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Polar Bears on Thin Ice

In former United States Vice President Al Gore's Oscar-nominated climate change movie, "An Inconvenient Truth," an animated polar bear is depicted swimming for its life after the polar ice cap that forms its habital melts. The recent calving off of 87 square kilometers of Greenland's ice shelf, as reported in January by the Canadian Ice Service, is dramatic testimony that the fate shown in the film is a real possibility (which is lucky for Gore, given his recent nomination for a Nobel Prize).

While we all love the cute and cuddly polar bear, certainly more than arctic habitats are being affected. According to a new climate change study reported in *Science*, the melting of Greenland's ice sheet would raise the oceans by seven meters, threatening to submerge cities located at sea level, from Los Angeles to London. Even a partial melting of the ice sheet could have catastrophic consequences for low-lying countries like Bangladesh.

As global warming and its effects continue to plague the environment— and engage public audiences, policy makers, and research granting agencies archaeological science stands to make a significant contribution to understanding the problem. We offer considerable expertise in paleoclimate studies, soil isotope analyses, geoarchaeology, and other research domains aimed at reconstructing ancient landscapes and the climates that shaped them.

In this issue of the *SAS Bulletin*, we feature two research articles that exemplify some of the ways in which archaeological scientists can provide paleoenvironmental data for creating and testing models of long-term climate change and human behavior. In "Late Quaternary Environment in the Teotihuacan Valley, México, Inferred from d13C in Soils," Elena Lounejeva and colleagues from the Institute of Geology of Mexico's National Autonomous University report the results of their analysis of stable carbon isotopes in soil organic matter from highland central Mexico, which allows them to track regional paleoenvironmental changes over the past 13,000 years.

Also in this issue, Craig Fertelmes and C. Michael Barton of Arizona State University's School of Human Evolution and Social Change offer a satellite view of vegetation change in the American Southwest in their contribution on "Using Remote Sensing to Assess the Impact of Prehistoric Agriculture on Modern-Day Vegetation Cover in the U.S. Southwest."

While these kinds of studies can (and often do) create mountains of data as large as the Greenland ice shelf, the trick is orienting the information to the right audiences. So please share this issue of the *Bulletin* with your colleagues in the social and earth sciences who you think would benefit from a dose of archaeological science!

E. Christian Wells

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percents above 3%. For the basaltic clay, weight loss percent is above 2% at 800°C (2.2%). Hence, most Aztec plainwares were likely fired above about 800°C but below 900°C. The weight loss percents for the basaltic test tiles between 600°C and 800°C range from 2.2% to 4.6%. Thus, we conclude that the lower-fired Aztec plainwares with weight loss percent in the range of 2.5% to 5% were likely originally heated between 600°C and 800°C.

Conclusion

TGA is a useful tool for interpreting original firing temperatures for archaeological ceramics, especially when combined with experimental studies or other materials science analyses, such as XRD. TGA also holds promise in defining and understanding firing technology in prehistoric pottery production, a key topic that is generally absent from ceramic studies. TGA provides insights into craft specialization and technology.

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Understanding Chronology in Historic Period Navajo Textiles: Red Dye Analysis

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Chemical identification of the red dyes used in historic textiles in the southwestern United States can aid in determining the production age of the handwoven textiles. In the mid-nineteenth century Navajo weavers unraveled yarn from cloth (bayeta) that was brought via government annuities and trading into the Southwest to use in their own handwoven blankets and garments (Wheat and Hedlund 2003). These raveled yarns came from a variety of sources and may contain imported red insect dyes– lac, cochineal, and kermes. Along with fabric texture, yarn spin direction and ply numbers, and stylistic features, dye testing may add to information used to determine the chronology of a textile. The presently accepted chronology shows that prior to 1860, commercial red yarn that was imported into the Southwest was primarily dyed with lac. Between 1860 and 1865, a mixture of lac and cochineal was common, and by 1865 pure cochineal dominated until the synthetic dyes were introduced in the late 1870s and 1880s (Wheat and Hedlund 2003).

