

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

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Mass spectrometry (MS) identifies the molecular formula of an analyte but typically requires physically sectioning objects and consuming sample material by dissolution or pyrolysis, resulting in irreparable damage. Ambient MS ion sources can sample from an intact object at atmospheric pressure, but they require the analyte to be close to a MS inlet and therefore cannot accommodate objects significantly larger than a microscope slide. Larger objects must be positioned farther away, but signal from ions generated at the analyte surface decreases dramatically with the length of the transport to the MS inlet. To avoid such loss, neutral molecules should be transported instead of ions.

To thermally desorb neutral analyte molecules, we supplied nitrogen at up to 200 °C from a custom-built probe angled at 45° and mounted from overhead. An Arduino-operated shutter was positioned between the neutral gas probe and a lower sampling area to control the exposure time for a sample surface. Desorbed molecules were collected with a 150 °C, SilcoNert-coated stainless steel sample line connected to a differentially-pumped inlet on a LTQ Orbitrap Velos mass spectrometer (Thermo Fisher). A custom-mounted IonSense DART 100 source operated by an SVP controller was sealed orthogonally to a tee with the transfer line and inlet.

The dimensions of the impact area on a sample surface exposed to heated nitrogen from the non-proximate flow probe were characterized using thermal paper, optimizing a variety of factors to maximize mass spectral abundance. Wooden blocks and test splints that were uncolored or vat-dyed with indigo were exposed to heated flow from the non-proximate probe for different times and temperatures, determining upper limits to prevent discoloration. Optimized sampling parameters were checked by analyzing indigo-dyed splints and examining impact areas for visual or microscopic damage. A colored cloth bookmark, representative of larger samples planned for future analyses, was mounted below the nitrogen probe to identify indigo on particular areas.