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*Museum Conservation Institute*

# Ambient Mass Spectrometry Open Lab Report

**MCI request number:** 6575.4 (Open lab)
**Title / Object:** wig
**Accession number:** 2012-18-43
**Maker:** Senegalese
**Geographic region:** Senegal
**Date:** n.d.
**Materials:** dyed raffia fiber

**Requested by:** Janelle Batkin-Hall, Andrew W. Mellon Conservation Fellow

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**Unit:** NMAfA

**Analyst(s):** G. Asher Newsome, (newsomeg@si.edu).

**Analysis date:** 17th October 2018

## Introduction

Blue-colored dyed fiber samples from a Senegalese wig were provided by Janelle Batkin-Hall, Andrew W. Mellon Conservation Fellow at the National Museum of African Art (NMAfA), to test for the presence of indigo and/or identify the dye material used.

## Methods

*DART-MS (Direct Analysis in Real Time mass spectrometry)*

DART ionization is a method for ambient mass spectrometry in which materials are rapidly sampled at atmospheric conditions with little or no preparation. DART systems flow helium through a cell where an electrical discharge between a needle and disk electrodes produces a plasma of ions, electrons, and metastable ions (Figure 1). The plasma further flows through a heated cell and a grid at a set voltage to remove all charged species except for helium metastable ions.[1] The reactive metastable ions exit the DART through a port in a ceramic cap and interact with both the sample itself and water in the

ambient atmosphere. Analyte molecules are thermally desorbed off a sample surface and ionized. The vacuum of the mass spectrometer itself or a supplemental vacuum pulls the ionized analyte into a ceramic transfer tube to the mass spectrometer ion optics for analysis. In transmission mode the DART probe is directed straight at the mass spectrometer inlet with samples held in between.[2]

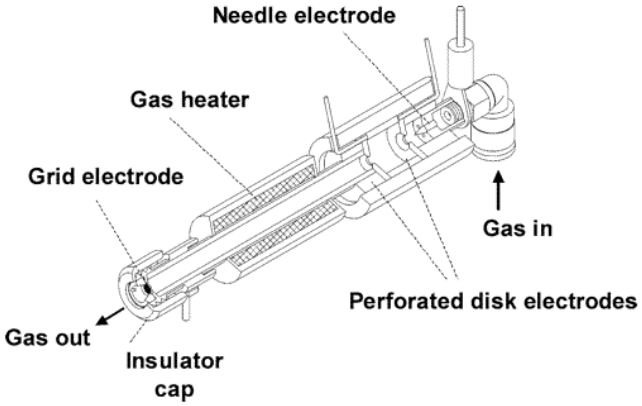


Figure 1. Diagram of DART optics. (Cody, R. B.; et. al. *Anal. Chem.* **2005,** *77* (8), 2297-2302).

*Fiber sampling*

The DART was mounted in trasmission mode in front of a LTQ Orbitrap Velos mass spectrometer (Thermo Fisher Scientific, Waltham, MA) fitted with a differentially-pumped Vapur interface. The ceramic insulator cap of the DART was set back 7 mm from the ceramic transfer tube of the interface. The helium ionization gas was set to a heater temperature of 200 and 350 °C, with optimum signal oberved at 300 °C. Individual fibers were held by precision steel forceps, which were themselves clamped to an independent micrometer stage mounted below the ion source (Figure 2). Fibers were translated axially between the ceramic cap and the transfer tube for analysis. MS data was acquired at 30,000 resolving power with a maximum ion trap fill time of 100 ms. The forceps were cleaned with solvent and exposed to DART without fibers in between analyses to prevent contamination.

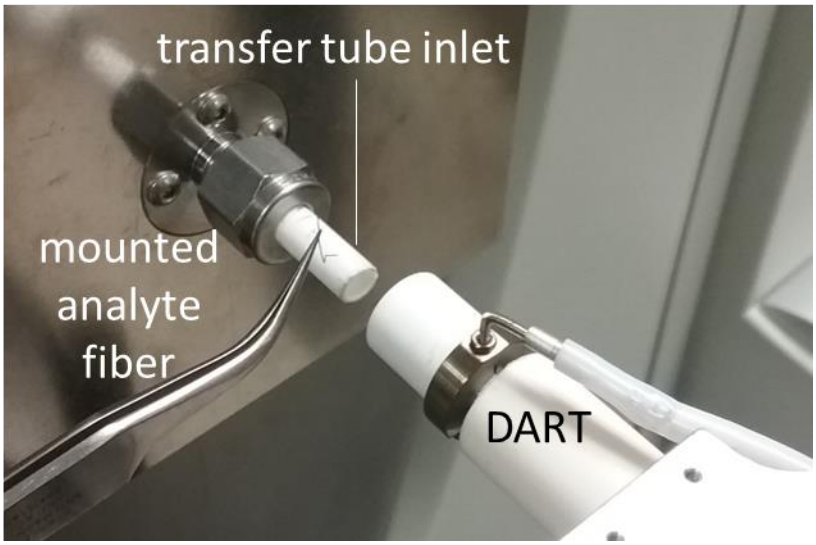


Figure 2. Single analyte fiber mounted in forceps before being translated into DART gas stream.

## Results

Observations from the wig fibers are summarized in Table 1. All observed ions had the form of protonated molecules. Indigo signal was observed above background at *m/z* 263 and 265 but was not one of the most abundant ions; a representative mass spectrum is shown in Figure 3. Although DART-MS is not quantitative without very careful controls, signal from intact indigo was low compared to other analyses of single fibers. Slightly more signal was observed from the reduced form leuco-indigo. Many of the most abundant ions came from compounds naturally present in plant materials like raffia, such as linolenic acid and ricinoleic acid. The overall most abundant ions were $C_{27}$ species, which could be synthetic materials or oxygenated forms of cholesterol.

