.12	17.37	23.16	137.2	1.3459
192		w61b	17.54	172.07	19.42	25.89	175.8	1.7246
193		w46a	12.26	120.27	11.42	15.23	68.8	.6745
194		w46b	12.89	126.45	12.60	16.80	73.9	.7252
195		w14a	15.19	149.01	14.93	19.91	115.5	1.1331
196		w14b	15.07	147.84	14.59	19.45	112.6	1.1046
197		w86a	16.85	165.30	15.74	20.99	145.4	1.4264
198		w86b	16.87	165.49	16.24	21.65	155.5	1.5255
199		w2a	13.65	133.91	12.73	16.97	85.8	.8412
200		w2b	14.35	140.77	13.79	18.39	99.4	.9753
201	W-5A	w23a	2.23	21.88	3.48	4.64	3.3	.0328
202		w23b	2.17	21.29	3.39	4.52	2.9	.0289
203		w71a	2.27	22.27	4.78	6.37	3.7	.0363
204		w71b	1.87	18.34	4.41	5.88	2.5	.0245
205		w84a	1.79	17.56	4.02	5.36	2.9	.0284
206		w84b	2.12	20.80	4.39	5.85	2.9	.0284
207		w6a	2.56	25.11	4.37	5.83	3.8	.0373
208		w6b	1.95	19.13	3.86	5.15	2.7	.0265
209		w83a	2.06	20.21	4.07	5.43	2.9	.0284
210		w83b	2.50	24.53	4.39	5.85	3.4	.0334
211	W-5B	w56a	12.76	125.18	13.41	17.88	73.3	.7190
212		w56b	13.27	130.18	13.33	17.77	77.3	.7583
213		w37a	14.29	140.18	12.82	17.09	89.4	.8770
214		w37b	13.80	135.38	13.40	17.87	91.9	.9015
215		w88a	14.44	141.66	13.31	17.75	98.5	.9663
216		w88b	14.28	140.09	13.41	17.88	99.9	.9800
217		w25a	16.03	157.25	14.72	19.63	126.5	1.2410
218		w25b	13.71	134.50	13.49	17.99	96.2	.9437
219		w32a	14.23	139.60	13.50	18.00	91.9	.9015
220		w32b	13.72	134.59	14.10	18.80	93.6	.9182

	group	specimen	dl	da	db	de	overhang	flexrig
112		w48b	.	.	.	.	4.100	49.36
113		w69a	.40	-.01	-.08	.41	4.150	51.19
114		w69b	.	.	.	.	3.675	35.55
115		w50a	-.34	.02	.04	.34	3.925	43.31
116		w50b	.	.	.	.	3.950	44.14
117		w18a	-.01	-.05	-.05	.07	3.875	41.68
118		w18b	.	.	.	.	3.675	35.55
119		w33a	.09	.01	.07	.11	3.500	30.71
120		w33b	.	.	.	.	3.975	44.99
121	W-1A	w4a	-2.01	.17	4.29	4.74	3.675	35.55
122		w4b	.	.	.	.	3.700	36.28
123		w8a	-1.81	.09	4.44	4.80	3.400	28.15
124		w8b	.	.	.	.	3.375	27.54
125		w41a	-2.05	.12	4.49	4.94	3.950	44.14
126		w41b	.	.	.	.	3.875	41.68
127		w73a	-1.87	.13	4.36	4.75	3.800	39.30
128		w73b	.	.	.	.	3.975	44.99
129		w28a	-2.39	.12	4.61	5.19	3.950	44.14
130		w28b	.	.	.	.	3.775	38.53
131	W-1B	w45a	-.52	.28	-.36	.69	4.050	47.58
132		w45b	.	.	.	.	4.075	48.47
133		w16a	-.33	.24	-.36	.54	3.525	31.37
134		w16b	.	.	.	.	3.575	32.73
135		w59a	-.61	.25	-.28	.72	3.800	39.30
136		w59b	.	.	.	.	3.775	38.53
137		w5a	.02	.25	-.47	.53	3.850	40.87
138		w5b	.	.	.	.	3.925	43.31
139		w1a	-.39	.29	-.45	.66	4.075	48.47
140		w1b	.	.	.	.	4.100	49.36
141	W-2A	w15a	-3.10	.47	5.33	6.18	3.600	33.42
142		w15b	.	.	.	.	3.650	34.83
143		w85a	-3.17	.51	5.62	6.47	3.725	37.02
144		w85b	.	.	.	.	3.575	32.73
145		w20a	-3.04	.51	5.28	6.10	3.650	34.83
146		w20b	.	.	.	.	3.725	37.02
147		w36a	-3.02	.61	4.74	5.65	4.250	54.98
