Application of laser mass spectrometry to art and archaeology

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Abstract:

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Application of REMPI Laser Mass Spectrometry to Art and Archaeology

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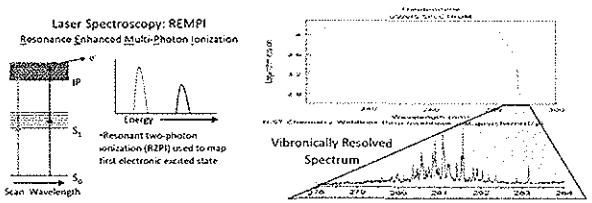
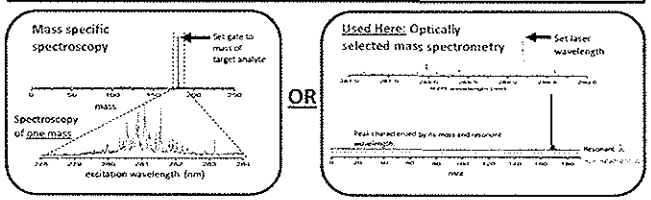
Abstract

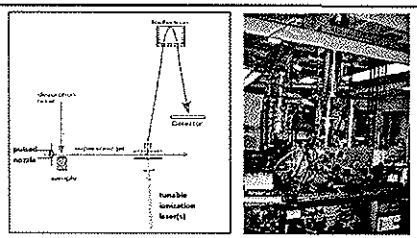
REMPI laser mass spectrometry is a combination of resonance enhanced multi-photon ionization spectroscopy and time of flight mass spectrometry. This technique enables the collection of mass specific optical spectra as well as of optically selected mass spectra. Analytes are jet-cooled by entrainment 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 laccaic acid in shellacs.



Methods[1]



Instrumental Set-up



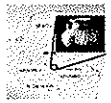
References:

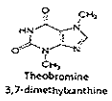
1. Meijer, de Vries, Hunziker, Wendt, REMPI Spectroscopy of Jet-Cooled Guanine, *Appl. Phys. B*, 1990, 51, 395-403.
2. Callahan, Gengeliczki, and de Vries, Resonant two-photon ionization mass spectrometry of phenolic acids and polyphenols. *Analytical Chemistry* 2008, 80, 2199-2033.
3. Henderson, Joyce, Hall, Hurst and McGovern. Chemical and archaeological evidence for the earliest cacao beverages. *PNAS*, 2007, *104*, 18937-18940.
4. Callahan, Gengeliczki, Svadlenak, Valdes, Hobza, and de Vries. Non-standard base pairing and stacked structures in methyl xanthine clusters. *PCCP*, 2008, *10*, 2819
5. Schmidt and Trentelman. 1064 nm Dispersive raman Micro-spectroscopy for the in-situ identification of organic red colorants. *e-PS* 2009, *6*, 10-21.

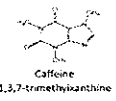
Why REMPI laser mass spectrometry?

- Eliminates the need for traditional chromatography methods. Utilization of resonant ionization 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 wine markers[2].
- Samples can often be run "as are" 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.

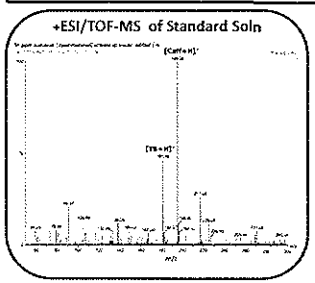
Initial Study: theobromine in cacao beverages



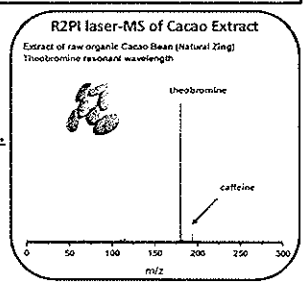


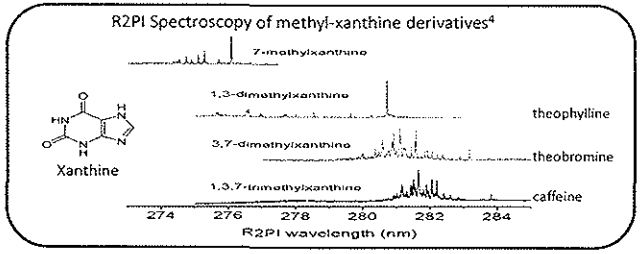


- In present day Honduras, McGovern et. al. uncovered ceramic pots believed to have contained the earliest known Mesoamerican cacao beverages. GC- and LC-MS were used to verify the pottery held the cacao beverage by testing for cacao molecular markers theobromine and caffeine[3].
- Callahan et. al. have extensively mapped the spectroscopy of Xanthine and its methyl derivatives, including both di-methylated theobromine and tri-methylated caffeine[4] (see bottom of column).
- Using theobromine's resonant ionization wavelength, the R2PI laser-MS of a raw cacao bean extract is shown to be fragment-free, as compared to the congested +ESI/TOF-MS of a simple aqueous theobromine and caffeine solution, as seen below:

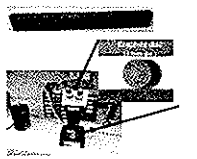


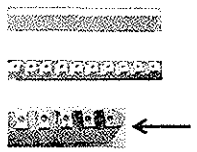
VS.

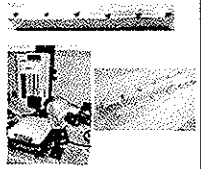




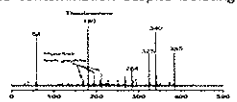
Method Development







- Graphite was used as a highly sensitive desorption substrate at 1064nm desorption laser wavelength; signal was observed off 200pg theobromine, but was prone to background contamination despite isolating the sample on discs.

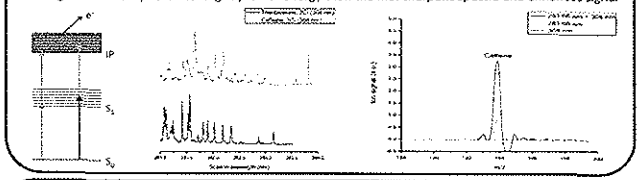


- Gold produced a clean background when used as substrate but decreased sensitivity at 1064nm. When the desorption wavelength was changed to 266nm sensitivity improved and modifications to the substrate surface were pursued to best isolate and consolidate sample. 100ng of theobromine were observed from the shallow-welled bar indicated at left, but deposition onto the basin-shaped surface led to uneven distribution of material onto edges:

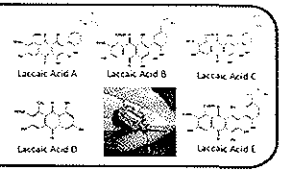
- Removable and disposable pegs were made out of stainless steel in 1.0 and 1.5mm diameters. Desorption at 266nm gave clean background. A motorized syringe pump was modified to automate and improve uniformity of sample deposition. The 1.5mm pegs were sensitive to 200ng of theobromine, while signal was observed from only 10ng off the 1.0mm peg due to consolidating all sample material within the diameter of the desorption laser spot. Pegs made out of carbon steel, Iconel (Ni/Cr alloy), and a silicon-bronze alloy gave similar results.

Future Work

Repeat experiments utilizing enhanced sensitivity of 2-color R2PI:
Setting second R2PI photon to slightly lower energy than the first sharpens spectra and enhances signal



- 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 *Coccoidea* insects, that was used in shellacs[5].



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