CHAPTER 7

ANALYSIS OF DYES IN ANCIENT TEXTILES

There are numerous rationales for performing dye and chemical analysis on samples taken from ancient textiles. The advantages to museums, responsible for the procurement, display, and conservation of prehistoric textiles, are many. Knowledge of the dyes present can assist the museum personnel in identifying, cleaning, and authenticating the specimen, as well as aiding the museum technician in decisions regarding lighting intensity and conservation procedures (Saltzman 1978, p. 181).

Too much light can critically affect the color and the tensile properties of some dyed textiles (Needles and Zeronian, eds. 1984, p. 22), and it is known that light-induced color changes in dyed and dyed-mordanted wool and silk fabrics are dependent upon the dye or dye-mordant combination used, as well as on the fiber type to which they were applied (For example: Dyed wool was less light sensitive than dyed silk.) (Needles and Zeronian, eds. 1984, p. 203).

Dye analysis was carried out on samples of purple yarns removed from materials made by the Mixtec Indians of southwest Mexico. The results revealed that three samples were dyed with cochineal, several were dyed with an early synthetic dye (fuchsine), and the remaining were dyed with synthetic dyes. This analysis signifies that colors which appear to be the same can be different, and that these different dyes possess different lightfastness. For example, textiles dyed with fuchsine can fade within weeks upon exposure to light (Saltzman 1978, p.181-182).

Through work conducted by Padfield and Landi, information about lightfastness of natural dyes has become known. They discovered the lightfastness of textiles dyed with natural dyes such as indigo, madder, and cochineal. They found that without mordanting cochineal demonstrated poor lightfastness (Saltzman 1978, p. 181).

Environmental Archaeology

Beyond the needs of the museum community, and more relevant to the scope of this thesis, is the need of the archaeologist to reconstruct the daily lives and environment of pre-literate cultures. The environmental archaeologist, through careful examination of the remaining material culture, attempts to obtain a more complete understanding of prehistoric man and his interrelationship with the environment (Butzer 1982, p. 5).

Through analysis of artifacts much can be learned. In many cases information acquired from cultural remains is not visually apparent, and a growing number of sophisticated tests, carried out by experts from a multitude of disciplines, must be conducted to assist the archaeologist in establishing proper conclusions about the life of the people once occupying an area at a particular period in time. There is also an increasing emphasis in archaeological pursuits towards gathering information about the daily lives of the common people of a culture: the farmers, workers, craftsmen, tradesmen, artisans, etc.

Dye analysis is one such sophisticated test which can assist the archaeologist in procuring invaluable information about the daily lives of a particular group of people. It is quite possible that the knowledge obtained through dye analysis of prehistoric burial textiles may not be acquired by any other means. Information obtained in this manner is essential to the validation of already existing data.

The results of dye analysis can reveal practices within a culture, which can then be used for comparisons to similar and diverse cultures. When compiled with other archaeological data, dye analysis can reveal much about the trade practices and the transfer of information between cultures. Some questions possibly answered by dye analysis are:

1. What was the environment of the area like at the time the textiles were dyed (ex. climate, types of snails, bugs, cacti, shell fish, etc.)?

2. How extensively did the people exploit their immediate environment?

3. Were the dye and mordants used obtained from the immediate environment or from trade?

4. Was there any interruption of the use of certain dyes over time, and could these interruptions be correlated to climatic conditions, interruption in trade, conquest, or exhaustion of available resources?

5. If the dye was obtained by trade, from how far away did the dye come?

6. How advanced were the textile dyeing techniques compared to known techniques of other cultures at the same period in time?

7. Were different dyes used more for the elite than for the commoner?

8. What was the range of colors used, and did these colors have any symbolic meaning?

9. Were any available dyes omitted from use, and if so why?

10. How available were the dyes which were used?

11. How valuable were the dyes which were used?

12. Was the culture in a state of decline or change as determined by the dyeing techniques and dyes used?

13. Was there a contact period with an exchange of cultural information from outside the Americas in pre-historic times?

This list is by no means complete. New discoveries of dyes present in ancient textiles often give rise to more questions than answers, requiring further dye analysis. One specific question raised by finding cochineal present in Pre-Inca textiles is: Did the use of cochineal originate in Peru and spread to Mexico, or originate in Mexico and spread to Peru; or did the use of cochineal develop in Peru and Mexico independently?

History of Dye Analysis

It has been known for over a century that dyes and pigments dissolved in various solvents give off characteristic colors (Saltzman and Keay 1963, p. 242). Solution spectrometry was first used for the analysis of dyestuff in the first part of the 20th century, by Professor Formanek of Prague. At that time, accuracy was a problem, and Formanek reported only a fifty percent accuracy in his test results (Mc Lean and Connell, eds. 1986, p. 29). Eventually, the technique of solution spectrophotometry became more exact and was used widely within industry. It was not until 1940 that it was used for archaeological investigation by Fester and Associates, who performed spectrophotometry on the colorants of the Paracas culture from Peru (Saltzman 1977, p. 173; after Fester 1940, 1943).

