Purple Dyes from the Carlos Museum Pre-Columbian Textiles Collection: Direct Mass Spectrometry and HPLC Analyses

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Introduction

In Fall of 2017, the Michael C. Carlos Museum of Emory University presented the exhibition, *Threads of Time: Tradition and Change in Indigenous American Textiles*. A grant from the Bank of America Conservation Project supported conservation of the objects prior to display. The conservation project included technical study of the textiles to seek information about materials and manufacture as well as cultural choices, available resources, trade, and provenance. We present here our investigations into the composition of purple dyes in order to better understand the materials and techniques used to achieve this color.

As part of a larger study on secondary colors (purple, green, and orange), samples were collected in May 2017 from a number of ancient Peruvian textiles in the Carlos collection. The objects are attributed to three distinct cultures, spanning nearly 1500 years. Secondary colors can be produced through several different methods, including direct dyeing with the desired hue, overdyeing (successively dyeing fibers with color and then a second), combining multiple dyes in a single vat (or dye-bath), and using different mordant/ dye mixtures.

Purple derived from mollusks is well known in the Old World, and was also used in Central and South America, though originating from a different species of marine snails. Red yarns were overdyed with blue, or vice versa, to produce purple. Red dyes in ancient Peru were generally derived from the roots of the *Relbunium* plant or from cochineal (*Dactylopius coccus*) insects. Shades of red vary by fiber type and can also be created through control of temperature and pH. The shade of red can be influenced further by selection of mordants. For example, cochineal dye can yield a purple color when copper is used as the mordant. Blue dye was obtained from the *Indigofera, Isatis* and *Polygonum* genera. All blue indigoids are prepared through reduction to form soluble leuco-indigo in the vat, followed by oxidation to blue indigotin (and other isomers) after the yarn or fibers have been removed from the relatively colorless solution. The complex chemistry of indigo dyeing likely precludes mixing of colors in the vat.

Research questions

- Is there evidence for the use of shellfish purple dyes, indicated by the presence of brominated indigoids?
- Were the purple colors achieved through overdyeing blue onto red?
- Do the red dyes – in various reddish shades as well as purple – originate from *Relbunium* or from cochineal?
- Are the red components consistent with previous findings of how the dye compositions change with time and location?

Can these questions be addressed through analysis of yarn samples by use of ambient ionization mass spectrometry and HPLC with diode array UV-vis detection?

Culture	Area of Peru	Time period	Red dye source[1]
Nasca	Southern	100-800 CE	*Relbunium*
Wari (Huari)	Southern and Central	500-1000 CE	Cochineal and *Relbunium*
Chancay	Central	1000-1470 CE	Cochineal

Materials and Methods

- Yarn fragments collected at the M.C. Carlos Museum (table, right)
- Red reference yarns dyed with *Relbunium* root and *Dactylopius coccus* (cochineal) from Saltzman Collection at UCLA
- Blue and purple reference alpaca yarns prepared at EMU: indigo (*Polygonum* sp.), shellfish purple, *Relbunium* and cochineal overdyed with indigo

Comparisons were carried out with pure compounds for each dye classification.

- Dry powders for DART-MS
- Solutions for PS-MS, UV-vis and HPLC

Dye	Primary colorant	Secondary colorants
Relbunium sp.	Xanthopurpurin	Purpurin, pseudopurpurin, munjistin
Cochineal (*D. coccus)*	Carminic acid	Glycosides of kermesic and flavokermesic acid
Indigo (*Polygonum* sp.)	Indigotin	Indirubin (isomeric with indigotin)
Shellfish purple	Dibromoindigo	Isomers of mono- and dibromoindigo and indirubin

