An Analytical Study of pre-Inca Pigments, Dyes, and Fibers

K. Maresuke KASHIWAGI

Department of Textiles and Clothing, Kyoritsu Women's University, Hitotsubashi, Chiyoda-ku, Tokyo 101

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The total analysis of 800-year-old Peruvian pigments with regard to the inorganic elements was carried out; some typical pigments, like mercury sulfide and iron oxide, are shown. Some characteristic pre-Inca (6—7 th century Tiahaunaco and 13—14 th century Chancay) dyes including cochineal, indigo, and probably logwood were identified from old fabrics by means of absorption spectroscopy and also chromatographic analysis. Two kinds of fiber constituting those fabrics were also investigated, and a few chemical analyses, including that of the amino-acid composition of protein fiber and that of the extent of the degradation of old cellulose fiber, were made.

Aside from the marvellous weaving technology of the pre-Inca period, which was developed at a very early date (2000 B.C.) and which remains in use today, the colors developed by those people present very interesting scientific problems today. Our present knowledge of those ancient dyestuffs is limited because the Incas did not leave any written documents and because those Indios who are their descendants have not yet been completely assimulated into Western culture.

Two kinds of dyed fabrics and five kinds of pigments were obtained by the courtesy of Mr. Yoshitaro Amano of the Museo Amano, Lima, Peru. One kind of fabrics was identified at the museum as from Chancay in the 13—14 th century, and the other, as from Tiahaunaco in the 6—7 th century. The pigments, all in powdered state, were found at Lauri, 87 km north of Lima, some time ago and were identified as of pre-Inca times (about 800 years ago).

Experimental

In addition to our previous methods–namely, paper chromatography[1,2] and the modern knowledge of organic chemistry,[3,4] all of which were successfully applied to the identification of certain dyestuffs in the old textiles, the present author adopted mass spectroscopy and high-frequency plasma spectroscopy of old inorganic pigments and absorption spectroscopy with regard to the extracted dyes.

Analysis of Pigments. About 10^{-2} g of each substance was dissolved by heating in a mixture of 0.5 ml of sulfuric acid and 2 ml of nitric acid, the mixture was then diluted to make a 20 ml solution. A Hitachi high-frequency plasma torch instrument, Model 300, was used to measure the characteristic spectra of each element at temperatures higher than 6000 °C. The mass spectroscopic measurements were carried out by the use of a Hitachi Mass Spectrometer, RNU6MG.

Analysis of Dyes. Dye extraction from the fabrics was made mostly according to Saltzman's method[5] using sulfuric acid, which destroyed the substrate fiber. However, we sometimes used our previous method for extraction employing ethanol and a small amount of hydrochloric acid.[2] Paper chromatography experiments were carried out at 30 °C with a developing solvent composed of butanol–acetic acid–water (4–1–1 by volume) except for the blue dyes of the indigo type. The developing solvent for the blue dye was composed of the supernatant solution from a mixture methyl acetate–2-propanol–25% aq. NaOH (45–35–20). The absorption spectra of those extracted dyes were measured by means of a Shimadzu Spectrophotometer, MPS-50L.

Analysis of Fibers. The fabrics were composed of Peruvian cotton and animal fiber of a Llama or Alpaca type, both of which could easily be recognized under a microscope.[6] The two kinds of fiber were further examined under a scanning electron microscope, Shimadzu EMX-SM. To estimate the extent of deterioration of the cellulose fiber, a small amount of white cellulose was removed from one of the Chancay fabrics and nitrated to measure the degree of polymerization by way of viscometry.[7] The amino acid composition of the protein fiber was determined by the use of the JLC-5AH analyzer at the Kanagawa Industrial Research Institute.

Results and Discussion

The analytical results for those pigments are shown in Table 1, together with some additional data from mass-spectroscopic measurements. According to Table 1, showing information which is here disclosed for the first time, we may suppose that the pre-Inca people did have a good knowledge of iron, contrary to a common belief that they did not know how to use iron.

Among the possible red dyes used in those days, cochineal was very widely known in this area.[8,9] Other possible dyes were kermes, lac-dye, and a mixture of those with cochineal.[9] Those dyes are known to contain compounds structurally related to one another, all being derivatives of anthraquinone, as is shown in Fig. 1.[10,11] Beside those, a shell fish dye called purpula could supply red color depending on the kind of mordant used.[9]

The dyes extracted from the red parts of the Chancay and Tiahaunaco fabrics gave a single red spot at values between 0.51 and 0.54 of R_f on a paper chromatogram, while cochineal itself showed a single red spot at 0.54. The absorption spectra of those red dyes in dilute sul-

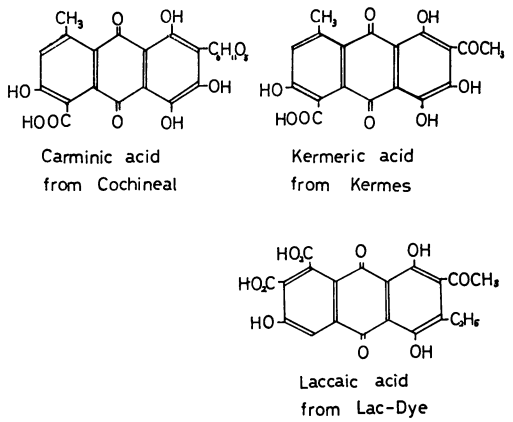


Fig. 1. Some anthraquinone dyes.