Procedures for Dye and Pigment Analysis of Ancient Textiles

Procedures for determining the dye present in ancient textiles can be very simple or complex. Regardless of the process, the overriding consideration for dye analysis is the availability of accurate standards by which the test results are compared. Having appropriate standards available for comparison with dyes present in prehistoric specimens is an involved matter, and the collection of materials for standards from the region of interest can be a very costly and time consuming. In spite of the difficulty, once these standards are acquired they serve as an invaluable measure by which unknown dyes are evaluated (Carter 1977, p. 174).

Dye Standards

Dye standards consist of samples of fibers (fibers must be the same as those from which the textile was woven; for example alpaca, wool, cotton, silk, etc.), dyed with the dyes and techniques known to have been used in the place and time of the textile's origin. Procurement of the necessary ingredients to replicate the ancient procedures on known fibers can be difficult, as these substances are not easily found commercially.

Botanical expeditions to the geographic location of the specimen's extraction may be necessary to procure the fiber and dyes needed for analysis. These costly expeditions may utilize the majority of the funds available for dye analysis. In addition, to assure a full range of standards, these standards must be made of all possible combinations of dyes and dyeing techniques used by the particular culture responsible for the dyed textile. Today, increasing numbers of prehistoric textiles are being analyzed in an increasing number of laboratories. As the number and type of available standards for comparison with ancient dye samples grows, accuracy has increased and costs are reduced.

Contamination of Ancient Textiles

Archaeological samples present a unique challenge to the persons conducting dye analysis, because consideration must be made for the reduction of color which takes place throughout time. This degradation depends greatly upon the circumstances to which the textile has been subjected. Archaeological specimens retrieved from burial sites and other locations have frequently been exposed to severe conditions such as moisture, bacteria, yeast, algae, and fungi. These agents not only caused discoloration and deterioration of the dyed specimen, but may also have facilitated the contamination of the textile with substances present in the burial environment.

Burial causes darkening and extremely large changes in shade of color in most dyed fabrics. Mordanted-dyed fabrics show less deepening and change (mordants have a profound effect on the shade and depth of shade of the fiber). Wool, acid-dyed with cochineal, underwent extensive darkening during burial, and the color shifted to purple, presumably because of soil ion-induced mordanting. Copper and chromium mordanted-dyed textiles prevent burial-induced damage to textiles, because of the antibacterial properties of these more stable complexes which are less susceptible to ion exchange during soil burial. Invaluable information about the mordant, dye, and fiber used in burial textiles provides an indication of the probable degree of deterioration (Needles and

Zeronian, eds. 1984, p. 200-210).

It is of interest to note here that certain metals or salts will affect the fiber. Textiles wrapped around an iron object may have been completely disintegrated, but have remained as a discernible iron oxide. When the same textile was wrapped around bronze, copper, or silver, the oxidation process often served to preserve them in the patina which is formed. This held true as long as no ammonia was produced during the process. It is of interest that the dyed wool fabrics resting near metal objects or ornaments showed less degradation, and actually appeared to benefit from the antimicrobial properties of such metals as iron and copper (Needles and Zeronian, eds. 1987, p. 200; Robinson 1969, p. 18). In the Indus Valley, archaeologists have discovered scraps of cotton preserved in contact with copper for over 2,000 years (Robinson 1969, p. 18).

Textiles under fairly dry conditions are amongst the toughest substances known. Humidity of any kind, on the other hand, will destroy textile faster than most other agents (Robinson 1969, p. 18). The ideal preserver of ancient fabrics has been in the salt mines of dry regions, and the sandy and alkaline soils of the drier deserts of North Africa, the Near East, and the Central American coastal strips (Robinson 1969, p. 18). Thus the condition of textiles differs because of such burial conditions as nearness to metals, climatic conditions, soil conditions, burial contamination, duration of burial, type of fiber, mordant, and dye used. Even if the coloring matter of the dyed artifact has been severely altered, the chemical foundation of the dyestuff is still preserved and usually can be detected (Diehl 1972, p. 28).

Because of the unique circumstances to which archaeological specimens have been subjected, simple color comparisons of dyes found in prehistoric textiles to a standard is not always satisfactory (McLean and Connell 1986, p. 27). The practice of using an overlay of dyes to achieve a desired color outcome (for example, a blue dye such as indigo can be overlaid with the red dye cochineal to produce purples, as in the case of the yarn from Bar Kochba Cave) can be deceiving in simple color comparison. Therefore, when preparing for dye analysis, it may be advisable to chemically analyze the substances extracted from the specimen (Saltzman and Keay 1967, p. 360).

Dye Analysis Procedures

When unknown colorants are dissolved in suitable solvents, they give solutions of characteristic color which are well defined by their spectral absorption. Removing the dye from sample fibers and preparing solutions with appropriate solvents is the first step in the spectrophotometric procedure (Goffer 1980, p. 183). With organic colorants fixed in appropriate solvents, both pure dyes and mixtures of dyes can be identified with the aid of solution spectra. In this method, spectrophotometric curves of the solution of the unknown colorant is compared with the spectra of known materials or standards. The spectrophotometric equipment is relatively simple to operate and is available in many chemical testing laboratories.

