Application of laser mass spectrometry to art and archaeology

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Abstract:

REMPI laser mass spectrometry is a combination of resonance enhanced multiphoton ionization spectroscopy and time of flight mass spectrometry. This technique enables the collection of mass specific optical spectra as well as of optically selected mass spectra. Analytes are jet-cooled by entrainment in a molecular beam, and this low temperature gas phase analysis has the benefit of excellent vibronic resolution. Utilizing this method, mass spectrometric analysis of historically relevant samples can be simplified and improved: Optical selection of targets eliminates the need for chromatography while knowledge of a target’s gas phase spectroscopy allows for facile differentiation of molecules that are in the aqueous phase considered spectroscopically indistinguishable. These two factors allow smaller sample sizes than commercial MS instruments, which in turn will require less damage to objects of antiquity. We have explored methods to optimize REMPI laser mass spectrometry as an analytical tool to archaeology using theobromine and caffeine as molecular markers in Mesoamerican pottery, and are expanding this approach to the field of art to examine laccic acid in shellacs.
Application of REMPI Laser Mass Spectrometry to Art and Archaeology

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Abstract

REMPI laser mass spectrometry is a combination of resonance enhanced multi-photon ionization spectroscopy and time of flight mass spectrometry. This technique enables the collection of mass specific optical spectra as well as of optically selected mass spectra. Analyzes are jet-cooled by entrainment in a molecular beam, and this low temperature gas phase analysis has the benefit of excellent vibronic resolution. Utilizing this method, mass spectrometric analysis of historical relevant samples can be simplified and improved: Optical selection of targets eliminates the need for chromatography while knowledge of a target's gas phase spectroscopy allows for facile differentiation of molecules that are indistinguishable in the aqueous phase considered spectroscopically indistinguishable. These two factors allow smaller sample sizes than commercial MS instruments, which in turn will require less damage to objects of antiquity. We have explored methods to optimize REMPI mass spectrometry as an analytical tool to archaeology using theobromine and caffeine as molecular markers in Mesoamerican pottery, and are expanding this approach to the field of art to examine local acids in shells.

Why REMPI laser mass spectrometry?

- Eliminates the need for traditional chromatography methods. Utilization of resonant excitation allows for facile isolation of target molecules within mixtures.
- Vibronically resolved gas phase spectroscopy offers clear differentiation of molecules that are considered spectroscopically indistinguishable by liquid phase techniques, such as the phenolic acids commonly used as archaeological markers.
- Samples can often be non-'as is' without extensive preparation in the form of extractions, etc. Therefore, less sample is necessary for analysis.
- Reducing the amount of sample required for analysis ultimately will result in less destruction caused to singular objects of antiquity in the name of analysis.

Method Development

- Graphite was used as a highly sensitive desorption substrate at 2864nm desorption laser wavelength; signal was observed off 200ng theobromine, but was prone to background contamination despite isolating the sample on-disc.
- Gold produced a clean background when used as substrate but decreased sensitivity at 1064nm. When the desorption wavelength was changed to 2864nm sensitivity improved and modifications to the substrate surface were pursued to keep isolate and consolidate sample. 100ng of theobromine were observed from the shallow-welled bar indicated at left, but deposition onto the bimetallic surface led to uneven distribution of material onto edges.
- Additional molecular markers of interest to art and archaeology are to be identified. Mapping their spectroscopy will allow them to be added to the REMPI laser-MS canon.
- Preliminary work has begun examining Laccaic Acid, a pigment historically created from Coccaidae insects, that was used in shellac².

Initial Study: theobromine in cacao beverages

- In present day Honduras, McGovern et al. uncovered ceramic pots believed to have contained the earliest known Mesoamerican cacao beverages. GC and LC-MS were used to verify the pots held the cacao beverage by testing for cacao molecular markers theobromine and caffeine.
- Callahan et al. have extensively mapped the spectroscopy of Xanthine and its methyl derivatives, including both di-methylated theobromine and tri-methylated caffeine² (see bottom of column).
- Using theobromine's resonant ionization wavelength, the REMPI-MS of a raw cacao bean extract is shown to be fragment-free, as compared to the congested ESI/TOF-MS of a simple aequous theobromine and caffeine solution, as seen below:

Future Work

Repeat experiments utilizing enhanced sensitivity of 2-color REMPI:
- Setting second REMPI photon to slightly lower energy than the first sharpens spectra and enhances signal
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- Preliminary work has begun examining Laccaic Acid, a pigment historically created from Coelidae insects, that was used in shellac².