AMBIENT MASS SPECTROMETRY ANALYSIS OF ALIZARIN DYED TEXTILE AND DYE TRANSFER TO PAPER

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ABSTRACT

Nondestructive and minimally destructive analytical chemistry techniques are valuable tools to the conservation field. Direct analysis in real time (DART) is an ambient ionization method that uses a heated helium post-plasma gas stream to desorb and ionize molecules from a sample surface that then enter a high-resolution mass spectrometer (MS). DART-MS has been used for many different applications, but recent literature in the field of conservation has focused on new methods for the dye analysis of historic textiles. In the current work, we present our DART-MS analysis of historic textiles related to madder dyeing on cotton, including samples removed from accessioned textiles and from intact samples mounted in swatch books. Our data demonstrates that DART-MS can detect compounds associated with textile processing, in addition to the dye chromophore. These additional compounds may provide insight into the complexity associated with historic textile production, use, and degradation.

INTRODUCTION

During the late 18th century and 19th century, spurred on by continuing developments in dye chemistry, monochromatic and polychromatic printed cottons with detailed imagery were wildly popular in Western Europe and the United States, available in a variety of styles and colors. With active innovative manufacturing and competition among printers, dye manufacturers, and distributors of this new industry, textbooks and chemical clarifications did not always stay current or have all the necessary procedures enumerated precisely. Consequently, a perusal of 19th and early 20th century dye swatch books can often find several examples where the image printed onto the cotton swatch, now pasted into the textbook, produced, over time, an image transfer or off-set on the adjacent page. In one Smithsonian museum, a set of bed hangings were found to be transferring an actual *colored* ghost image, a shadowy dyed print or off-set, directly onto adjacent tissue or mat board (figure 1). In some instances, these images may well be leaching or off gassing of volatile materials, unfixed auxiliaries or dyes, but without chemical analysis there can be no definitive identification. Even uncolored ghosts images are known to be difficult and time consuming to replicate and identify (Heald et al., 1994; Padfield and Erhardt, 1987).

In the field of conservation and preservation, where analytes or samples are often too rare or too precious to be physically sectioned from intact objects, nondestructive and minimally destructive analysis methods are especially important. For example, X-ray fluorescence spectroscopy (XRF) can identify inorganic elements associated with mineral dyes or mordants. Until recently, the most comparable analytical method for organic compounds has been Fourier transform infrared spectroscopy (FTIR), which identifies species by the spectral pattern of covalent bonds. Identification by FTIR is complicated by the simultaneous detection of all materials present in a single spectrum. In order to determine the color component, a mere 0.2-3.0% by weight of the

fabric itself, the dye must first be separated from the fiber. The most accurate and precise organic dye analysis for dyed and printed fabric requires the removal and processing of a small dyed sample by high performance liquid chromatography (HPLC) coupled to ultraviolet-visible (UV-Vis) spectroscopy, a diode array detector (DAD), or mass spectrometry (MS). Unlike FTIR, LC separates the chemical components for individual detection, and known chromophores are characterized by absorbance, chromatographic retention time, and/or molecular mass. The finding is confirmed by its congruency to a library of references, containing known dye standards each previously characterized.

Ambient mass spectrometry describes a set of techniques performed at atmospheric pressure with little or no sample preparation or sectioning. Chromatography is not employed, and high mass resolution distinguishes compounds that are not separated in time. (Gross 2011) DART ionization is one such technique. Helium flows through a heated cell where an electrical discharge creates metastable ions (figure 2), which exit through a port in a ceramic cap in a plume of gas and interact with both the sample and water in the ambient atmosphere. (Cody et al. 2005) Analyte molecules are thermally desorbed off a sample surface, ionized, and pulled through a transfer tube into the mass spectrometer vacuum for analysis. The DART experiment can be performed in transmission mode, in which the DART probe is directed straight at the transfer tube with samples held in between (figure 3a) (Cody et al. 2005); or in reflection mode, in which the DART probe is directed at an angle to a horizontal sample surface positioned in front of the mass spectrometer (figure 3b). (Gross 2014; Habe et al. 2015; Newsome et al. 2018) DART ionization has been used for a variety of small molecule applications, including dye analysis. (Armitage et al. 2015a, 2015b)

Three examples of DART-MS analysis are described in this paper. First, a comparison with the HPLC-DAD/MS results was made using a part of the same sample removed from a set of bed hangings and related printed textiles (figures 1, 4a). Second, the identification of the colored ghost image on paper associated with these hangings (figures 1, 4b) was confirmed, including cases where the colorant ghost itself had dissipated throughout the paper to imperceptivity. Lastly, an offset stain associated with a dyed swatch sample in a dye manufacturer's swatch book of sample dyes was analyzed. The offset images were found on the cover and facing papers across from the dye when the book was opened (figures 5a, left and 5b left).