The Spectrophotometric Analysis

Development of the spectrophotometric technique for textiles analysis first took place in the early 1940s by Stearbs and Associates at the American Cyanamid Co. (Saltzman and Keay 1967, p. 361). The method is based on the fact that all organic colorants will dissolve to a sufficient degree in at least one solvent to give a colored solution. A "spot test" of the solution can give a clue to the identity of the material. Final determination of the dye takes place with the use of the spectrophotometer. Light absorption of colored solution gives a characteristic curve. Additional refinement takes place with the use of log density curve (log 1/T) available on some spectrophotometers. This is carried out by plotting the logarithm of the absorbency vs. the wavelength. By use of the log-density curve, the photometry curve produced by the dye solution is independent of the concentration (Saltzman and Keay 1967, p. 362).

Though a variety of red dyes, of both vegetable and animal origin, were known in antiquity, only a few ever attained technological importance (Goffer 1980, p. 184). Four of these natural red dyes (brazilwood, madder, relbunium, and cochineal) have been detected in one Peruvian textile. Through the use of spectrophotometry and the comparison of spectral wavelengths, it is possible to differentiate between these red dyes even when they are present in one solvent (Saltzman 1978, p.183).

Solutions derived from red fibers removed from textiles can be analyzed for cochineal by boiling for a few seconds in sodium hydroxide, adding acid immediately, and then extracting the coloring matter with butanol (carminic acid is soluble in butanol). The solution is isolated, cleared with a centrifuge, shaken with diluted sodium hydroxide (soluble in carminosin-red). The specimen is then submitted to spectroscopic analysis. Absorption of carmine acid lies at 571, 528, and 495nm (Fester 1954, p. 241).

While spectrophotometry was the dye analysis procedure selected for the research conducted on the samples of the Peruvian textile reported in this thesis, it is important to mention that there are other satisfactory tests which can be used for the detection of dyes in archaeological textiles. A discussion of these tests will not be attempted in this paper with the exception of a test for the differentiation of the scale insect red dyes by chemical analysis. For further information about dye analysis, I refer the reader to the bibliography and a booklet written by Helmut Schweppe which was published by the Smithsonian Institution. This booklet contains practical information on the identification and differentiation of dyes on historic textile materials, and can be obtained upon request from the Smithsonian Institution (Schweppe 1988, p. 1-20).

Chemical Analysis of Dyes

Four scale insects of the superfamily Coccoidea produce a red dye which is chemically similar and produces approximately the same range of red hues, but which differ in chemical composition. These four insects are: Dactylopius coccus (American cochineal), Kermes vermilio (kermes), Porphyrophora polonica (Polish cochineal or kermes), and Porphyrophora hamelii (Ararat cochineal) (Gerber 1978, p. 23; Wouters and Verhecken 1988, p. 189). These scale insect dyes can be differentiated with the knowledge of the chemical composition of each dye.

Kermes was still in wide use in Europe prior to the discovery of the New World in the fifteenth century, but was quickly replaced by American cochineal when the Spanish exported this dye from New Spain in large quantities (Taylor 1987, p. 143). Two other widely-used red dyes were Polish cochineal and Armenian cochineal. The importance of these dyes to archaeological investigations is in the differentiation of kermes, Armenian cochineal, and Polish cochineal from American cochineal in the analysis of red dye in prehistoric and historic textiles.

The chemical composition of Polish cochineal, American cochineal, and kermes has been analyzed by G. W. Taylor, R. Pfister, M. G. Whiting, et al. Their results have been presented as a means to determine the presence or absence of these red colorants in old textiles. The differentiation of these red dyes is based on the fact that Polish cochineal, American cochineal, Armenian cochineal, and kermes consist of carminic and kermesic acids in differing proportions. The establishment of these proportions aided in the differentiation of these dyes, and can be used to assist in the determination of the presence of these dyes.

Armenian cochineal was found by High Performance Liquid Chromatography and computerized UV-VIS diode array detection (this detection system consists of a photo diode array detector and a device for storage, manipulation, and retrieval of data) to consist primarily of carminic acid. Kermesic acid was not detected, and if present would have been less than 1%. Kermes was found to consist primarily of kermesic acid. Polish cochineal consisted of both carminic and kermesic acids, with the latter present, but being the lesser component (carminic acid 80%, kermisic acid 20%). There is a close chemical similarity between Armenian cochineal and American cochineal, with both containing a large proportion of carminic acid. It is difficult to distinguish between dye of Armenian cochineal and American cochineal without the detection of the differences in the proportion of carminic and kermesic acid (Taylor 1987, p. 144).

In the detection of dyes present in forty Egyptian textiles from the fifth to seventh centuries, ten contained an insect red dye with carminic acid present and kermesic acid absent. Due to the absence of kermesic acid, kermes and Polish cochineal were eliminated as possibilities (Taylor 1987, p. 145). While efforts to chemically analyze dyes goes back to the early nineteenth century, there still remains an incomplete understanding of the red dyes produced by these scale insects (see Table 5; Wouters and Verhecken 1988, p. 189).

