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Nanometer-Scale Proximal Probe Thermal Desorption Coupled with Laser Mass Spectrometry

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The analysis of cultural heritage materials presents a number of obstacles which impose limitations on the range of analytical techniques that can be utilized in their analysis: limited, and extremely small samples, complexity of sample structure, the importance of maintaining spatial integrity and, most importantly, the preciousness of the samples. These limitations present particular challenges for the identification of dyes and pigments within microscopic painting cross sections, in which complex mixtures and thin (often only a few microns) layers of organic material are common.

Discerning organic compounds with high spatial resolution may help clarify aspects of cultural histories, and may assist in the conservation of works of art since these organic molecules are often prone to degradation due to moisture, light or other environmental conditions. A variety of spatially resolved analytical techniques for identification of elemental composition (e.g. SEM-EDS and micro-XRF) are well established and extensively used in cultural heritage science, but are not molecularly specific[1]. Molecular analysis such as SERS is well suited for the identification of organic molecules, but is often limited by relatively large spatial resolution (~25 μm for SERS), and sometimes struggle to identify spectroscopically similar molecules[2]. Therefore, there remains a need for the development of complementary techniques that can provide spatially resolved, molecularly-specific, and unambiguous identification of cultural heritage materials.

Recently, Berkel et al. reported sub-micrometer scale atomic force microscopy (AFM) proximal probe thermal desorption (Anasys Instruments) of organic molecules, and subsequent detection via electrospray ionization MS[3]. Here we describe a new approach that extends this combination by decoupling the AFM thermal desorption (TD) step from the MS step. Our MS scheme combines jet-cooled, vibronic laser spectroscopy through resonant-enhanced-multi-photon-ionization coupled with mass spectrometry (REMPI-MS). The inherent optical resolution in low temperature laser spectroscopy can often be much higher than the mass resolution in a typical mass spectrometer[4]. We also employed a non-resonant laser ionization (LDMS) method to demonstrate the flexibility created by decoupling TD and MS.

This three step process is achieved by: (1) Use of an AFM mounted microscope to identify target features, followed by proximal probe TD on selected locations and transfer of desorbed material to a sample bar through a heated capillary. (2) Physical transfer of the sample bar to the laser mass spectrometer for laser desorption of molecules, followed by jet cooling of the desorbed molecules, (3) ionization and detection, which is accomplished via REMPI-MS or non-resonant laser MS. Spatial resolution of the TD craters, as measured using topographical images of all examined samples range from 500-1500nm, a significant improvement compared to current methods.

Initial experimentation used a thin film of caffeine on a silica wafer as an analyte. TD was used to evenly distribute analyte in four separate spots on the sample bar, which was then utilized for REMPI-MS. The parent peak of caffeine appears at m/z 194, seen in Figure 1, indicating a successful transfer of the material onto the sample bar following TD without thermal degradation.

To illustrate the diversity of experiments that can be performed on the desorbed material, an additional set of experiments was done using LDMS. Both traditional (alizarin crimson) and 'modern synthetic' (PV19 and PO43) organic dyes with significance in cultural heritage were chosen to construct microscopic cross sections representative of samples taken from works of art.

A microscopic image alizarin dye cross section, and the mass spectrum of alizarin samples can be seen in Figure 2 (parent peak m/z 240). Other species were also observed, indicative of the complex nature of these natural organic dyes. Additional experiments suggest most fragmentation occurs in the TD step. The mass spectra seen in Figure 3 were produced from a layered sample of PV19/PO43, shows the PV19 parent peak at m/z 312 and the PO43 parent peak at m/z 412, respectively.

The decoupling of the TD and MS steps allows for unparalleled flexibility in choosing appropriate analysis methods for each particular sample. The result is a powerful approach to identifying organic molecules with high spatial resolution coupled with unprecedented precision and sensitivity. This approach is extendable to other fields of research as well [5].

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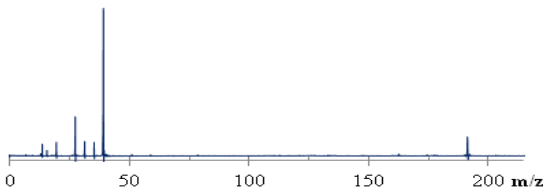

Figure 1: REMPI mass spectrum of caffeine sample

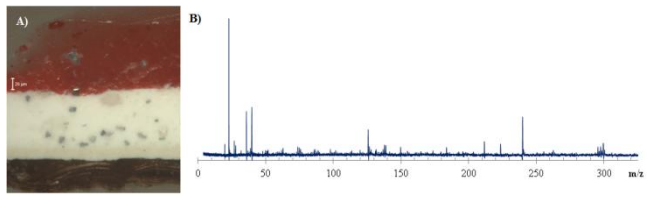

Figure 2: A) Microscopic image of alizarin crimson dark dye B) Mass spectrum of alizarin sample

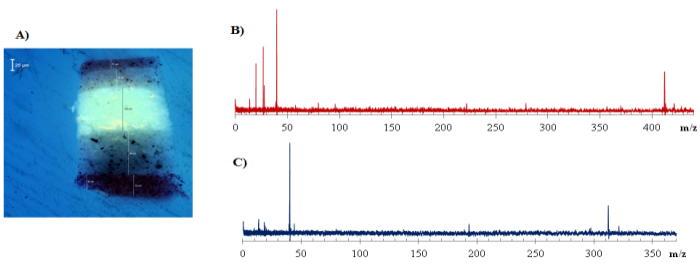

Figure 3: A) The lower two layers contain the dyes relevant to this experiment, PV19(lower) and PO43(upper). Mass spectra of B) PO43 and C) PV19.

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