Non-proximate Ambient Mass Spectrometry Sampling of Large, Intact Cultural Heritage Objects

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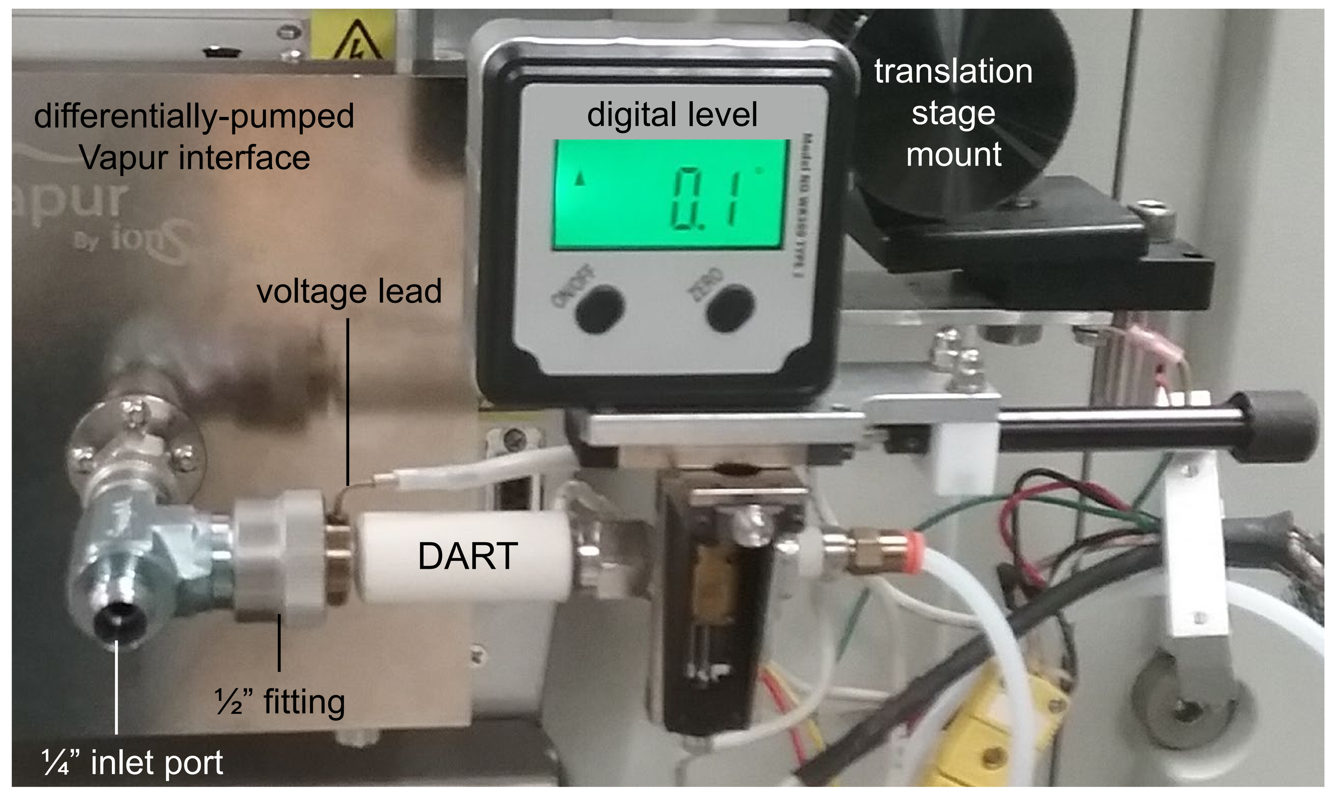
Overview

- Large, intact objects cannot fit close enough to a mass spectrometer to be efficiently sampled by common ambient analysis techniques such as direct analysis in real time (DART) or DESI
- With large object necessarily placed far from MS, signal from ions generated at surface decreases logarithmically with length of atmospheric pressure transfer tube to MS inlet
- Continuous solvent-based transport [1, 2] deprecated for analyte objects that cannot be wetted
- Ionization is separated from thermal desorption sampling to transfer neutral gaseous analyte
- Timed, discontinuous exposure to neutral, heated gas used to minimize sample damage [3]
- Temperatures and flow rates optimized to transfer desorbed analyte 2 m to DART ion source
- Indigo and related compounds observed from non-proximate, dyed fabric and wood splints
- Methodology to be used for intact cultural heritage objects – woven basket, wooden sculpture