Table 5. The amount of carminic and kermesic acid present in four scale insects.

Presence or Absence of Carminic Acid and Kermesic Acid		
Scale Insect Dye	Carminic Acid	Kermesic Acid
Cochineal	+	- (1% or less)
Kermes	-	+
Polish cochineal	+ (80%)	+ (20% or less)
Armenian cochineal	+	-

Source: Wouters and Verhecken 1988, p. 189.

Spectrophotometric Analysis

Ten Peruvian specimens were selected for spectrophotometric analysis. This selection was made because of the fortunate preservation of textiles found in burial remains in arid regions of Peru, as well as the availability of samples which had not been previously analyzed for dye content, but in which the presence of cochineal was suspected. An eleventh sample, an Iranian camel bag, was selected because there was a possibility that the red fibers used in weaving the camel bag had been dyed with cochineal. The ten Peruvian burial textile remnants were obtained from the Materials Conservation Laboratory, Texas Memorial Museum, University of Texas at Austin. The ten specimens ranged in age from 400 B.C. to 1532 A.D., and from six cultures: Tihuanaco; Nazca; Tiahuanacoid (coastal); Chimu; and Chancay. The samples were selected from a wide range of cultures because the results of the analysis would give a better picture of the extent of use of cochineal in Pre-Inca, Peru (see Table 6; see Figures 9, 10, 11, 12, 13). The camel bag sample was woven in Iran and is of unknown age. It was from my private collection of ethnic weavings.

Samples

Each sample consisted of a one-eighth to one-fourth inch long small bundle of fibers, individually bagged and labeled with the accession number of the textile from which it was removed. After collection, the samples were mailed to David A. Wenger, Professor of Medicine, Biochemistry, and Molecular Biology at Jefferson Medical College. Spectrophotometric dye analysis was conducted to determine if cochineal was used as the dyestuff, either in combination with another dyeing substance, or as a single dyeing agent. Dr. Wenger was selected to perform the analysis because his testing procedure uses a very small sample size, and because of his extensive work in analysis of prehistoric and historic textiles. Dr. Wenger has analyzed more than 1,000 specimens, and has been able to identify most of the dyes in Navaho, as well as Central and South American textiles.

Table 6. List of the eleven samples submitted for dye analysis.

Dye Analysis Test Samples		
Culture	**Date of Culture**	**Textile Description**
1. Nazca	400 B.C. - 540 A.D.	Geometric pattern, gold and red throughout.
2. Tihuanaco	800 - 1000 A.D.	Red and gold, bars with a geometric pattern.
3. Nazca	400 B.C. - 540 A.D.	Irregular dusty rose with gold and brown birds.
4. Chimu	1000 - 1400 A.D.	Blue, gold, red, and brown with a geometric pattern.
5. Chancay	1000 - 1400 A.D.	Mustard, green and gold bird with gold, green, rose and pale pink background.
6. Chancay	1000 - 1400 A.D.	Gold and shades of rose, with a piano keys-like pattern.
7. Chancay	1000 - 1400 A.D.	Rose background with a geometric pattern in gold.
8. Inca?	1200 - 1532 A.D.	Rectangular red and gold, with a horizontal red border.
9. Chimu	1000 - 1400 A.D.	Brown, rose, gold and shades of color with a random pattern.
10. Tiahuanacoid	1000 - 1100 A.D.	Irregular little pattern, red and gold little men.
11. Iranian	1856 or later	Navy, tan, and red camel bag with a geometric pattern and a rectangular border.