Museum code	Textile	Color/sample	Culture
2002.1.100	Snake band	Purple	Nasca
2002.1.3	Hummingbirds	Purple	Nasca
2002.1.148	DWW	Purple	Wari
2002.1.148	DWW	Purple2	Wari
2002.1.148	DWW	Red	Wari
2002.1.1	DWW	Blue/Purple	Wari
2002.1.1	DWW	Red	Wari
2002.1.16	Tunic	Salmon	Wari
2002.1.16	Tunic	Pink/red	Wari
2002.1.83	Fragment	Red	Tihuanaco Wari
2003.40.5	Band	Purple	Wari
2003.40.5	Band	Red	Wari
2002.1.126	Yarn ball	Brown (red?)	Chancay

DART-MS

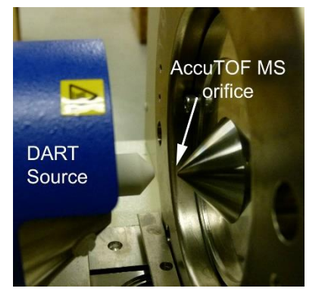
- Approx. 1-2 mm of yarn removed and divided into two bundles
  - Direct analysis of bundle 1
  - Formic acid (80%) added to bundle 2
  - Fibers held in tweezers, introduced into gap.
- Source @ 450 ºC, orifice 1 set to -30V to minimize fragmentation
- Highest sensitivity in negative ion mode[2-3]

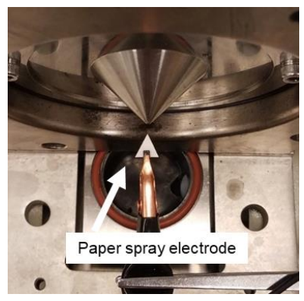
PS-MS

- Approx. 1 mm of yarn extracted in 1:1 0.1% Na_2EDTA:DMF
  - Preserves glycoside compounds.[4]
- Paper spray in positive ion mode (3500 V)
- Analogous to ESI-MS

HPLC-UV-Vis

- Same extract as used for PS-MS
- Extraction solvents removed via vacuum desiccation
- Resuspended in 1:1 DMF:MeOH
- Diode array detection from 200-900 nm; spectrum used for identification along with retention time.





Cochineal reference materials

DART-MS:

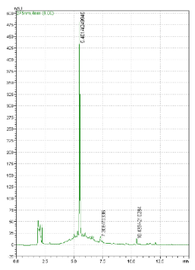
- Hydrogen bonding between –OH groups in glycoside on carminic acid, does not readily ionize by DART.
- Formic acid + high temperature cleaves glycosidic linkage (bond between glucose moiety and anthraquinone), yielding kermesic acid (aglycone of carminic acid).

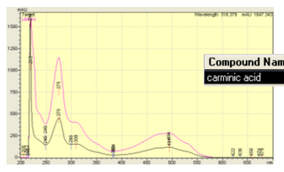
PS-MS:

- Two peaks correspond to five possible components.
- Carminic acid, DCIV and DCVII are isomeric: all may be peak at m/z 515
- HPLC results justify identifying m/z 515 as Na adduct of carminic acid, indicative of cochineal dye

HPLC-UV-Vis:

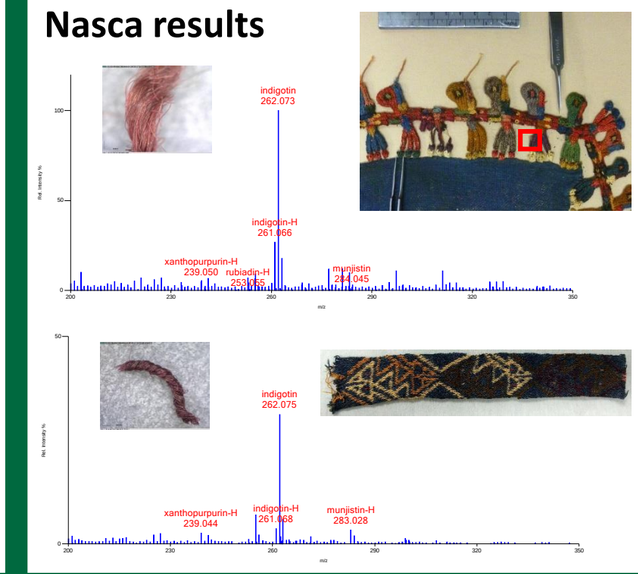
- Largest component peak for cochineal dye @ ~5 min
- UV-vis spectrum consistent with carminic acid
- More carminic acid present than other components