EXPERIMENTAL

Samples. HPLC-DAD/MS results had previously established the chromophores on a printed toile as chemical components of alizarin dye: alizarin, purpurin, and three other anthraquinones, analogs of purpurin--anthrapurpurin, flavopurpurin and an unknown, along with ellagic acid, present in tannic acid based dyes. (Mouri, 2017)[1] In preparation for comparable analysis using the DART-MS, several sources of alizarin were used as standards: 1) muslin cloth dyed with madder that had been post-treated with $SnCl_2$; 2) powdered alizarin (Aldrich, 97%) dried onto

[1] NASM permitted sampling from the interior of a valence (T20140072370) from a set of bed hangings and associated fabric fragments. See Ballard, M. 2017. "MCI # 6652 Fiber, Yarn, Weave, & Fabric of the Balloon Fabric" unpublished internal report, Museum Conservation Institute, Smithsonian Institution.

Whatman paper; 3) madder root (Kremer pigments); and 4) fibers from wool yarn dyed with madder and post-treated with $SnCl_2$.

No sample preparation was performed for the extant samples of the toile textile. A fragment of tissue paper containing a colored ghost image had been set aside, folded into a small, compacted sample and wrapped tightly in aluminum foil. As of October 2017, the offset had faded, dispersed throughout the paper within the confines of the aluminum foil; although contained, they were now rendered almost imperceptible. For more distinctive, conventional offsets, the dye swatch book *Les Couleurs d'Alizarine** was selected and its Swatch #36 "Noir d'Alizarine R, en pate" (figure 5a, right) and its offsets (figures 5a left and 5b left) were tested [BASF, no date]. Because of the size of this object, reflection mode was used for DART-MS analysis.

Instrumentation. A DART 100 probe operated by an SVP controller (IonSense, Saugus, MA) was custom-mounted in front of a LTQ Orbitrap Velos mass spectrometer (Thermo Fisher Scientific, Waltham, MA) fitted with a differentially pumped Vapur interface. Mass spectra data were acquired at 30,000 resolving power with a maximum ion trap fill time of 100 ms. In transmission mode, a flat ceramic insulator cap was offset from the ceramic transfer tube by 7 mm (figure 3a). There can be a limit to the size of the sample, but this configuration provides the greatest ion sensitivity. In reflection mode, an electronically-controlled shutter (Newsome et al. 2018) was mounted beneath the insulator cap and transfer tube and above sample surfaces. A tapered ceramic insulator cap with a 0.5 mm orifice was positioned approximately 5 mm in front of the transfer tube and 45° to and 0.5 mm above the sample surface. Samples were exposed to the DART gas plume 3 s using the shutter (figure 3b). This configuration provides a greater protection from temperature for the object. Several helium gas temperatures were tested to determine optimum signal intensity. Optimum signal was observed with a helium gas temperature of 400 °C.

RESULTS & DISCUSSION

Madder Standards for DART Muslin cloth dyed with madder and post-treated with $SnCl_2$ was examined by DART-MS in transmission mode at various temperature settings for the presence of alizarin and derivatives. Signal abundance from alizarin increased with DART helium temperature setting up to 400 °C. No alizarin was detected at 100 °C. To prevent thermal damage to samples at 400 °C, most samples were run with a helium temperature setting of 300 °C. The discrete samples, like the madder materials, also were run in the transmission mode.

Formulas of alizarin derivatives and their respective exact mass values are shown in table 1. Table 2 lists the samples tested in this study. In the madder root sample, signal from alizarin derivatives dominated the mass spectrum, shown in figure 6. For all other samples (including the alizarin reference and madder-dyed samples), alizarin and/or its structural isomers were a trace signal in the spectrum at *m/z* 241.0504 (figure 7). Balloon printed fabric samples remaining from dye analysis with HPLC-DAD/MS were then analyzed (figures 8 and 9). With permission for destructive analysis of the tissue paper wrapping, the balloon offset was examined at 400 °C. The mass spectrum is given in figure 10, with the inset showing the alizarin peak. In figure 11, the selected ion signals for several alizarin derivatives are plotted over collection time. The mass-

resolved analyte signal was observed when the sample was placed between the DART source and the inlet tube with zero background signal otherwise. The results are generally consistent with the HPLC data; DART-MS was able to detect alizarin and its derivatives, including on the invisible offset on acid free tissue.

Dye swatch books containing "alizarin" swatches were also occasionally found to contain offset stains on paper directly in contact with the swatches. In the book *Les Couleurs d'Alizarine, Vol. II*, one particular offset stain from swatch 36 (dye: Noir d'Alizarine R) was present on both the glassine tissue paper in direct contact with the swatch and on paperboard that covered the tissue (figure 5a and b). Because of the large size and dark discoloration of the offset, it was chosen for analysis by DART-MS. Analysis in reflection mode was collected on the swatch, the tissue offset, and the paperboard offset. As a control, data was also taken in unaffected areas of the tissue and the paperboard where no discoloration was observed. A summary of the mass spectral data for these five sample sets are shown in table 3. The results indicate the presence in the textile of ricinoleic acid and linoleic acids—components of castor oil soap, recommended as an auxiliary or assist in the dyeing of Alizarines, synthetic anthraquinones (BASF, no date; Hummel, 1906; Knecht et al., 1910; Pellew, 1918). In addition, resin acids (rosin) were detected on both the swatch and the papers containing the offset, which may be associated with the paper processing (Adams, 2011). The presence of rosin suggests that the offsets or discolorations may travel from the paper to the textile and not just from the textile to paper.