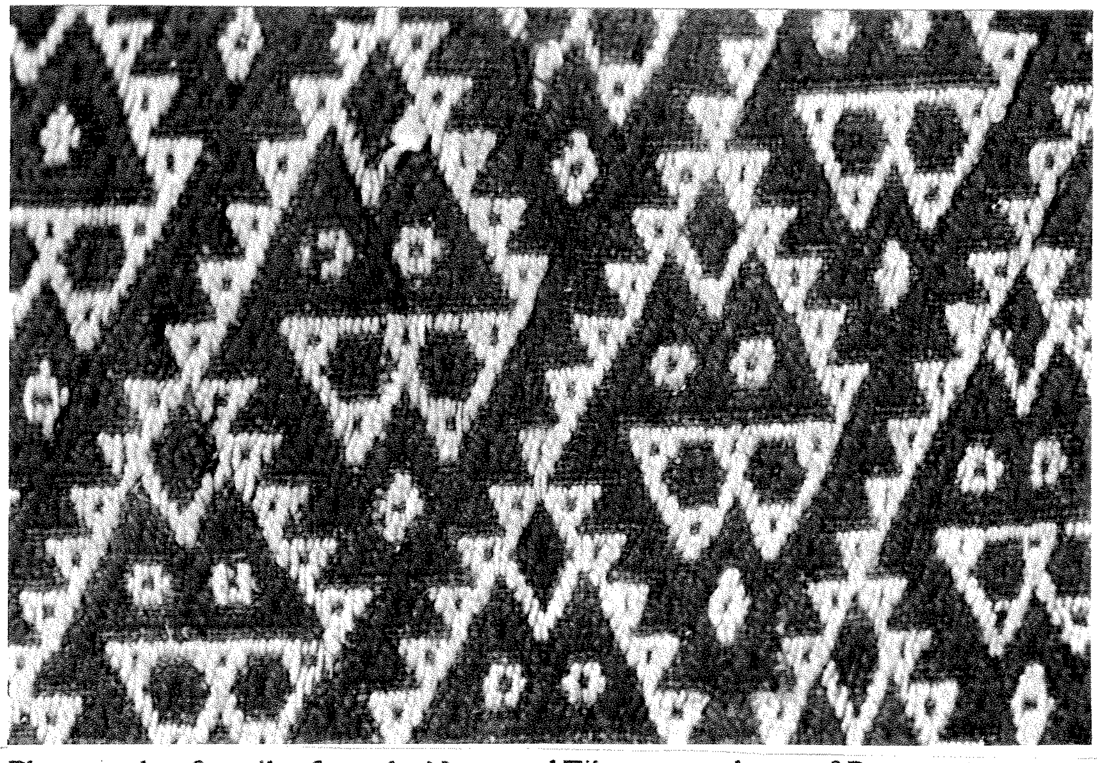


Figure 9. Photographs of textiles from the Nazca and Tihuanaco cultures of Peru.

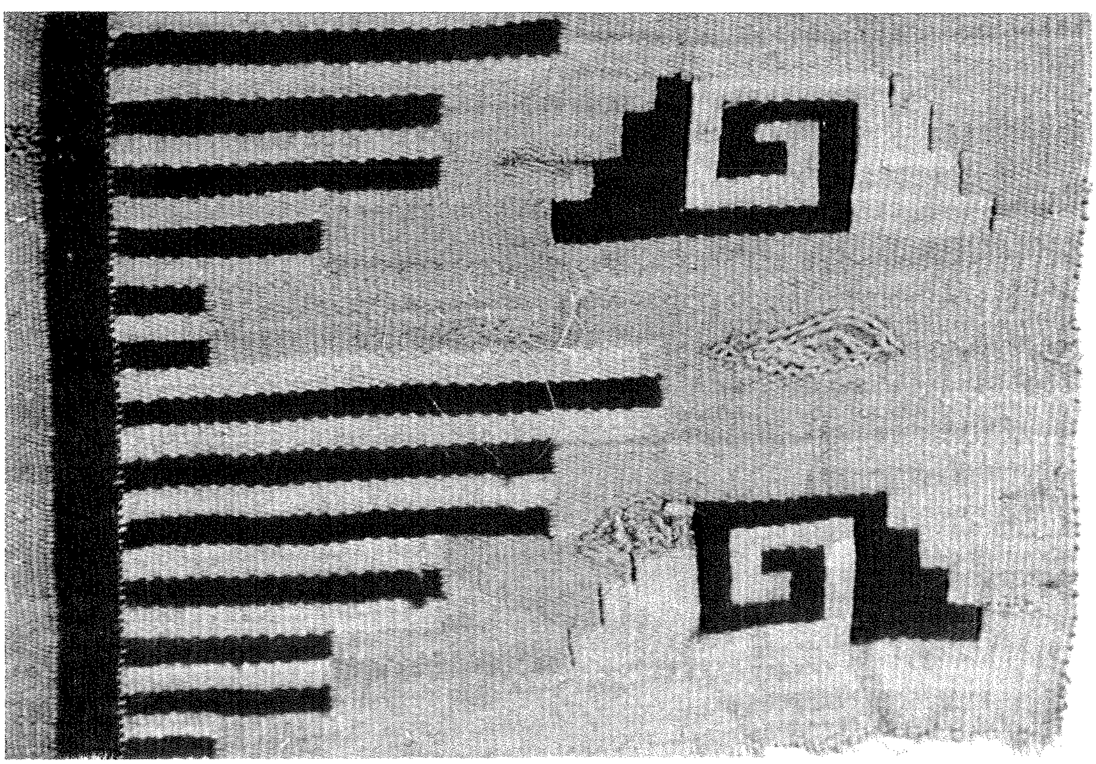
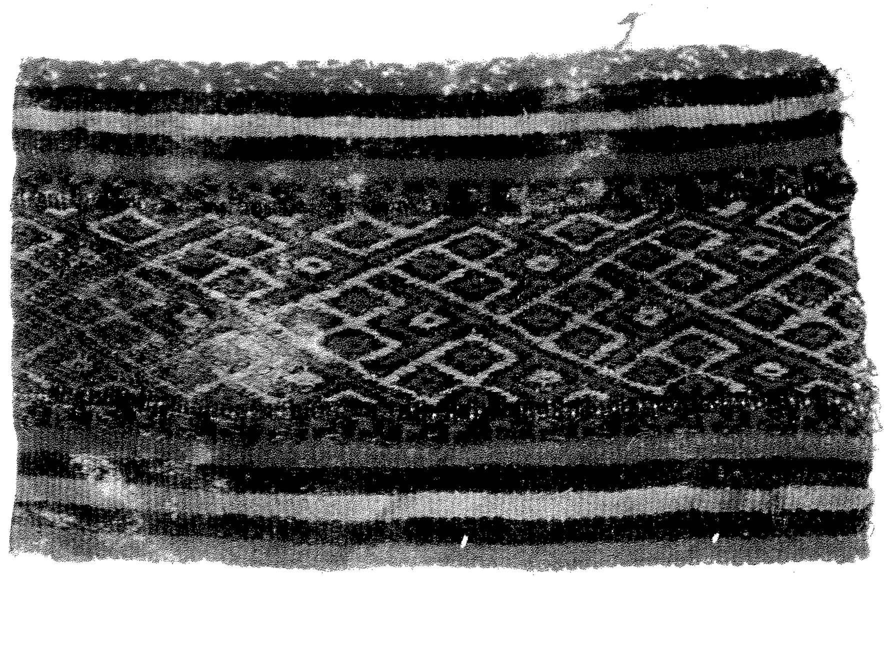