Code	Name	Formula	Adduct	Mass
CA	carminic acid	$C_{22}H_{20}O_{13}$	+Na	515.080
DCOFK	flavokermesic acid glycoside	$C_{22}H_{20}O_{12}$	+Na	499.085
DCII	flavokermesic acid glycoside	$C_{22}H_{20}O_{12}$	+Na	499.085
DCIV/DCVII	kermesic acid glucofuranosides	$C_{22}H_{20}O_{13}$	+Na	515.080

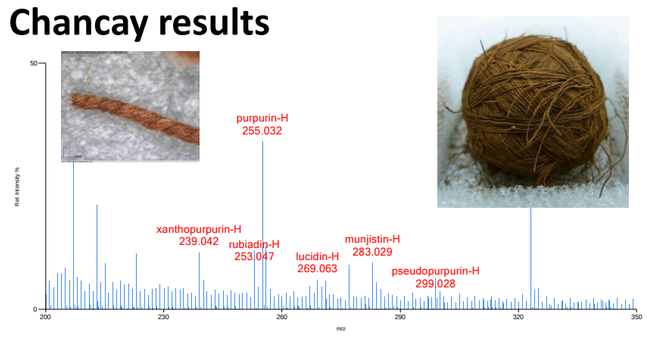
Nasca results



Cross-knit looped textiles

- Purples appear to be overdyeing of red from *Relbunium* and indigo.
- No traces of shellfish-derived pigments.
- No evidence of cochineal aglycones in DART-MS with acid
- The use of *Relbunium* is consistent with previous studies of Nasca textile colorants.

Chancay results



- Brown-red yarn shows evidence for *Relbunium* dye by DART-MS.
- Due to the extreme sensitivity of DART-MS for indigo, blue and green yarns from the basket show primarily indigotin.
- FTIR of yarns from the colored balls showed both cotton and wool.

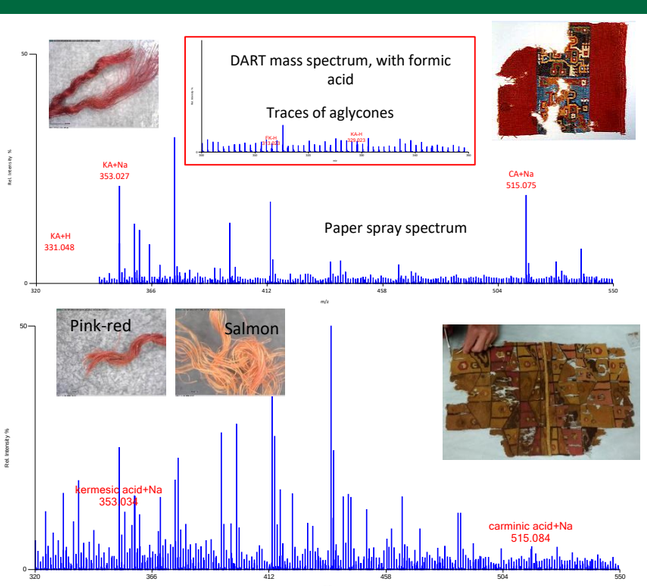
Yarn description	FTIR interpretation
Large blue	cotton (cellulose)
Brown-red	cotton (cellulose)
Small blue	wool (protein)
Dark green	wool (protein)
Light green	wool (protein)
Yellow-brown	wool (protein)
"white"	cotton (cellulose)