148		w36b	.	.	.	.	4.125	50.27

	group	specimen	dl	da	db	de	overhang	flexrig
149		w66a	-2.85	.51	4.99	5.77	4.000	45.84
150		w66b	.	.	.	.	4.025	46.70
151	W-2B	w65a	.24	.23	-.69	.77	3.975	44.99
152		w65b	.	.	.	.	3.700	36.28
153		w68a	-.08	.28	-.63	.69	3.600	33.42
154		w68b	.	.	.	.	3.725	37.02
155		w70a	-.07	.25	-.60	.65	4.225	54.02
156		w70b	.	.	.	.	3.925	43.31
157		w9a	.08	.28	-.65	.71	3.475	30.06
158		w9b	.	.	.	.	3.550	32.04
159		w31a	.27	.22	-.68	.76	4.075	48.47
160		w31b	.	.	.	.	4.525	66.36
161	W-3A	w12a	-4.57	.93	7.62	8.93	3.825	40.08
162		w12b	.	.	.	.	3.850	40.87
163		w47a	-4.63	.96	7.70	9.04	4.375	59.98
164		w47b	.	.	.	.	4.575	68.59
165		w7a	-4.45	.96	7.33	8.63	4.600	69.72
166		w7b	.	.	.	.	4.250	54.98
167		w77a	-4.64	1.04	7.87	9.20	4.175	52.12
168		w77b	.	.	.	.	3.975	44.99
169		w53a	-4.51	.99	7.32	8.65	4.200	53.07
170		w53b	.	.	.	.	4.025	46.70
171	W-3B	w17a	-.02	.33	-.82	.88	3.275	25.16
172		w17b	.	.	.	.	3.400	28.15
173		w27a	-.58	.34	-.62	.91	3.475	30.06
174		w27b	.	.	.	.	3.375	27.54
175		w40a	-.15	.28	-.67	.74	3.750	37.77
176		w40b	.	.	.	.	3.825	40.08
177		w57a	-.11	.32	-.67	.75	3.650	34.83
178		w57b	.	.	.	.	3.575	32.73
179		w29a	.05	.27	-.66	.71	3.875	41.68
180		w29b	.	.	.	.	3.600	33.42
181	W-4A	w89a	-5.13	.72	10.07	11.32	4.150	51.19
182		w89b	.	.	.	.	4.125	50.27
183		w38a	-4.62	.77	10.02	11.06	4.725	75.56
184		w38b	.	.	.	.	4.725	75.56
185		w21a	-4.61	.76	9.36	10.46	4.350	58.96

	group	specimen	di	da	db	de	overhang	flexrig
186		w21b	.	.	.	.	4.175	52.12
187		w42a	-4.92	.70	10.48	11.60	4.475	64.19
188		w42b	.	.	.	.	4.300	56.95
189		w52a	-5.11	.90	8.87	10.28	4.300	56.95
190		w52b	.	.	.	.	4.250	54.98
191	W-4B	w61a	-.42	.18	.16	.48	4.025	46.70
192		w61b	.	.	.	.	4.000	45.84
193		w46a	-.24	.29	-.17	.41	4.300	56.95
194		w46b	.	.	.	.	4.025	46.70
195		w14a	-.08	.23	-.20	.32	3.300	25.74
196		w14b	.	.	.	.	3.400	28.15
197		w86a	-.01	.16	-.10	.19	3.975	44.99
198		w86b	.	.	.	.	3.800	39.30
199		w2a	-.40	.15	.03	.43	3.500	30.71
200		w2b	.	.	.	.	3.600	33.42
201	W-5A	w23a	-6.10	.91	11.62	13.16	5.425	114.36
202		w23b	.	.	.	.	5.275	105.13
203		w71a	-6.28	.96	11.64	13.26	5.675	130.91
204		w71b	.	.	.	.	5.625	127.48
205		w84a	-6.40	.96	11.25	12.98	5.125	96.42
206		w84b	.	.	.	.	4.950	86.87
207		w6a	-6.50	.84	12.65	14.25	5.100	95.01
208		w6b	.	.	.	.	4.900	84.27
209		w83a	-6.09	.95	11.41	12.97	5.775	137.95
210		w83b	.	.	.	.	5.450	115.95
211	W-5B	w56a	-.44	.39	-.02	.59	3.475	30.06
212		w56b	.	.	.	.	3.575	32.62
213		w37a	-.32	.40	-.13	.53	3.800	39.30
214		w37b	.	.	.	.	3.725	37.02
215		w88a	-.12	.34	-.21	.42	4.325	57.95
216		w88b	.	.	.	.	4.050	47.58
217		w25a	-.42	.38	.08	.57	3.725	37.02
218		w25b	.	.	.	.	3.675	35.55