Figure 10. Photographs of textiles from the Nazca and Chimu cultures of Peru.



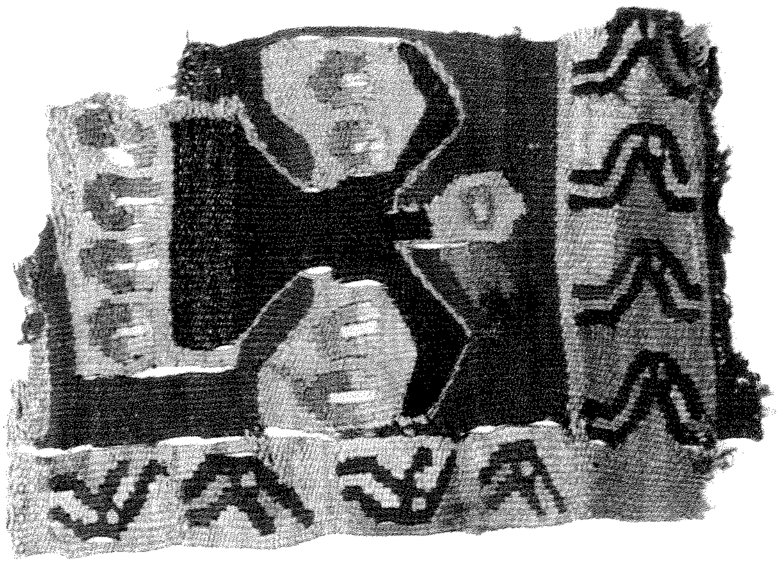
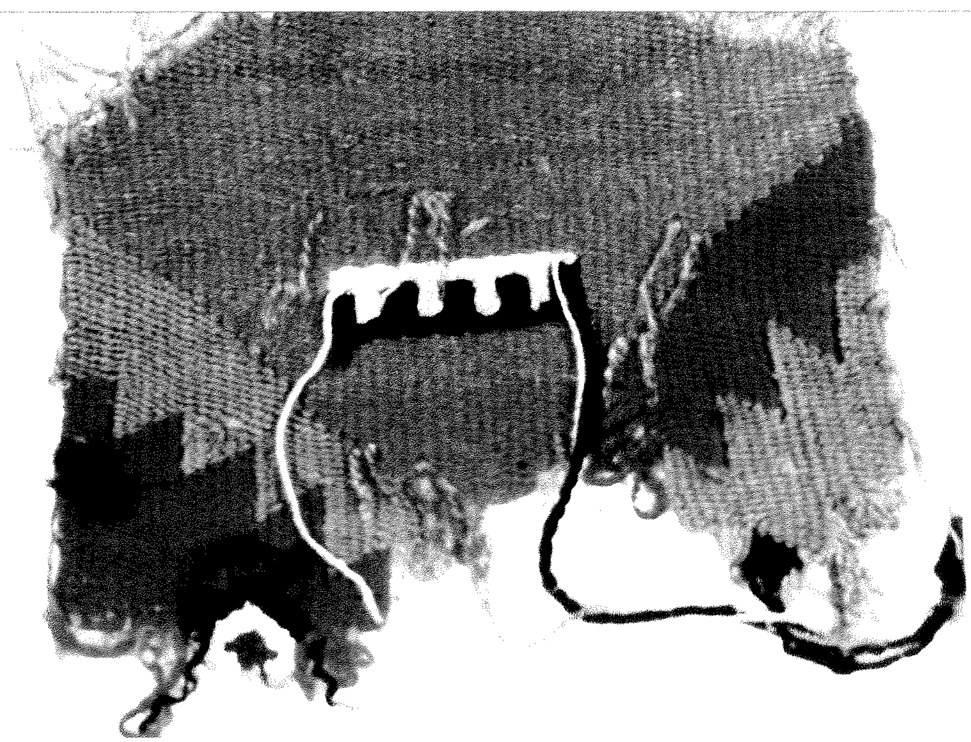


Figure 11. Photographs of textiles from the Chancay culture of Peru.