Table 1. Observed ions and identified chemical formulae.

| intact mass | neutral chemical formula | database id |
|---|---|---|
| 189.1113 | $C_9H_{16}O_4$ | Heptanedioic acid, dimethyl ester isomer |
| 226.1790 | $C_{13}H_{23}NO_2$ | Glutarimide, N-(2-octyl)- isomer |
| 228.1971 | $C_{13}H_{25}NO_2$ | Carbonic acid, monoamide, N-ethyl-, menthyl ester or isomer |
| 238.1214 | $C_{16}H_{15}NO$ | Cyheptamide isomer |
| 245.1381 | $C_{12}H_{20}O_5$ | Succinic acid, butyl 3-oxobut-2-yl ester isomer |
| 250.0853 | $C_{16}H_{11}NO_2$ | Phenyl(5-phenyl-3-isoxazolyl)methanone isomer |
| 263.0816 | $C_{16}H_{10}N_2O_2$ | indigo |

| | | |
|---|---|---|
| 263.2357 | $C_{18}H_{30}O$ | Linolene aldehyde |
| 265.0964 | $C_{16}H_{12}N_2O_2$ | leuco-indigo |
| 279.2305 | $C_{18}H_{30}O_2$ | Linolenic acid |
| 281.2458 | $C_{18}H_{32}O_2$ | linoleic acid; m/z 299.2579 water loss |
| 297.2405 | $C_{18}H_{32}O_3$ | Carbonic acid, but-2-yn-1-yl tridecyl ester |
| 299.2561 | $C_{18}H_{34}O_3$ | ricinoleic acid |
| 327.0767 | $C_{18}H_{15}O_4P$ | Triphenyl phosphate, flame retardant in plastics |
| 338.3397 | $C_{22}H_{43}NO$ | erucamide (polyethylene slip agent) |
| 357.2978 | $C_{21}H_{40}O_4$ | Sebacic acid, isohexyl 3-methylbut-2-yl ester isomer |
| 367.3340 | $C_{22}H_{42}N_2O_2$ | |
| 383.3288 | $C_{27}H_{42}O$ | Cholesta-4,6-dien-3-one isomer |
| 399.3254 | $C_{27}H_{42}O_2$ | |
| 401.3384 | $C_{27}H_{44}O_2$ | Cholesterol, 7-oxo- isomer |
| 417.3331 | $C_{27}H_{44}O_3$ | Tigogenin isomer |
| 431.3121 | $C_{27}H_{42}O_4$ | 1,2-Cyclohexanedicarboxylic acid, 3,5-dimethylphenyl undecyl ester isomer |
| 433.3277 | $C_{27}H_{44}O_4$ | Phthalic acid, 2,4-dimethylpent-3-yl dodecyl ester isomer |
| 445.2088 | | |
| 447.3490 | $C_{28}H_{46}O_4$ | Didecyl phthalate isomer |
| 507.2236 | $C_{32}H_{30}N_2O_4$ | |

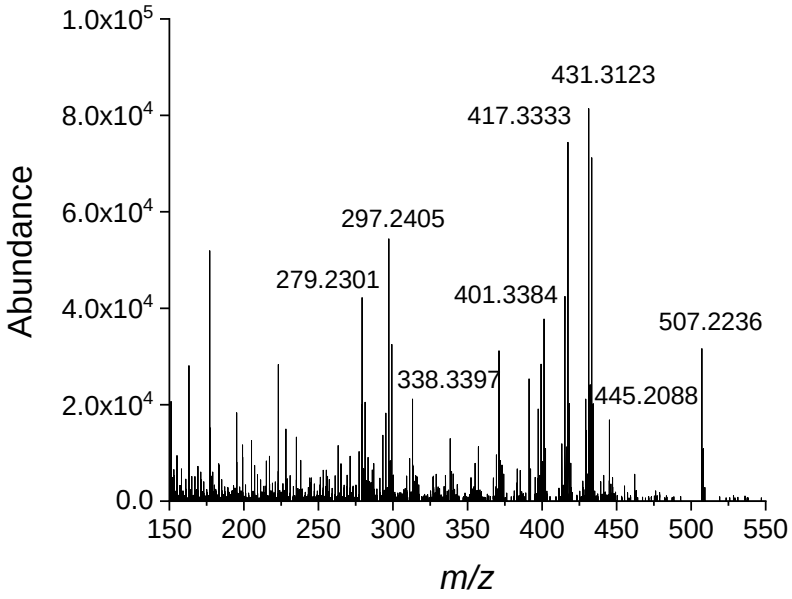


Figure 3. Ions with identified molecular formulas from 300 °C DART of wig fibers.

## Conclusions

Indigo and the reduced form of indigo were identified in low abundance from dyed raffia fiber samples. Although the analysis was not quantitative, indigo may not be the primary colorant. Most of the signal arose from the raffia material itself.

## References

1. Cody, R. B.; Laramee, J. A.; Durst, H. D., Versatile new ion source for the analysis of materials in open air under ambient conditions. *Analytical Chemistry* **2005,** *77* (8), 2297-2302.
2. Gross, J. H., Direct analysis in real time-a critical review on DART-MS. *Analytical and Bioanalytical Chemistry* **2014,** *406* (1), 63-80.