The lac insect (*Laccifer lacca*) is native to India and Southeast Asia (Wheat and Hedlund 2003). The lac dyestuff was imported into England by the late eighteenth century. There are four chemical species within the lac beetle that produce

the red dye: laccaic acid A, B, C and D, with A being most abundant. The cochineal insect (*Dactylopius coccus*) is native to the Americas, where the insects live on prickly pear cactus (*Opuntia*) pads (Hogue 1993). Kermes (*Kermes vermilio*) is a parasite that feeds on Mediterranean oak (Cardon 1990), found in the Mediterranean region of southern Europe and Turkey. Kermesic acid (kermes) is the aglycone of carminic acid (cochineal), and both acids are responsible for producing the red color of the dyes (Bingham and Tyman 2000). Figure 1 shows the chemical structures of these red dyes. Due to the importation of commercial cloth into the Southwest from eastern American as well as European woolen mills, there is the possibility that each of these dyes may have been incorporated into Navajo textiles.

Extensive analysis has been previously done on Navajo textiles and, more specifically, on red dyes in these textiles. Anthropologist Joe Ben Wheat (Wheat and Hedlund 2003) devoted considerable effort to working on this topic and collaborated with biochemist David Wenger (2003) for the dye analysis. An extensive database was compiled from their results, focusing on lac, cochineal, and the synthetic dyes. The goal of the present project is to enhance and perhaps add another level of sensitivity to the established chronology by probing for the insect dye kermes, which was not previously sought.

Materials and Methods

The dyed fiber standards in this study were created directly using the dried insects. Lac (*Coccus laccu*) and cochineal (*Dactylopius coccus*) were obtained from Maiwa Craft Supply (Vancouver, BC, Canada), and kermes (*Kermes vermilio*) was obtained from German dye chemist Harold Böhmer. The wool (carded and spun Churro wool from Howard's Handwerk Haus, Tucson, AZ) was mordanted and dyed using standard methods (Fereday 2003). Both alum (potassium aluminum sulfate) and tin (stannous chloride) mordants were used (obtained from Aurora Silk). After samples were dyed, two extraction methods were carried out. The EDTA extraction method used a 1:1 mixture of DMF with 0.1% aqueous H_2EDTA with heat (100°C water bath, 30min) to extract the dye from the fiber (Tiedemann and Yang 1995; Zhang and Laursen 2005). The sulforic acid extraction method utilized concentrated sulfuric acid (1hr) to extract the dye (Wenger 2003). The UV-Visible spectrophotometry analysis was performed using an Agilent 8453 spectrophotometer. A Hewlett Packard/Agilent 1100 series HPLC was used with an Agilent Zorbax RX-C8 4.6 x 150mm, 5µm analytical column. The initial solvent system was on a gradient: 0 min- 80%A 20%B, 20 min - 5%A 95%B (A: H_2O with 0.1%TFA, B: MeOH) (Hayashi and Saito 2001). The chromatographic data was taken with the detector set at both 254nm and 495nm. Raw data are reported in Table 1.

Results and Discussion

Wenger's (2003) previous analysis of Navajo textiles utilized strong acidic conditions to extract the dyes from the wool fibers, followed by analysis and identification using UV-Visible spectrophotometry. Previously it was thought that by reacting cochineal with strong acid, complete cleavage of the glucose ring would occur and thus cochineal and kermes would not be identifiable, since cochineal and kermes are chemically distinguishable only by the presence or absence of a glucose sugar (Wenger, personal communication 2005). However, since the glucose ring is attached to the base structure via a C-C bond, not a C-O bond, it is more resistant to cleavage. It is true the acid will hydrolyze part of the glucose ring, but it is not cleaved all the way to the base structure (Allevi et al. 1987). Nevertheless, chemical species that are very similar in structure, such as the incomplete cleavage product of cochineal and kermes, are very difficult to identify in a UV-visible spectrum. Therefore, two changes were made to the dye extraction and analysis procedure. This study uses a metal chelating compound