Table 1. Analysis of pigments used 800 years ago in chancay area

Specimen	Color	Elements found (principal constituent and other minor ingradients)	Main constituent
1	red	Hg≫Sr, Na, Zn, Fe, Mg, Cu, Ni, Cr, Ca, Al, K	HgS
2	brown red	Fe≫Na, Zn, Mn, Mg, Cu, Ca, Al, K, Sr, Pb	Fe_2O_3
3	green	Cu≫P, Zn, Fe, B, Si, Mn, Mg, Ni, Cr, Ti, Mo, Ca, Al, K, Sr, Na	$CuCO_3Cu(OH)_2$ Marachite
4	dark yellow	mainly organic, metals found are Cu, Zn, Fe, Mg, Ca, Al, K, Na	lake with absorp. max. at 230 and 270 nm in acidic media
5	yellow	Fe≫Zn, Mg, Cu, Ca, Al, K, Sr, Na	$Fe_2O_3 \cdot H_2O$ or FeOOH

Other evidences found by Mass Spectra are:

1. Isotope conposition of Hg are the following.

Atomic wt.	Ratio%
198	10
199	16
200	23
201	13
202	30
203	0
204	7

4. Important constituent is organic.

furic acid were quite similar to that of cochineal, as is shown in Fig. 2. Moreover, the pH shifts of the absorption maxima of the dyes were quite identical to that of conhineal; they all exhibited maxima at 490 nm in acidic, 520—530 nm in neutral, and 550—560 nm in alkaline media.

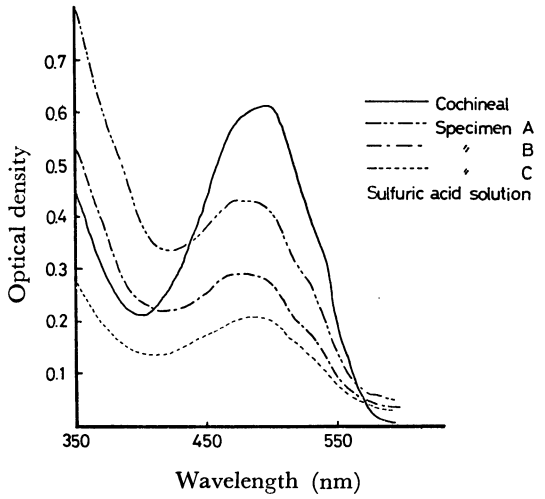


Fig. 2. Absorption spectra of the pre-Inca dyes and cochineal.

The blue dyes were extracted from the blue part of the old fabrics with sulfuric acid and chloroform. The extracts showed one blue spot at values from 0.68 to 0.72 of R_f in a paper chromatograph, while synthetic indigo showed one at 0.69.

The absorption spectra of those solution containing the blue dye extracted from fabrics and that of synthetic indigo are compared in Fig. 3. There seems to be little doubt that the blue dyes from the old fabrics were indigo; therefore, we can conclude that those blue colors must have been from a certain indigo-producing plant.

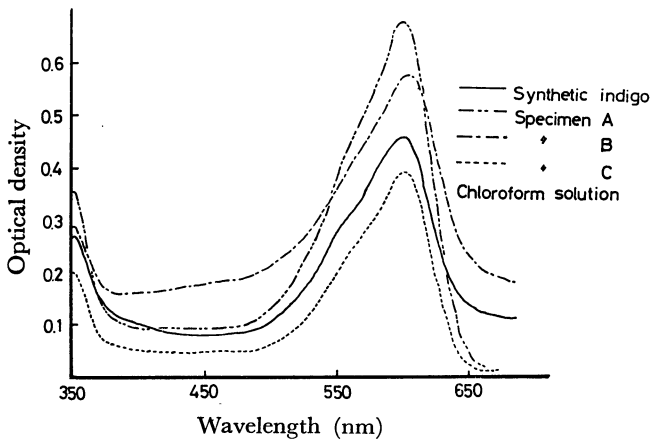


Fig. 3. Absorption spectra of the pre-Inca blue dyes and synthetic indigo.

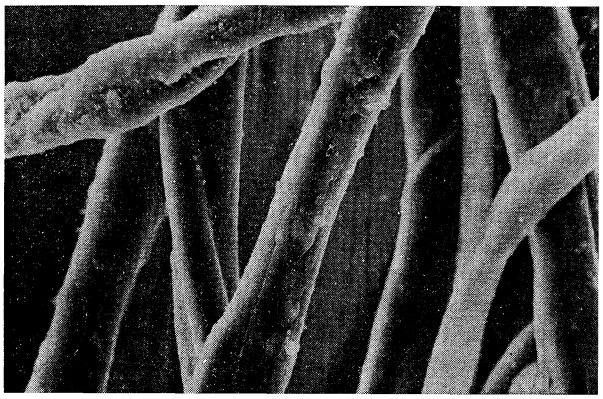
Beside this indigo spot, another red spot with an R_f value of 0.84 appeared on the paper chromatogram. We tried to assign this red dye to some flavonoid compound by means of absorption spectra[12] and also by a few spot tests,[13] but we have not succeeded thus for. The pre-Inca people might, as in some other parts of the world, have attempted to produce a purple color from red and blue (mostly indigo),[9,14] as well as the famous purpula.