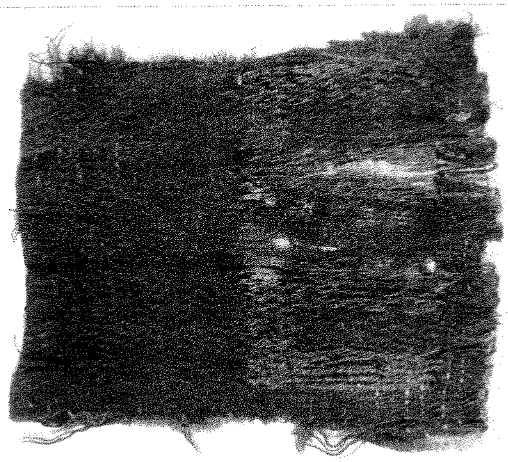
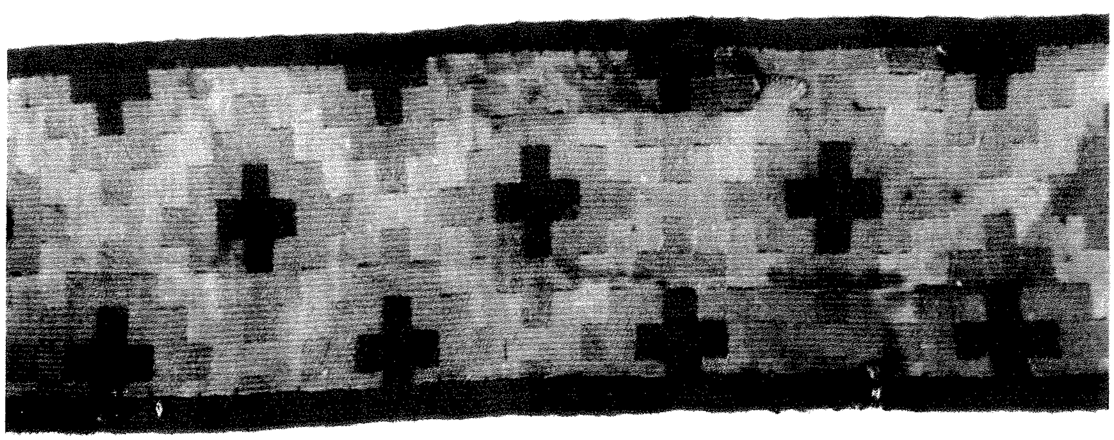


Figure 12. Photographs of textiles from the Chancay and Inca (?) cultures of Peru.