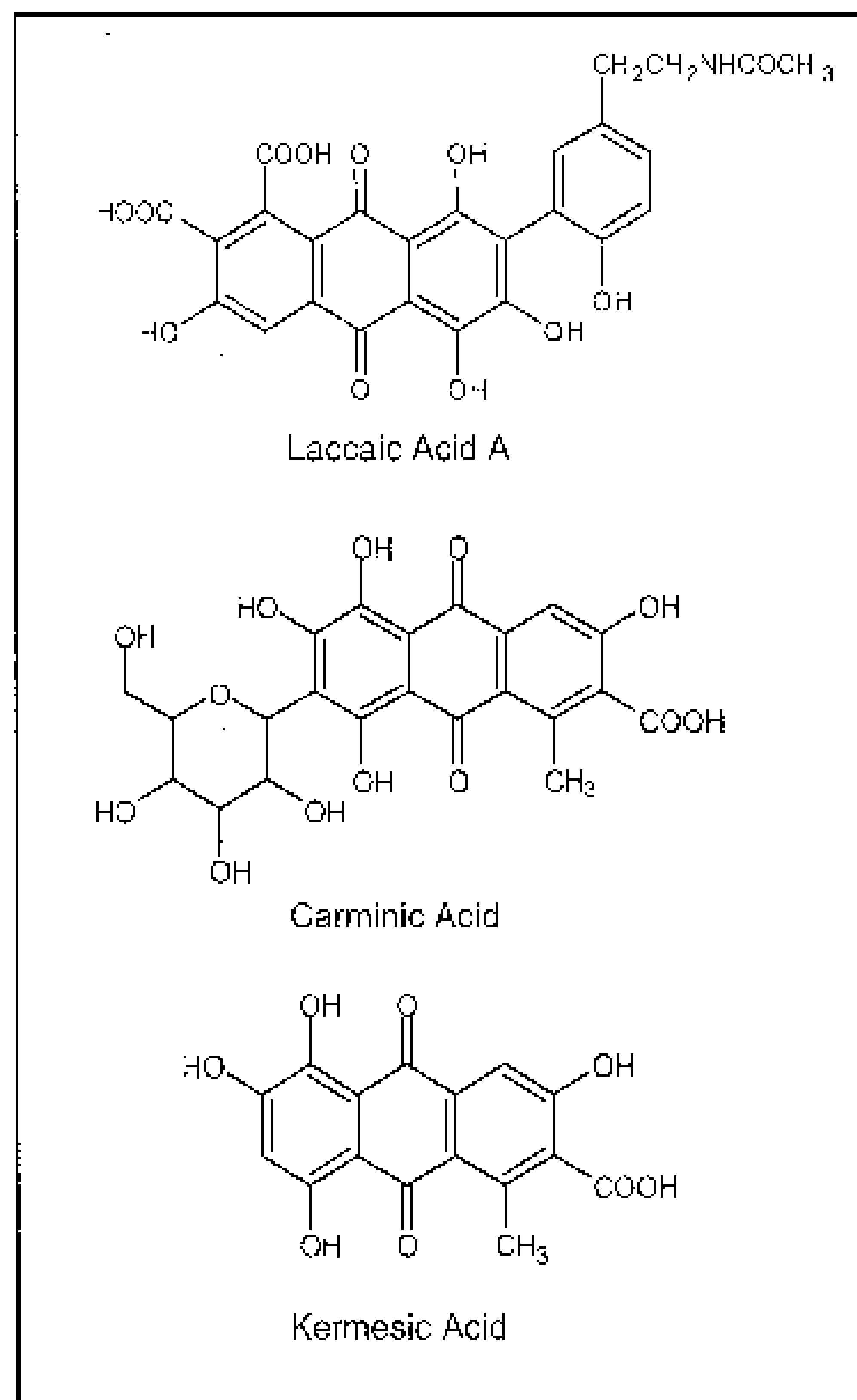

Figure 1. The chemical structures of the red anthroquinone insect dyes: lac (laccaic acid A), cochineal (carminic acid) and kermes (kermesic acid).

Table 1: The dye analysis results for the Southwest textiles from the Arizona State Museum. All the analyzed textiles were Navajo, except for E-9990 which was Acoma.

Sample	Previous Analysis	Results
8407-light	never tested	cochineal 11: lac 57
8407-dark	never tested	cochineal 15: lac 85
8418-red	cochineal 45: lac 55	cochineal 60: lac 40
8418-dark	cochineal 30: lac 70	cochineal 52: lac 48
8420-rose	never tested	synthetic
8420-maroon	never tested	cochineal
22077-bright	cochineal 90: lac 10	cochineal
22077-dark	cochineal	cochineal
22078-tassel	never tested	cochineal
22078-red	never tested	cochineal 85: lac 15
E-1201	cochineal	cochineal
E-2167	never tested	cochineal
E-2211-pink	never tested	cochineal 41: lac 17: syn 42
E-2211-maroon	never tested	cochineal 37: lac 63
E-2270	never tested	cochineal 7: lac 93
E-2853-red	cochineal	cochineal
E-2853-maroon	cochineal	cochineal
E-2856	cochineal 95: lac 5	cochineal 68: synthetic 32
E-2859-red	cochineal 55: lac 45	cochineal 54: lac 46
E-2859-pink	synthetic	synthetic
E-2867(pink)	cochineal	cochineal
E-3266-orange	synthetic	synthetic 95: cochineal 5
E-3760-maroon	cochineal	cochineal
E-9990-rust	never tested	cochineal 80: lac 30

to extract the dyes instead of the concentrated acid, followed by High Performance Liquid Chromatography (HPLC) analysis instead of UV-Visible spectrophotometry.