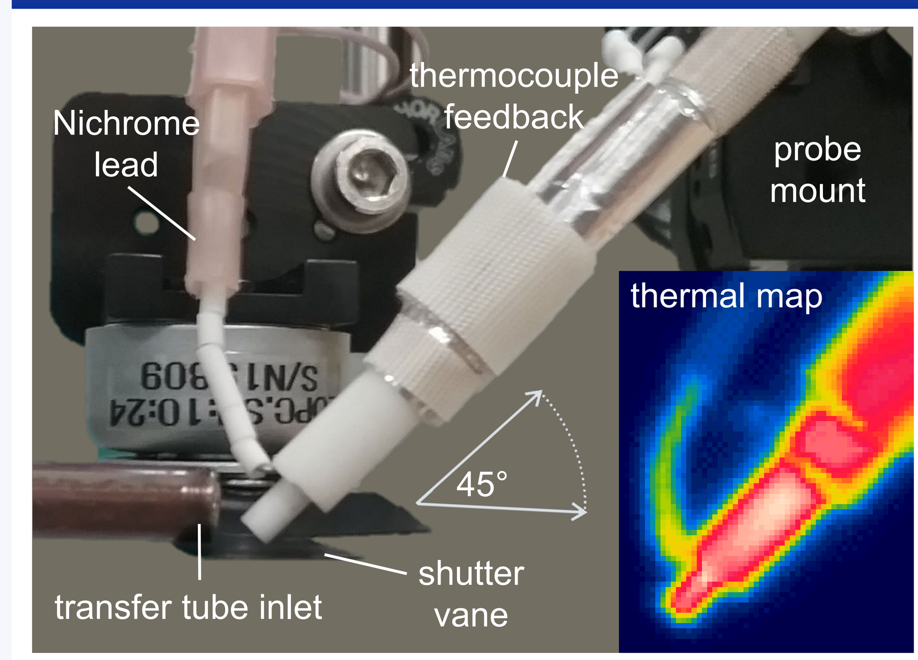
Experimental: MS-proximate Ionization

- MS Analysis with LTQ Orbitrap Velos (Thermo Fisher) at 30,000 resolving power
- DART 100 source (IonSense) with flat 2.5 mm orifice cap, operated by SVP controller, case shielding removed, independently mounted from above on multi-dimension translation stages



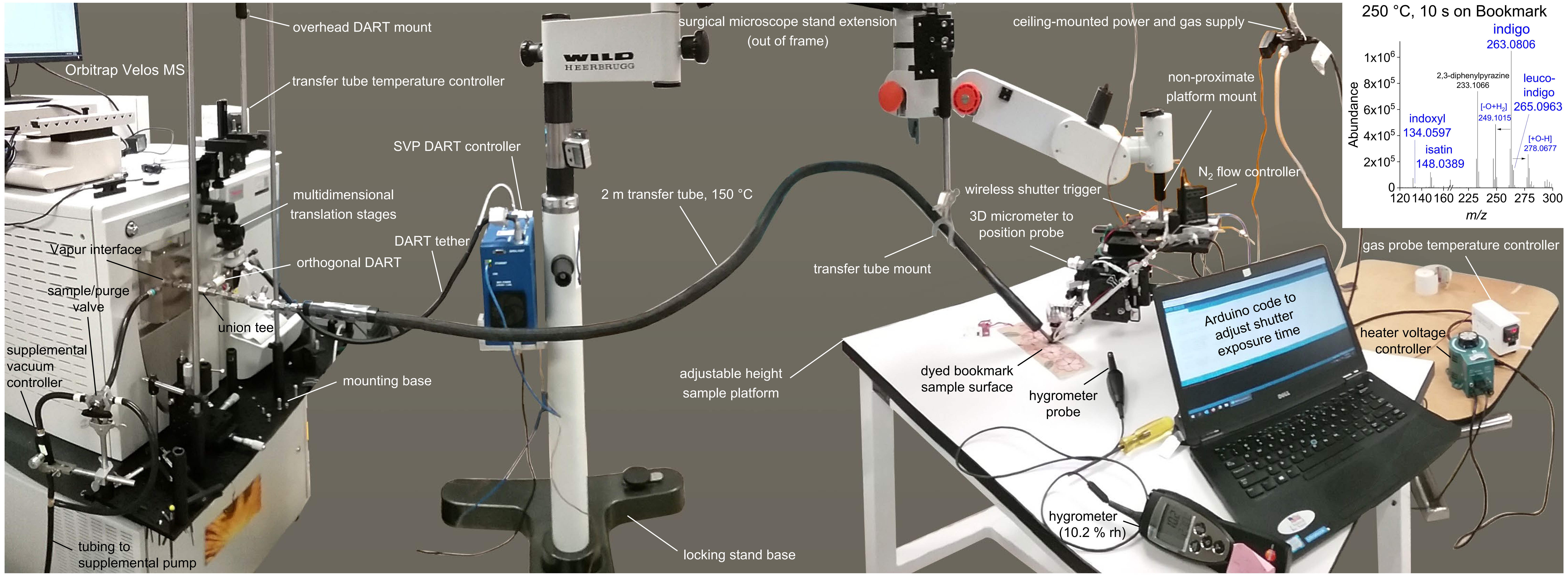
- DART probe mounted orthogonal to inlet, helium plasma set to 50 °C for source stability
- Stainless steel union, coated with SilcoNert to prevent sample carryover, connects Vapur and orthogonal DART probe to sample inlet port
- Ceramic orifice cap sealed to union tee with ½" UltraTorr fitting, isolated from voltage lead