219		w32a	-.73	.34	.28	.85	3.700	36.28
220		w32b	.	.	.	.	3.725	37.02

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
1	control	u53a	17.93	175.89	19.42	25.89	208.6	2.0464
2		u53b	18.41	180.60	19.39	25.85	214.3	2.1023
3		u61a	16.88	165.59	18.79	25.05	190.2	1.8659
4		u61b	18.27	179.23	18.88	25.17	202.3	1.9846
5		u84a	18.29	179.42	18.95	25.27	204.8	2.0091
6		u84b	18.24	178.93	18.99	25.32	207.7	2.0375
7		u19a	18.16	178.15	19.44	25.92	205.0	2.0111
8		u19b	18.29	179.42	18.67	24.89	197.7	1.9394
9		u48a	17.09	167.65	18.03	24.04	181.5	1.7805
10		u48b	17.85	175.11	18.13	24.17	197.1	1.9336
11	U-1A	u1a	16.88	165.59	16.75	22.33	169.4	1.6618
12		u1b	16.76	164.42	17.00	22.67	167.8	1.6461
13		u88a	17.39	170.60	18.17	24.23	194.6	1.9090
14		u88b	17.11	167.85	17.88	23.84	184.6	1.8109
15		u11a	15.91	156.08	15.69	20.92	150.4	1.4754
16		u11b	16.19	158.82	16.42	21.89	156.7	1.5372
17		u55a	16.95	166.28	17.63	23.51	180.6	1.7717
18		u55b	17.12	167.95	16.41	21.88	157.0	1.5402
19		u22a	16.59	162.75	17.26	23.01	169.8	1.6657
20		u22b	17.70	173.64	18.00	24.00	184.1	1.8060
21	U-1B	u17a	18.10	177.56	19.77	26.36	217.1	2.1298
22		u17b	18.28	179.33	19.39	25.85	210.0	2.0601
23		u4a	17.44	171.09	18.52	24.69	192.9	1.8923
24		u4b	17.41	170.79	18.45	24.60	192.5	1.8884
25		u15a	17.62	172.85	19.26	25.68	204.2	2.0032
26		u15b	18.05	177.07	18.50	24.67	192.2	1.8855
27		u27a	17.83	174.91	17.98	23.97	198.4	1.9463
28		u27b	16.68	163.63	18.12	24.16	190.8	1.8717
29		u33a	16.70	163.83	17.40	23.20	177.0	1.7364
30		u33b	17.90	175.60	17.13	22.84	177.1	1.7374
31	U-2A	u41a	16.13	158.24	15.44	20.59	144.3	1.4156
32		u41b	16.73	164.12	15.43	20.57	148.9	1.4607
33		u85a	15.65	153.53	15.48	20.84	134.4	1.3185
34		u85b	15.86	155.59	16.54	22.05	150.7	1.4784
35		u29a	16.22	159.12	16.55	22.07	158.9	1.5588
36		u29b	16.48	161.67	16.27	21.69	155.5	1.5255
37		u40a	15.80	155.00	15.02	20.03	138.1	1.3548

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
38		u40b	15.46	151.66	15.38	20.51	139.6	1.3695
39		u35a	14.80	145.19	14.45	19.27	123.9	1.2155
40		u35b	15.20	149.11	14.32	19.09	122.2	1.1988
41	U-2B	u63a	17.34	170.11	19.20	25.60	206.2	2.0228
42		u63b	18.53	181.78	19.33	25.77	214.4	2.1033
43		u36a	17.18	168.54	16.30	21.73	170.0	1.6677
44		u36b	16.84	165.20	16.09	21.45	161.6	1.5853
45		u83a	16.40	160.88	16.86	22.48	169.6	1.6638
46		u83b	15.68	153.82	13.72	18.29	127.0	1.2459
47		u57a	17.40	170.69	18.32	24.43	195.9	1.9218
48		u57b	17.64	173.05	17.99	23.99	196.4	1.9267
49		u12a	17.21	168.33	18.03	24.04	189.7	1.8610
50		u12b	17.13	168.05	18.04	24.05	179.7	1.7629
51	U-3A	u10a	13.99	137.24	13.71	18.28	104.7	1.0271
52		u10b	13.93	136.65	13.50	18.00	104.9	1.0291