The insect dyes lac, cochineal and kermes are mordant dyes, which utilize a metal ion to form a chemical complex between the dye and the desired fiber, which may be cotton or wool (Figure 2) (Timar-Balazsy and Eastop 1998). Because the dye is only held onto the fiber by binding to the metal ions,

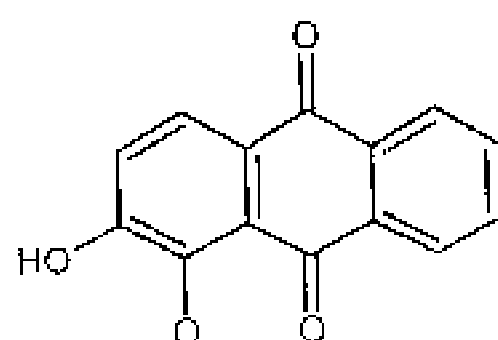

Figure 2. In mordant dyes metal ions are used to bind the dye to the fiber. In this example, chromium (III) is bound to cotton, the anthroquinone dye and two water molecules are the other chelating agents.

there is an alternative way to extract the dye from the fiber without the use of strong acid. Using a metal chelator instead of a strong acid to cleave the dye/metal/fiber bonds should leave the dye molecules intact and lead to better chemical analysis. Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand chelator that will bind to the metal ion with a stronger affinity than the anthroquinone dye, which will cause the dye to be released from the fiber. This extraction method does not chemically alter the glucose ring on cochineal, and so allows the chemical structure to be analyzed more accurately.

HPLC analysis of the extracted dye adds a further level of sensitivity to the analysis of the dyes. HPLC utilizes a separation step prior to the absorbance detection of the analyte, which allows base-line resolution of the analyte peaks that is unachievable with UV-Visible spectrophotometry. Figure 3 shows the UV-Visible spectra for both the sulfuric acid and EDTA extracts, as well as the chromatogram of the EDTA dye extracts. The sulfuric acid extracts could not be analyzed with HPLC due to the inability of the stationary phase in the HPLC column to withstand the low pH of the sulfuric acid. However, the results show that baseline resolution and reproducibility are achieved with HPLC, and the UV-Visible spectrophotometry results are not as diagnostic.

A diverse range of Navajo textiles was sampled in order to encompass the time span, designs, and yarn types that might involve kermes as a contributing dye source. The textile samples from the Arizona State Museum were extracted using the EDTA method and analyzed by HPLC. The most significant finding was that kermes was not found in any of the textiles sampled. However, this conclusion is logical because by this time cochineal was abundant in Europe and had mostly replaced kermes as the dyestuff of choice due to its higher dye content (Wheat and Hedlund 2003). The dye compositions (percentages) were compiled for the textiles tested by integrating the analyte peaks on the HPLC chromatograms. A subset of the samples tested were textiles previously analyzed by Wenger. Comparing the results from this study with previous findings showed a strong positive correlation. Only two samples' results differed enough to require further investigation. The first anomaly was a two-piece Navajo dress (E-2856) for which the estimated chronology was 1850-1865. However, results from this study showed the presence of synthetic dye, thus suggesting a later estimated date range. The other interesting piece was a Navajo chief's blanket which was found to contain lac and cochineal, as well as synthetic dye. It seems unlikely that all three dyes were used on the same fibers. More work needs to be done, but the probable explanation for this was the use of yarns from different sources in the same blanket, and a procedural error in sampling. Overall, the present study strongly supports Wenger's previous analysis, as well as adds to the database of dye testing for Southwestern textiles.

