
Mass Spectrometric Fingerprinting of Tank Waste Using Tunable, Ultrafast Infrared Lasers

Project ID: 65425

Dr. Richard F. Haglund, Jr., Vanderbilt University

Dr. Wayne P. Hess, Pacific Northwest National Laboratory

Executive Summary

During the past year, we have initiated systematic studies of mass spectrometry of model tank-waste materials using both conventional nanosecond, single-frequency and tunable, subpicosecond mid-infrared lasers. In addition to making initial measurements, we have also constructed several new items of equipment for the experiment and begun to develop a model of the processes which lead to efficient desorption and ionization of organic molecules (*e.g.*, toluene, benzene, crown ethers) from sodium nitrate. Comparisons of nanosecond and picosecond lasers, and of infrared and ultraviolet lasers, have been especially instructive. These accomplishments are detailed in the following paragraphs.

Key experimental results. The main thrust of our effort is understanding the mechanisms of matrix-assisted laser desorption and ionization (MALDI) using NaNO_3 itself as the matrix. Most of the experiments involve using a tunable infrared free-electron laser to create ions by tuning into resonant vibrational bands of the matrix materials. The motivation for doing this is fundamentally to avoid having to dilute tank-waste materials with some other matrix material, thus generating a potential secondary waste stream. We have concentrated our experimental efforts on three particular aspects of the problem we set ourselves in the proposal:

- Demonstrating that we can detect desorbing organic molecular ions from NaNO_3 crystals and powders using tunable, infrared light from a free-electron laser;
- Comparative studies of ultraviolet and infrared MALDI, including studies in which exogenous matrix materials are added to the NaNO_3 .
- Developing a physical model of the processes of desorption and ionization which can be used both to underpin quantitation and to give insight into the MALDI mechanism.

Our experiments and model-building in these three areas have confirmed the following results:

First, we can indeed detect molecular ions desorbed from NaNO_3 with high sensitivity, and there is a linear regime within which one could hope to obtain relatively accurate quantitation. While we are presently only in the low ppm range in terms of sensitivity, we are aware of a number of things we can and will do to enhance the sensitivity by several orders of magnitude. It may be of particular interest that we find the crown ethers, upon desorption, also can abstract and carry away an attached Na atom which shows up very clearly in the time-of-flight spectrum.

Second, particularly efficient ion production is obtained if one irradiates doped NaNO_3 at 248 nm after adding an appropriate ultraviolet MALDI matrix material (*e.g.*, dihydroxybenzoic acid). On the contrary, however, the addition of infrared MALDI matrices (*e.g.*, succinic acid or 4-hydroxy- α -cyano-cinnamic acid) to the NaNO_3 does not materially affect the ion yield, even though the added matrix materials have significant absorption at the 7.1 μm wavelength used to excite the NO_3 stretching vibration. We believe the difference between uv-MALDI and ir-MALDI in this respect may result from the comparatively greater efficiency for generating photoelectrons in the ultraviolet.

Third, the “phase explosion” model proposed by a number of researchers seems to describe our results quite nicely – but one should note that this is the first time there has been any experimental evidence for this in the infrared.

The fundamental picture of the phase explosion is this: If the optical absorption depth of the material is short compared to the characteristic thermal diffusion length, it is possible to create very high volumetric density of vibrational excitation at high intensity, because of the strong thermal confinement. Indeed, in experiments on CaCO_3 , the isoelectronic cousin to NaNO_3 , we have shown that the free-electron-laser pulses deposit two vibrational quanta in every CO_3 group in the optical absorption depth. Under these circumstances, the irradiated material reaches the critical temperature T_c for explosive vaporization before the deposited thermal energy has time to equilibrate, leading to the so-called “phase explosion.” This should be especially productive of highly energetic ions and neutrals, and gives extremely efficient material removal from surfaces.

Development of laboratory apparatus. In our proposal, we stated our intent to construct a novel miniature time-of-flight mass spectrometer which would also be suitable for post-ionization studies of neutral atoms and molecules emitted during laser-induced desorption. This apparatus has now been constructed and will be commissioned in the laboratory during the summer of 1999. It is expected to provide much of the data needed to test our conjecture about the mechanism of desorption and ionization in the infrared, in particular, the “phase explosion” hypothesis described above.

Training of graduate students. During this past year, we have had two students who have participated actively in the MALDI studies: Michael Papantonakis and Michelle Baltz-Knorr. Mr. Papantonakis is approximately a year and a half away from completing his dissertation; he is spending the summer this year working with Drs. Michael Alexander and Wayne Hess in the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory. His focus is on problems of quantitation associated with tank waste and the potential for the use of compact ion-trap mass spectrometers with MALDI ion sources. Ms. Baltz-Knorr is just at the beginning of her dissertation program, but has become increasingly skilled in experiments and will continue actively working on the program during the coming year.

Publications and conference contributions A number of conference contributions and publications have been or will be prepared and presented as a result of this year’s work. These include the following:

1. Plenary lecture, “The Future of Tunable, Ultrafast Lasers in Materials Analysis and Processing,” R. F. Haglund, Jr., American Society for Mass Spectrometry, Dallas, TX, June 1999.
2. Invited talk, “The Role of Vibrational Excitation in Desorption and Ionization from Molecular Solids,” Conference on Laser Ablation (COLA’99), Goettingen, Germany, July 1999.

Contributed papers will be presented in sessions dedicated to the scientific basis of nuclear waste analysis and management at the American Chemical Society meeting (New Orleans, August 1999), and Fall Meeting of the Materials Research Society (Boston, December 1999). Papers on MALDI studies of organic molecules on sodium nitrate have been or are in the process of being submitted to *Chemical Physics Letters*, *Thin Solid Films* and *Applied Surface Science*.