53		u69a	12.68	124.39	13.33	17.77	81.5	.7995
54		u69b	14.09	138.22	13.17	17.56	94.7	.9290
55		u59a	13.03	127.82	12.34	16.45	86.4	.8476
56		u59b	14.23	139.60	13.61	18.15	104.4	1.0242
57		u52a	13.59	133.32	13.56	18.08	103.1	1.0114
58		u52b	13.32	130.67	12.49	16.65	89.5	.8777
59		u56a	14.01	137.44	12.43	16.57	91.2	.8949
60		u56b	13.58	133.22	12.57	16.76	89.0	.8731
61	U-3B	u70a	17.95	176.09	18.27	24.36	193.7	1.9002
62		u70b	17.21	168.83	18.69	24.92	188.6	1.8502
63		u7a	17.79	174.52	18.40	24.53	187.5	1.8394
64		u7b	18.77	184.13	18.91	25.21	216.9	2.1278
65		u13a	16.94	166.18	18.18	24.24	185.8	1.8227
66		u13b	17.27	169.42	17.97	23.96	182.0	1.7854
67		u76a	18.08	177.36	18.24	24.32	198.7	1.9492
68		u76b	17.87	175.30	18.51	24.68	[illegible]	1.9179
69		u5a	17.64	173.05	18.44	24.59	188.6	1.8502
70		u5b	17.69	173.54	18.70	24.93	196.4	1.9267
71	U-4A	u9a	10.44	102.42	8.90	11.87	42.1	.4130
72		u9b	10.76	105.56	9.09	12.12	42.0	.4124
73		u32a	10.84	106.34	9.36	12.48	48.1	.4723
74		u32b	11.18	109.68	9.37	12.49	49.8	.4880

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
75		u75a	9.55	93.69	7.84	10.45	32.7	.3205
76		u75b	10.79	105.85	9.05	12.07	44.3	.4344
77		u24a	10.85	106.44	8.84	11.79	44.3	.4343
78		u24b	11.70	114.78	9.93	13.24	54.9	.5382
79		u20a	10.26	100.65	8.97	11.96	40.0	.3928
80		u20b	10.76	105.56	9.52	12.69	44.9	.4405
81	U-4B	u45a	16.23	159.22	15.32	20.43	142.2	1.3950
82		u45b	18.09	177.46	16.82	22.43	187.8	1.8423
83		u66a	17.44	171.09	18.56	24.75	183.8	1.8031
84		u66b	18.55	181.98	19.05	25.40	208.0	2.0405
85		u30a	17.64	173.05	18.41	24.55	199.3	1.9551
86		u30b	18.50	181.49	18.43	24.57	206.9	2.0297
87		u72a	17.19	168.63	17.40	23.20	179.1	1.7570
88		u72b	17.26	169.32	16.84	22.45	165.6	1.6245
89		u67a	17.68	173.44	19.01	25.35	204.4	2.0052
90		u67b	18.07	177.27	19.24	25.65	208.5	2.0454
91	U-5A	u16a	5.79	56.80	5.55	7.40	9.6	.0942
92		u16b	6.50	63.77	6.67	8.89	13.2	.1295
93		u51a	5.20	51.01	4.73	6.31	7.9	.0777
94		u51b	5.97	58.57	5.29	7.05	10.0	.0978
95		u65a	6.52	63.96	5.86	7.81	12.2	.1198
96		u65b	7.11	69.75	6.42	8.56	16.1	.1577
97		u8a	6.30	61.80	5.72	7.63	11.1	.1088
98		u8b	6.72	65.92	5.71	7.61	12.4	.1216
99		u26a	3.29	32.27	4.05	5.40	4.9	.0479
100		u26b	5.33	52.29	5.22	6.96	8.3	.0813
101	U-5B	u54a	17.65	173.15	18.58	24.77	178.1	1.7472
102		u54b	17.40	170.69	18.26	24.35	190.7	1.8708
103		u38a	17.39	170.60	16.07	21.43	167.4	1.6422
104		u38b	16.85	165.30	16.30	21.73	162.1	1.5902
105		u58a	17.16	168.34	15.85	21.13	152.4	1.4950
106		u58b	17.20	168.73	17.31	23.08	174.2	1.7089
107		u68a	18.08	177.36	19.24	25.65	197.4	1.9365
108		u68b	17.83	174.91	18.90	25.20	198.5	1.9473
109		u3a	17.76	174.23	17.90	23.87	191.7	1.8806