Discontinuous, Neutral Desorption and Transfer

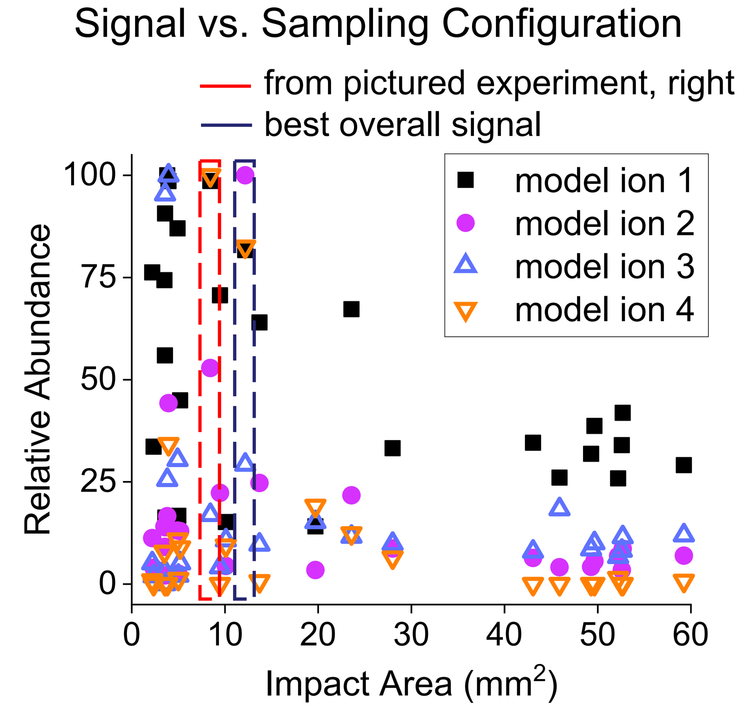


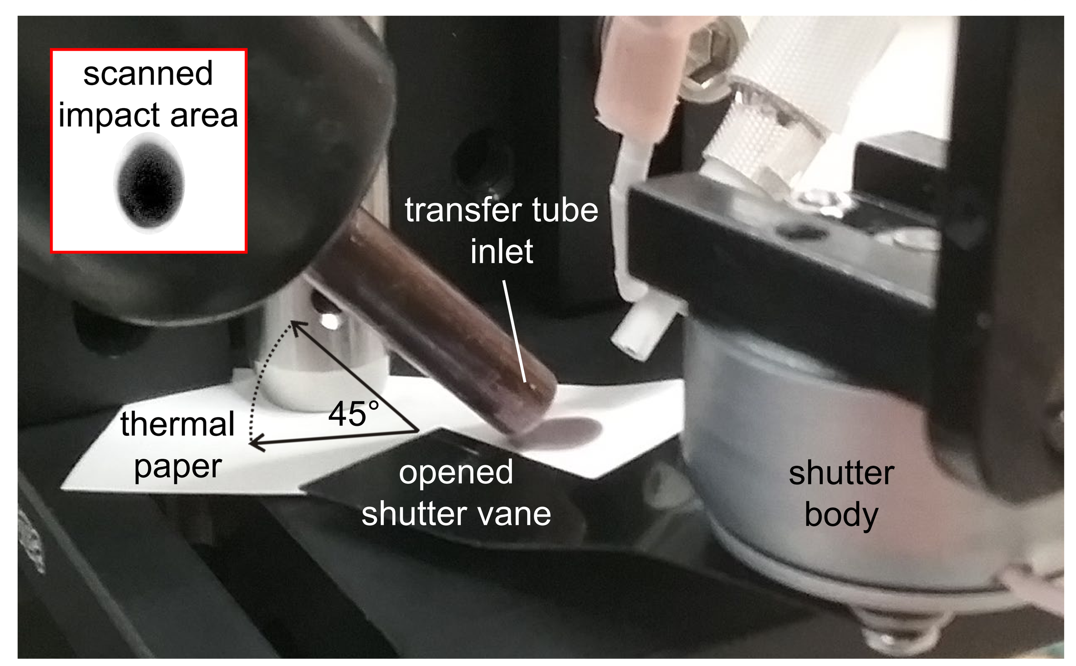
- Probe built from ¹⁄₁₆" od copper tubing within ⅛" od alumina tubing, within 22 gauge NiChrome wire coil, within ¼" alumina tubing
- Probe mounted 45° to normal from above on micrometers on overhead stand
- Continuous neutral nitrogen supplied by flow controller connected to rear
- Thermocouple wrapped to probe body feeds back to temperature controller relaying 15.5 V AC to heater coil (leads protected by alumina beads)
- ¼" od stainless steel transfer tubing, SilcoNert-coated and regulated at 150 °C (Clayborn Lab)
- Arduino-controlled shutter protects sample during object mounting until timed exposure

Wide-angle Perspective of Non-Proximate Thermal Desorption System (right) and 2 m Transfer Tube to MS-proximate DART (left)



Flow Rate, Temperature, and Position Optimization

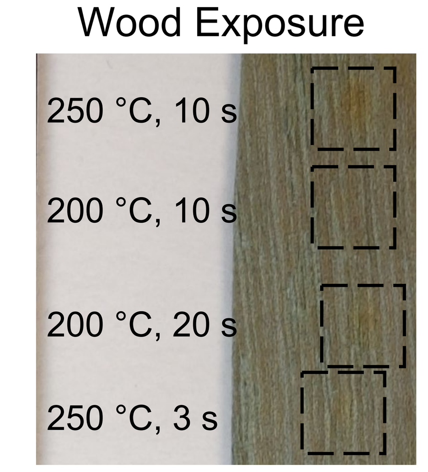




- 150 °C gas probe trained on thermal paper coupon, imaging impact area and desorbing analyte for transfer to DART
- Maximizing impact area does not guarantee high MS signal if transfer tube cannot collect desorbed analyte efficiently
- Impact area reduced by: lower N_2 outflow rate, higher transfer tube inflow rate, moving gas probe closer to surface
- Minimum transfer tube inflow rate (set by supplemental IT vacuum status also increases signal by extending mixing time with DART reagent flow, makes it easier to maintain transfer tube temperature
- 12 mm² impact area from 5 s exposure yields best overall signal, produced by: 0.2 L/min nitrogen flow probe, positioned 3.0 mm away from inlet angled 45° to normal, 2.0 mm above the sample surface, with a 1.2 L/min transfer tube inflow

Conclusions and Future Work with Wood Samples and Sculptures

- The desorbing nitrogen gas outflow rate from the probe must be paired to transfer tube inflow rate to optimize collection of gaseous analyte for transfer to MS-proximate DART
- Not all analytes are desorbed with equal efficiency by one set of sampling conditions
- Indigo-dyed splints (right) demonstrate qualitative wood analysis without visible damage
- Future applications to museum collections include identifying indigo dye on large Native American baskets and fingerprinting wood species [4] used to carve African sculptures
- The non-proximate sampling system has implications for future fieldable and portable MS systems, which would similarly be used around large and irregularly shaped objects
- For a Zoom meeting with authors, email newsomeg@si.edu



References and Acknowledgements

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