Black and golden yellow colors were often found in those fabrics. The dye extracted from the black parts of the fabrics exhibited two spots paper-chromatographically, one at 0.54 and the other at 0.34 of R_f, both of a dark yellow color. Moreover, the extracted golden yellow dye showed exactly the same spots as the black. This is taken to show that both colors originate from the same material, probably only the difference being the kind of mordant used. We further found that those two spots agreed with those from logwood extracts (R_f: 0.35 and 0.53). Logwood is well known to contain haematoxylin, which, on exposure to air, becomes

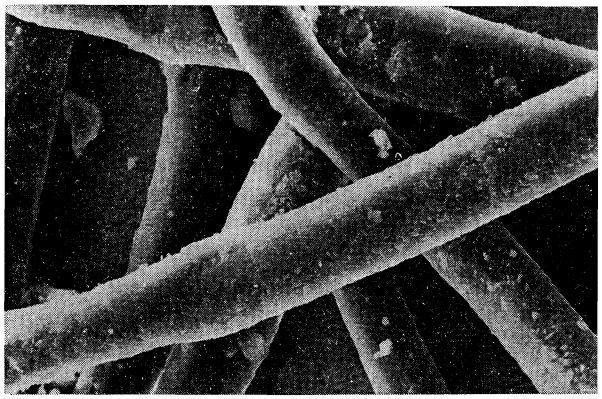
oxidized to haematein.

In addition, a series of dyeing experiments were undertaken, in them, among other items of interest, only logwood (Haematoxylon capechianum L.) exhibited both black as a result of the mordanting of $CuSO_4$ with a small amount of Fe and golden yellow color as a result of the use of acetic acid on silk cloth. We have not yet been successful in obtaining dependable absorption spectra and there is even a possibility that this dye polymerizes,[15] but it appears that both the black and golden yellow colors in those fabrics are probably from logwood.

Many pre-Inca fabrics were composed of cotton and animal protein fiber, one as warp and the other as weft, but sometimes the fabrics were interwoven in a more complicated manner. Those two kinds of fibers from one of the Chancay fabrics are shown in Fig. 4.



Cotten fiber.



Animal protein fiber.

Fig. 4. Two kinds of old Peruvian textile fibers.

Many soil particles were often found everywhere along the fiber surfaces, and surface scratches were found under close examination. This evidence probably indicates that the fabrics had deteriorated over the long period of aging. To investigate the deterioration more quantitatively, both the degree of polymerization of cellulose (DP) and the total amino acid composition of the protein fiber were determined. The average DP for the old cellulose fiber thus calculated was 585, which was obviously lower than for natural cotton fiber. The following relation may approximately hold for cellulose deterioration under limited conditions.[16]

$1/DP - 1/DP_0 = kt$, where DP is the degree of polymerization at a certain time, DP_0 is the initial DP of cellulose, k is a constant, and t is the number of years elapsed. If k is assumed to be 1.86×10^{-6} and if DP_0 be 3500,[16] then we get $t=766$ years which corresponds to the early 13 th century. Table 2 shows the amino acid composition of pre-Inca protein fiber from fabrics which are known to be of the Llama type.

TABLE 2. AMINO ACID COMPOSITION OF PROTEIN FIBER (mol/10^5 g)

Amino acid	pre-Inca fiber	Llama	Camel	Merino wool
Lys.	14.7	19.3	20.9	20.6
His.	2.4	4.0	3.8	5.9
Arg.	50.6	55.8	56.0	52.0
Asp.	43.0	50.1	45.8	52.4
Thr.	43.1	47.2	47.5	53.6
Ser.	60.1	80.0	77.7	99.6
Glu.	120.0	109.0	114.0	94.7
Gly.	48.7	59.0	56.8	73.6
Ala.	38.2	40.4	39.8	44.7
Cys.	10.9	43.6	44.3	40.1
Val.	35.5	35.9	35.4	43.0
Met.	4.0	3.7	4.7	3.6
iso Leu.	19.9	20.8	20.0	21.5
Leu.	51.6	56.9	55.9	62.0
Tyr.	14.2	20.9	19.0	31.3
Phe.	15.1	24.1	16.4	23.9
Pro.	86.0	80.0	83.0	56.4

For comparison, the amino acid analyses of three other fresh protein fibers—llama, camel, and merino wool—was carried out; the results are shown in Table 2. From Table 2 it appears that the pre-Inca protein fiber was more similar to that of camel rather than that of llama, except for the difference in cystine content (10.9/44.3). Whether this and other minor differences in amino acid content are attributable to selective degradation due to long aging, or, to the pre-Incan people's use of other kinds of animal fiber, like vicuna or alpaca, is not clear at this stage.

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