110		u3b	17.19	168.63	17.62	23.49	172.1	1.6883
111	wcontrol	w48a	15.74	154.41	15.34	20.45	119.0	1.1674

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
112		w48b	15.16	148.72	15.68	20.91	116.3	1.1466
113		w69a	16.89	165.69	20.16	26.88	183.4	1.7992
114		w69b	17.36	170.30	18.44	24.59	166.6	1.6343
115		w50a	15.85	155.49	18.02	24.03	138.7	1.3606
116		w50b	17.91	175.70	22.40	29.87	207.2	2.0326
117		w18a	17.09	167.65	18.22	24.29	171.9	1.6863
118		w18b	17.20	168.73	18.53	24.71	175.6	1.7226
119		w33a	16.57	162.55	17.90	23.87	152.0	1.4911
120		w33b	16.78	164.61	19.30	25.73	171.4	1.6814
121	W-1A	w4a	13.01	127.63	13.43	17.91	82.8	.8127
122		w4b	14.89	146.07	16.33	21.77	123.7	1.2135
123		w8a	12.30	120.66	13.14	17.52	77.1	.7560
124		w8b	15.25	149.60	15.29	20.39	120.6	1.1831
125		w41a	14.46	141.85	13.24	17.65	95.7	.9391
126		w41b	14.07	138.03	15.47	20.63	111.2	1.0909
127		w73a	14.73	144.50	14.19	18.92	102.4	1.0045
128		w73b	14.70	144.21	14.75	19.67	106.6	1.0457
129		w28a	15.18	148.92	14.47	19.29	108.1	1.0605
130		w28b	14.60	143.23	15.94	21.25	117.6	1.1537
131	W-1B	w45a	13.36	131.06	13.51	18.01	86.5	.8487
132		w45b	15.03	147.44	15.22	20.29	108.3	1.0624
133		w16a	15.81	155.10	17.80	23.73	156.6	1.5362
134		w16b	16.97	166.48	18.68	24.91	183.1	1.7962
135		w59a	14.40	141.26	15.61	20.81	101.3	.9938
136		w59b	15.80	155.00	17.87	23.83	136.2	1.3361
137		w5a	18.60	182.47	19.97	26.63	206.9	2.0297
138		w5b	17.76	174.23	20.51	27.35	207.2	2.0326
139		w1a	16.36	160.49	17.83	23.77	151.8	1.4892
140		w1b	15.95	156.47	17.80	23.73	149.6	1.4676
141	W-2A	w15a	11.45	112.32	10.98	14.64	53.6	.5261
142		w15b	12.99	127.43	12.91	17.21	79.0	.7747
143		w85a	11.85	116.25	11.33	15.11	63.6	.6242
144		w85b	10.94	107.32	9.63	12.84	47.9	.4703
145		w20a	12.00	117.72	10.84	14.45	58.2	.5706
146		w20b	12.21	119.78	11.65	15.53	67.4	.6611
147		w36a	10.67	104.67	10.22	13.63	44.1	.4328
148		w36b	10.45	102.51	10.26	13.68	43.9	.4304

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
149		w66a	12.34	121.06	11.96	15.95	66.6	.6531
150		w66b	12.46	122.23	12.22	16.29	66.2	.6498
151	W-2B	w65a	18.75	183.94	19.36	25.81	201.1	1.9728
152		w65b	16.68	163.63	16.79	22.39	149.0	1.4617
153		w68a	17.46	171.28	18.91	25.21	178.8	1.7540
154		w68b	17.85	175.11	19.73	26.31	189.7	1.8610
155		w70a	17.32	169.91	19.27	25.69	181.6	1.7815
156		w70b	16.48	161.67	19.35	25.80	169.5	1.6628
157		w9a	15.55	152.55	16.55	22.07	133.5	1.3096
158		w9b	16.29	159.80	16.72	22.29	141.8	1.3911
159		w31a	17.15	168.24	17.10	22.80	156.7	1.5372
160		w31b	16.66	163.43	15.49	20.65	138.5	1.3587
161	W-3A	w12a	7.69	75.44	7.32	9.76	18.6	.1822
162		w12b	8.21	80.54	8.02	10.69	23.9	.2341