Conclusions

No source of kermes was found in the Navajo textiles tested, although it was important to make the analyses with the

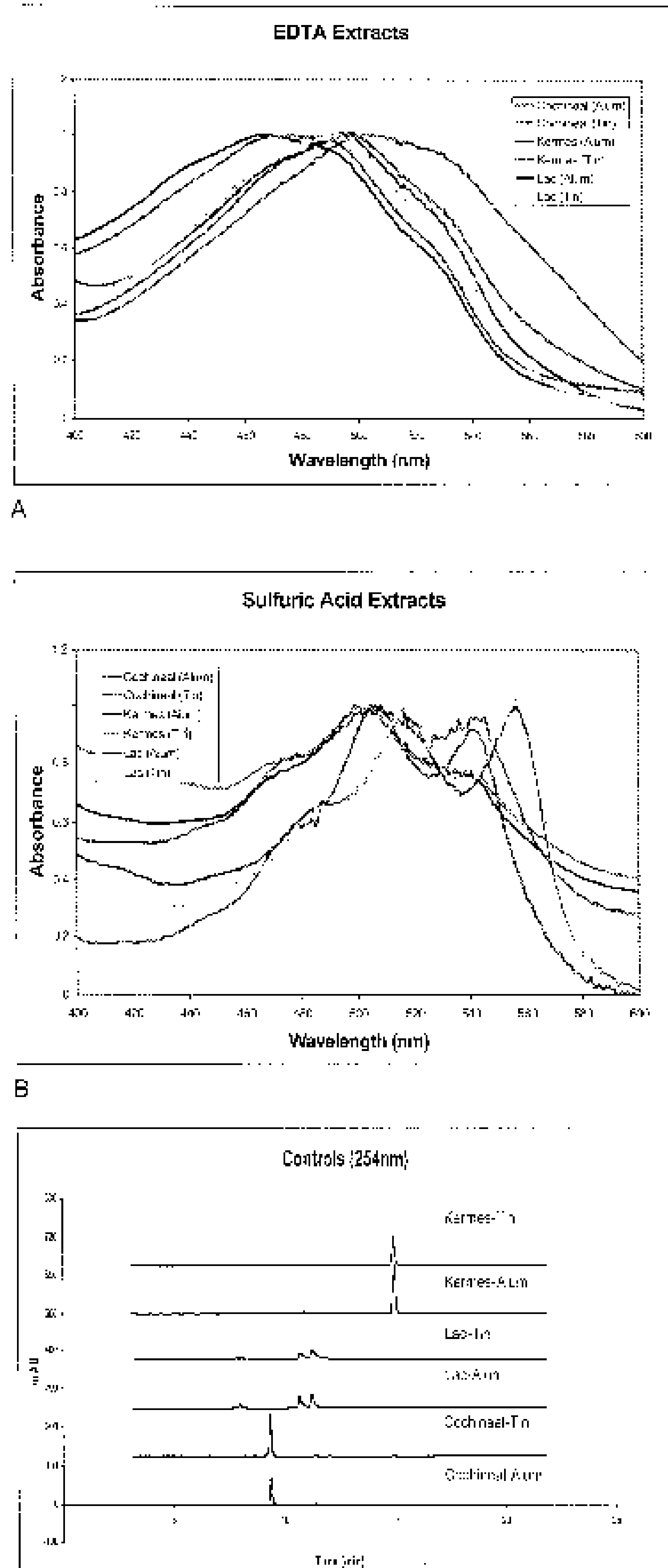

Figure 3. A and B show the UV-Visible spectra of the EDTA and sulfuric acid extracts, respectively; C shows the HPLC chromatogram of the dye standards at 254 nm.

revised method in order to distinguish between kermes and cochineal. Although not every textile can be sampled, it seems unlikely that kermes entered the Southwest on fabrics that were subsequently raveled and rewoven, since the sample set used in this study was derived from a broad set of characteristics. Testing for kermes has applications beyond textiles from the Southwest. For example, it has potential applications in the study of Middle Eastern carpets and textiles. Cochineal was not always available in Europe, and kermes was the red insect dye used prior to European contact with the New World. Expanding this type of testing may help to establish the period during which each dye was used. Given an improved chronology, this testing could refine certain dating techniques based on the presence or absence of kermes versus cochineal.

Acknowledgments

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Archaeological Ceramics

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The column in this issue includes six topics: 1) Reviews of Books on Archaeological Ceramics, 2) New British Archaeological Reports-International Series, 3) Previous Meetings, 4) Forthcoming Meetings, and 5) Internet Resources.