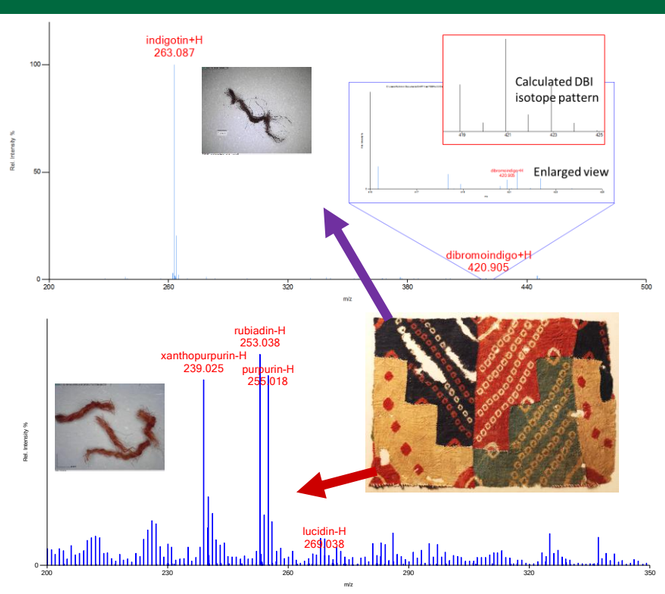
Wari results

- Wari tunics/fragments and band showed only traces of cochineal aglycones by DART-MS for the various red/pink/salmon colors
- Paper spray MS confirmed the presence of carminic acid, indicative of cochineal, in the red and purple yarns
- Indigo was observed in the purple yarn by DART-MS

Museum ID code	Textile	Color/Sample	DART results	PS results
2002.1.148	DWW	Purple	*Relbunium* and indigo	n/a
2002.1.148	DWW	Purple2	Dibromoindigo	n/a
2002.1.148	DWW	Red	*Relbunium*	n/a
2002.1.1	DWW	Blue/Purple	Indigo and *Relbunium*	n/a
2002.1.1	DWW	Red	*Relbunium*	n/a
2002.1.16	Tunic	Salmon	nd	CA, KA
2002.1.16	Tunic	Pink/red	nd	CA, KA
2002.1.83	Fragment	Red	?	CA, KA
2003.40.5	Band	Purple	Indigo	CA, KA
2003.40.5	Band	Red	nd	CA, KA

CA - Carminic acid, KA - Kermesic acid, n/a- not run, nd- nothing detected





Discontinuous warp and weft textiles

- No aglycones consistent with carminic acid were observed in the DART-MS for these objects.
- *Relbunium* appears to have been used for the reds, with traces of a shellfish-derived pigment in the purple areas of 2002.1.148.
- Clear evidence of overdyeing in some yarn samples.

Discussion

- Only a single sample showed traces of dibromoindigo, characteristic of shellfish-derived purple dye.
- All of the sampled purple colors were achieved through a combination of blue and red.
- *Relbunium* dye components were observed in the DART spectra of the Nasca purple yarns, which is consistent with previous findings.
- The tunic and band fragments that are securely attributed to the Wari Middle Horizon period showed evidence of cochineal use.
- The Wari-related discontinuous warp and weft textiles did not show evidence of cochineal. The reds were apparently prepared from *Relbunium*.
- The presence of *Relbunium* compounds in the Chancay red-brown yarn was unexpected. Cochineal was thought to be preferred as the red dye source by that time period.

Conclusions

- Ambient ionization MS methods are capable of rapidly differentiating between different classes of dyes present in purple textile yarns from ancient Peru.
- HPLC-DAD, considered the standard method for dyes analysis, helps to confirm the identity of compounds observed in both DART and PS-MS (e.g., carminic acid in cochineal)
- The purple dyes from the ancient Peruvian textiles sampled were generally combinations of indigo and either *Relbunium* plant red or cochineal derived from insects. The combinations were generally consistent with previous reports of dye usage during the corresponding time periods.
- Later use – from putative Wari and Chancay sources – of *Relbunium* dyes is interesting and suggests additional studies are warranted.

Future work

- Further HPLC characterization of *Relbunium* dyes to distinguish xanthopurpurin and alizarin
- Confirmation of dibromoindigo in Wari-related textile by HPLC-DAD
- Optimization of PS-MS parameters for maximum sensitivity to glycosides of *Relbunium* to better investigate possible mixtures of red dyes.

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