163		w47a	8.02	78.68	7.99	10.65	21.7	.2126
164		w47b	4.48	43.95	6.14	8.19	8.6	.0841
165		w7a	8.25	80.93	7.92	10.56	23.5	.2304
166		w7b	8.11	79.56	8.20	10.93	24.1	.2365
167		w77a	7.17	70.34	6.88	9.17	16.5	.1618
168		w77b	7.42	72.79	7.47	9.96	18.4	.1805
169		w53a	6.60	64.75	7.20	9.60	15.7	.1542
170		w53b	6.73	66.02	7.36	9.81	15.6	.1534
171	W-3B	w17a	15.52	152.25	17.01	22.68	144.8	1.4205
172		w17b	16.08	157.74	17.22	22.96	150.8	1.4793
173		w27a	17.70	173.64	18.52	24.69	175.2	1.7187
174		w27b	16.07	157.65	17.55	23.40	149.1	1.4627
175		w40a	16.17	158.63	19.20	25.60	166.2	1.6304
176		w40b	17.19	168.63	17.80	23.73	161.6	1.5853
177		w57a	14.20	139.30	15.55	20.73	102.2	1.0026
178		w57b	13.31	130.57	14.37	19.16	84.7	.8305
179		w29a	17.19	168.63	18.61	24.81	181.1	1.7766
180		w29b	17.38	170.50	18.43	24.57	172.2	1.6893
181	W-4A	w89a	5.70	55.92	5.87	7.83	10.4	.1016
182		w89b	6.67	65.43	6.14	8.19	13.8	.1353
183		w38a	4.75	46.60	6.63	8.84	9.3	.0909
184		w38b	4.51	44.24	6.24	8.32	8.1	.0792
185		w21a	5.71	56.02	6.30	8.40	10.5	.1031

	group	specimen	load	tenstr	elong	extensn	wrkrup	energy
186		w21b	5.70	55.92	5.99	7.99	10.3	.1014
187		w42a	3.94	38.65	4.67	6.23	5.9	.0578
188		w42b	4.65	45.62	5.36	7.15	7.7	.0751
189		w52a	4.64	45.52	6.70	8.93	9.3	.0916
190		w52b	4.85	47.58	6.70	8.93	9.2	.0902
191	W-4B	w61a	16.22	159.12	17.37	23.16	137.2	1.3459
192		w61b	17.54	172.07	19.42	25.89	175.8	1.7246
193		w46a	12.26	120.27	11.42	15.23	68.8	.6745
194		w46b	12.89	126.45	12.60	16.80	73.9	.7252
195		w14a	15.19	149.01	14.93	19.91	115.5	1.1331
196		w14b	15.07	147.84	14.59	19.45	112.6	1.1046
197		w86a	16.85	165.30	15.74	20.99	145.4	1.4264
198		w86b	16.87	165.49	16.24	21.65	155.5	1.5255
199		w2a	13.65	133.91	12.73	16.97	85.8	.8412
200		w2b	14.35	140.77	13.79	18.39	99.4	.9753
201	W-5A	w23a	2.23	21.88	3.48	4.64	3.3	.0328
202		w23b	2.17	21.29	3.39	4.52	2.9	.0289
203		w71a	2.27	22.27	4.78	6.37	3.7	.0363
204		w71b	1.87	18.34	4.41	5.88	2.5	.0245
205		w84a	1.79	17.56	4.02	5.36	2.9	.0284
206		w84b	2.12	20.80	4.39	5.85	2.9	.0284
207		w6a	2.56	25.11	4.37	5.83	3.8	.0373
208		w6b	1.95	19.13	3.86	5.15	2.7	.0265
209		w83a	2.06	20.21	4.07	5.43	2.9	.0284
210		w83b	2.50	24.53	4.39	5.85	3.4	.0334
211	W-5B	w56a	12.76	125.18	13.41	17.88	73.3	.7190
212		w56b	13.27	130.18	13.33	17.77	77.3	.7583
213		w37a	14.29	140.18	12.82	17.09	89.4	.8770
214		w37b	13.80	135.38	13.40	17.87	91.9	.9015
215		w88a	14.44	141.66	13.31	17.75	98.5	.9663
216		w88b	14.28	140.09	13.41	17.88	99.9	.9800
217		w25a	16.03	157.25	14.72	19.63	126.5	1.2410
218		w25b	13.71	134.50	13.49	17.99	96.2	.9437
219		w32a	14.23	139.60	13.50	18.00	91.9	.9015
220		w32b	13.72	134.59	14.10	18.80	93.6	.9182