3. CONCLUSIONS

Recent literature has suggested that using DART-MS for dye analysis could be achieved in a totally non-destructive fashion (Armitage, Day and Jakes, 2015b). Our data also demonstrate the utility of detecting by DART-MS compounds associated with textile processing, which in turn can provide insight into the complexity associated with historic textile production, the quality of the manufacturing, or the postproduction use and misuse, as well as fabric degradation. Indeed, DART-MS can also detect when the leachings have gone from the paper into the textile swatch, as seen in Table 3.

The DART-MS instrumentation can also provide varying levels of sensitivity depending upon the configuration and the setting temperature of the helium stream. With direct transmission, alizarin and its various analogs can be distinguished at temperatures between 300 and 400 C. With reflective mode, the actual chromophore remains obscured at lower temperatures, but the out-gassings or leachings are clearly represented. This reflective mode may provide book conservators, bibliophiles and antiquarians as well as textile conservators and scientists with insights into the gradual changes that can occur within a closed volume.

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Air and Space Museum; Dr. Chika Mouri (Mori) and Dr. Blythe McCarthy, Department of Conservation and Scientific Research, Freer/Sackler Galleries.

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ADDITIONAL READING

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SOURCES OF MATERIALS

DART 100 probe operated by an SVP controller
IonSense
Saugus, MA

LTQ Orbitrap Velos mass spectrometer
Thermo Fisher Scientific
Waltham, MA

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REGINA A. BAGLIA received her Ph.D. in chemistry at The Johns Hopkins University in 2016, where she worked with Prof. David P. Goldberg. Her research was focused on bioinspired synthetic inorganic chemistry. In 2017, she took up a post-doctoral internship at the Museum Conservation Institute working on LED lighting issues for the "Ruby Slippers" exhibition. She currently resides in Dallas, Texas. E-mail: regina.baglia@gmail.com

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LIST OF FIGURES

Table 1. Most common red colorant compounds in madder (Schweppe, 1989).

Compound	Neutral Formula (M)	Exact mass of protonated molecule ($[M+H]^+$)
alizarin	$C_{14}H_8O_4$	241.0501
purpurin	$C_{14}H_8O_5$	257.0450
pseudopurpurin	$C_{15}H_8O_7$	301.0348
xanthopurpurin	$C_{14}H_8O_4$	241.0501
Lucidin	$C_{15}H_{10}O_5$	271.0606
Rubiadin	$C_{15}H_{10}O_4$	255.0657

Table 2. Summary of alizarin derivatives detected in samples

Sample	Alizarin detected at *m/z* 241.0504	Purpurin detected at *m/z* 257.0453	Other derivatives detected
Madder on cotton muslin (after-treated with $SnCl_2$)	✓	✓	rubiadin
Alizarin powder	✓	✓	-
Madder root	✓	✓	Rubiadin, lucidin
Madder on wool yarn(after-treated with $SnCl_2$)	✓	✓	Rubiadin, lucidin
Printed toile (red)	✓	✓	Rubiadin, lucidin
Printed toile (brown)	✓	✓	Rubiadin
tissue paper offset	✓	✓	Rubiadin, lucidin

Table 3. Summary and Comparison of compounds detected in textile, its off-sets, and paper controls

Observed *m/z*	**Compound Class**	**Neutral Formula and Compound**	**Textile**	**Tissue Off-set**	**Tissue Control**	**Board Off-set**	**Board Control**
263.2364	Fatty aldehyde	$C_{18}H_{30}O$ Linolyl aldehyde	✓	✓			
281.2485	Fatty acid	$C_{18}H_{32}O_2$ Linoleic acid	✓	✓			
289.2534	Resin acid	$C_{20}H_{32}O$ Abietol	✓			✓	✓
299.2578	Fatty acid	$C_{18}H_{34}O_3$ Ricinoleic acid (castor oil)	✓	✓			
299.2014	Resin acid	$C_{20}H_{26}O_2$	✓	✓	✓	✓	✓
301.2161	Resin acid	$C_{20}H_{28}O_2$ Dehydroabietic acid	✓	✓	✓	✓	✓
303.2312	Resin acid	$C_{20}H_{30}O_2$ Abietic acid	✓	✓	✓	✓	✓
315.1945	Resin acid	$C_{20}H_{26}O_3$ 7-oxodehydro abietic acid		✓		✓	✓