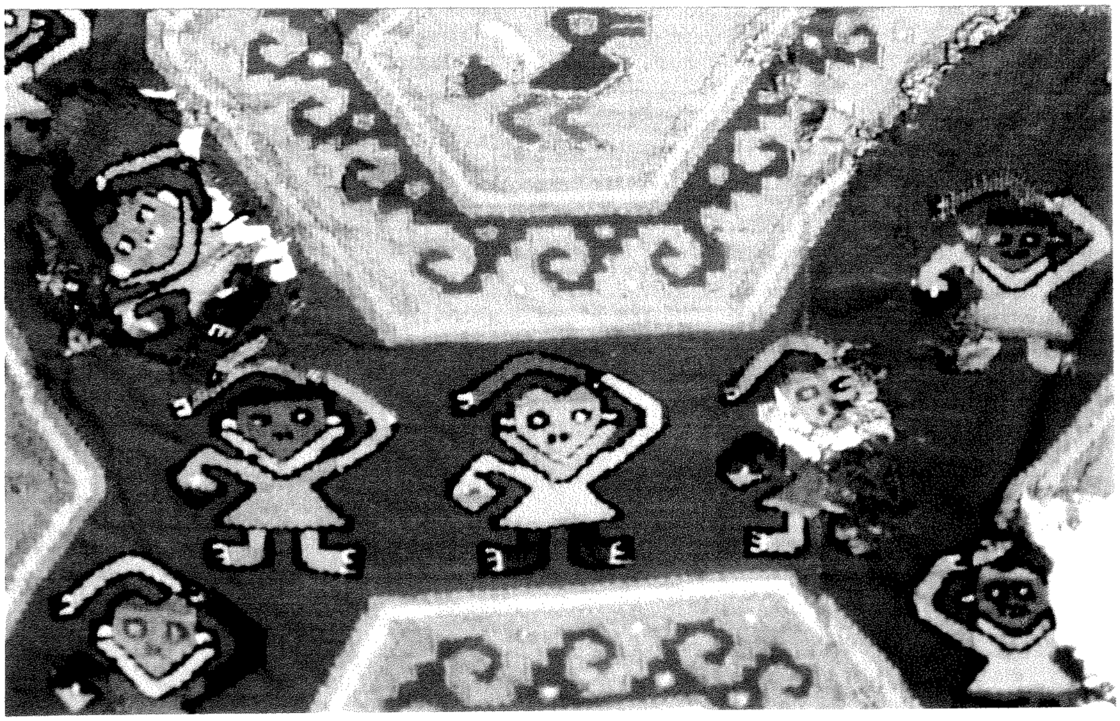
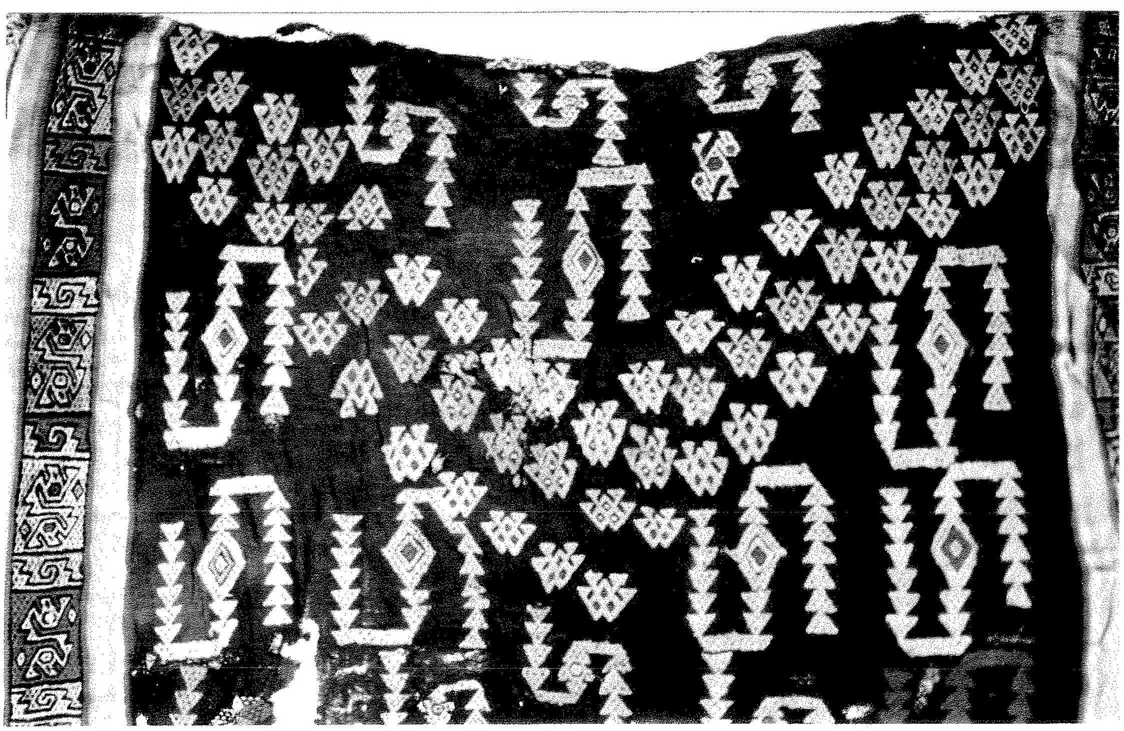


Figure 13. Photographs of textiles of the Chimu and Tiahuanacoid cultures of Peru.



Spectrophotemetric Test

A small sample of textile is placed in concentrated sulfuric acid for about 5 minutes. In this way, the dye is extracted from the fiber. After the dye is extracted, the mixture is filtered through glass wool to remove the fiber. The remaining solution, containing the extracted dye, is then subjected to spectrophotometric analysis, scanning from 600 to 450 nanometers. The resulting curves obtained are compared to the curves of known dyes for identification. This test is usually conducted on red dyes (Wenger 1991, personal communication).

Results

Dr. Wenger's report on the results of the spectrophotometric analysis stated that all ten of the Peruvian red fiber samples were positive for cochineal, and that there was no evidence for any other dyes present. His report on the Iranian or Turkish camel bag sample stated that the camel bag was dyed with a synthetic dye which was probably some type of azo dye (see Table 7; see Appendix V; Wenger 1991, personal communication).

Table 7. Results of the spectrophotometric analysis

SPECTROPHOTOMETRIC ANALYSIS			
ACCESSION NUMBER	CULTURE	AGE	TEST RESULTS
1608-279	Tihuanaco	800 - 1000 AD	Positive
1608-280	Nazca	400 BC - 540 AD	Positive
1608-282	Nazca	400 BC - 540 AD	Positive
1608-284	Tiahuanacoid	1000 - 1100 AD	Positive
1608-292	Chimu	1000 - 1400 AD	Positive
1608-297	Inca?	1200 - 1523 AD	Positive
1657-10	Chimu	1000 - 1400 AD	Positive
2389-81	Chancay	1000 - 1400 AD	Positive
2389-82	Chancay	1000 - 1400 AD	Positive
2402-1	Chancay	1000 - 1400 AD	Positive
Camel Bag		Post 1886	Negative

Source: Wenger 1991, personal communication.