Picosecond IR MALDI Mass Spectrometry of Organic Molecules on Nitrate Crystallites

Michael R. Papantonakis[1], David R. Ermer[2], Richard F. Haglund,Jr.[1]

[1]Department of Physics and Astronomy and W. M. Keck Foundation Free-Electron Laser Center, Vanderbilt University

[2]Department of Physics and Astronomy, Mississippi State University

INTRODUCTION

A critical problem in environmental science and engineering is tracking organic molecules and metal complexes in soils and other poorly characterized systems. We have extended the technique of MALDI mass spectrometry (MS) (see below), largely the province of biomolecular characterization, to analyze a complex system by directly exciting a vibrational resonance of the matrix, bypassing the need for adding an exogenous matrix. MALDI is an attractive protocol because it requires small sample sizes, provides rapid analysis, and minimal sample preparation compared to other techniques. Our focus has been on a simulant of the mixed hazardous tank waste (TW) resulting from nuclear fuel processing, and we have shown that we can identify and quantify the compounds of interest from a mixed sample.

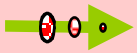
One challenge is to improve the protocol for characterizing the organic fraction of the tanks. The organic chelators, originally added to the tanks to form complexes with heavy metals, pose a combustion risk with oxidizers as the environment inside the tanks changes. A means of rapidly describing the abundances of the various organics present would improve the risk assessment necessary prior to waste treatment or relocation. We have demonstrated in principle that IR MALDI mass spectrometry can provide this necessary characterization.

MALDI TOF MS

A laser initiates desorption/ablation, producing a cloud of ions and neutrals...

The matrix isolates target molecules, absorbs laser light, and assists in ion formation

...the ions are accelerated by an applied field and then separated by charge-to-mass ratio through time-of-flight (TOF) ¨ t ~ $(m/z)^{1/2}$



Matrix
Assisted
Laser
Desorption
Ionization

Ion yield is proportional to specific energy deposition:

(E/V)~F¥a(w,I)

while the ionization rate is proportional to the k-photon cross section and intensity:

(dN/dt)~hN(t)Æ$_{(k)}$I^k

There is still no consensus about the mechanism of charge transfer in MALDI. Possibilities include collisional, photo-thermal, and photo-mechanical processes.

REFERENCES AND ACKNOWLEDGMENTS

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2. DR Ermer, MR Papantonakis, M Baltz-Knorr, RF Haglund, Jr. *Proc. SPIE-Int. Soc. Opt. Eng.* **3935**, 104 (2000).

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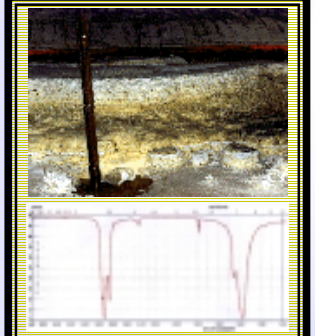
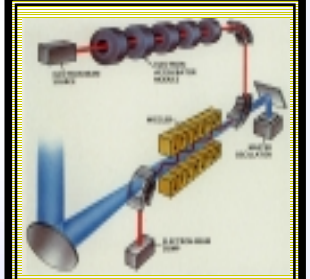
MATERIALS AND METHODS

A tunable, picosecond, free-electron laser was tuned to resonant vibrational modes of the systems studied. For nitrate studies, the wavelength used, 7.1 m, overla ps a group of six overlapping nitrate stretching modes. This is tantamount to using $NaNO_3$, the primary component of the saltcakes found in waste tanks (*see below*), as a matrix in a conventional IR-MALDI procedure. In addition to using tunable laser light, we also employ a free-electron laser with a novel temporal pulse structure incorporating a train of ps-duration pulses. The TW simulant, largely $NaNO_3$ and carboxylic chelating compounds, was based upon recipes found in the literature.[1]

Samples were prepared by drying an aqueous mixture of $NaNO_3$ and TW compounds under a stream of warm air. Mass spectra were acquired in a reflectron TOF MS (with a flight path of approximately 2 m) by applying a 5 kV delayed extraction acceleration pulse.



Top: A view of the saltcake capping the mixed hazardous waste tanks found at the Hanford Defense Site. Several of the 177 tanks, which can each hold one million gallons of waste, are leaking or in danger of exploding. *Bottom:* FTIR spectrum of $NaNO_3$.



Vanderbilt FEL parameters

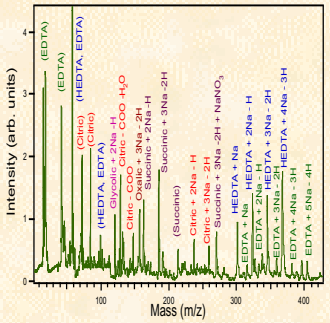
Tuning range: 2-10 m
Macropulse energy: 30-150 mJ
Micropulse energy: 3-15 J
Structure: 5 s train of 2.8 GHz, ps pulses

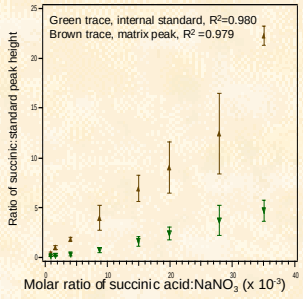
¨ We use a 100 ns slice of the pulse train for the TW simulant studies.

CONCLUSIONS

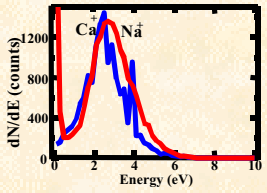
The ability to characterize and track molecular contaminants through the environment by mass spectrometry without adding exogenous matrix materials is highly desirable. Our work shows that in this case, it is possible to identify and quantitate organic components of simulated tank waste by tuning infrared light into resonant vibrational modes to desorb and ionize intact molecular species. Thus this variant on traditional IR-MALDI is an attractive tool for qualitative and quantitative analyses. Our studies with picosecond irradiation show the process to be intensity rather than fluence dependent, with desorption possibly initiated by electrostatic repulsion following rearrangement of local charge concentrations by vibrational excitation on fast time scales.[2] Vibrational-mode selectivity appears to be an important element in the formation of positive ions.

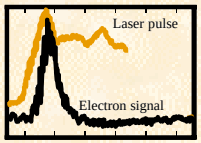
RESULTS



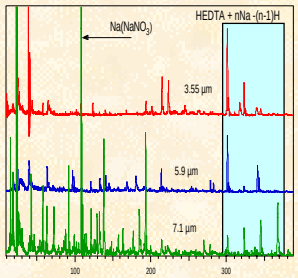


Speciation and calibration: Two needs for waste characterization are the ability to identify and to quantify the total organic content of the waste tanks. ***Above left*** is an equimolar spectrum of 5 chelators and their degradation products. Each additive is recognized, although at different intensities, and all major peaks of the spectrum are labeled. The $NaNO_3$ peaks have been erased. ***Above right*** is a calibration plot of succinic acid, a TW degradation product, in $NaNO_3$. We have found that both $NaNO_3$ peaks and internal standards can be used for calibration.





These graphs show ion energies from laser induced ion emission (λ=3.5 µm). The ***top figure*** shows ions from $NaNO_3$ and $CaCO_3$, while the ***bottom figure*** shows electron emission from a 2,5-DHB pellet as a function of laser intensity. Surprisingly, cation energies are up to 8 times the photon energy. The energy distribution is non-thermal and suggests a non-linear, intensity dependent process.



TW simulant samples were irradiated at 3.55 (overtone) and 5.9 µm (residual water). These wavelengths produced less consistent spectra than at 7.1 µm, yielded different matrix patterns, diminished degree of alkali attachment, and decreased ion production. While these results are distinctive, the specific relationship between ion production and mode selectivity requires further study.