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Compact two-step laser time-of-flight mass spectrometer for *in situ* analyses of aromatic organics on planetary missions

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RATIONALE: A miniature time-of-flight mass spectrometer measuring 20 cm in length has been adapted to demonstrate two-step laser desorption/ionization (LDI) in a compact instrument package for enhanced organics detection. Two-step LDI decouples the desorption and ionization processes, relative to traditional LDI, in order to produce low-fragmentation mass spectra of organic analytes. Tuning the UV ionization laser energy would allow control of the degree of fragmentation, which might enable better identification of constituent species.

METHODS: A reflectron time-of-flight mass spectrometer prototype was modified to allow a two-laser configuration, with IR (1064 nm) desorption followed by UV (266 nm) postionization. A relatively low ion extraction voltage of 5 kV was applied at the sample inlet.

RESULTS: The instrument capabilities and performance were demonstrated with analysis of a model polycyclic aromatic hydrocarbon, representing a class of compounds important to the fields of Earth and planetary science. Two-step laser mass spectrometry (L2MS) analysis of a model PAH, pyrene, was demonstrated, including molecular ion identification and the onset of tunable fragmentation as a function of ionizing laser energy. Mass resolution $m/\Delta m = 380$ at full width at half-maximum was achieved for gas-phase postionization of desorbed neutrals in this highly compact mass analyzer.

CONCLUSIONS: Achieving L2MS in a highly miniaturized instrument enables a powerful approach to the detection and characterization of aromatic organics in remote terrestrial and planetary applications. Tunable detection of molecular and fragment ions with high mass resolution, diagnostic of molecular structure, is possible on such a compact L2MS instrument. The selectivity of L2MS against low-mass inorganic salt interferences is a key advantage when working with unprocessed, natural samples, and a mechanism for the observed selectivity is proposed. Copyright © 2012 John Wiley & Sons, Ltd.

Compact mass spectrometers are of considerable interest for applications in national security, forensics, the search for natural resources, the detection and quantification of pollution on Earth, and for *in situ* chemical analysis on planetary missions. Polycyclic aromatic hydrocarbons (PAHs) are an important class of compounds for such applications. PAHs are found naturally on Earth, for example in crude oil and coal beneath the surface, and are also produced in the combustion of these fuels and other materials, contributing to pollution of soil, air, and water. Similar compounds are found in extraterrestrial materials that have been delivered to the Earth's surface, such as meteorites and returned cometary particles from the Stardust mission,^[1–7] and a diverse population of PAHs has been detected or hypothesized to occur in diverse planetary environments. Two-step laser desorption/ionization mass spectrometry (L2MS) has been shown to be a valuable technique for selectively probing the aromatic composition of solid materials, both terrestrial

and extraterrestrial, using laboratory-scale instrumentation on Earth.^[1–11] Here we demonstrate that L2MS can be adapted to a highly miniature instrument that could find use for *in situ* measurements on Earth and landed space-flight missions to planetary bodies.

In the simplest configuration, a compact laser desorption/ionization time-of-flight (LDTOF) mass spectrometer uses a single laser wavelength to desorb and ionize analytes from a solid sample. For mineralogical samples and simple organic mixtures, using a time-of-flight analyzer with this technique has been shown to be highly effective in determining sample composition.^[12–15] The spectral identification of specific organics in a complex sample presents challenges, however, due to mass interferences between molecular ions from parent molecules and common fragment ions, limited detector dynamic range, and degradation of the time-of-flight spectrum owing to the strong desorption/ionization efficiency of some dominant inorganic elements with low ionization energies. The specificity offered by the two-step laser ionization technique has been shown to be particularly effective at targeting the aromatic component of a more complex mixture, and this selectivity offers a route to differentiating between classes of organic in diverse samples.

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It has been shown that L2MS leads to a reduction in the laser pulse energy required for target analytes such as aromatic hydrocarbons, compared with single-laser LD-TOFMS. When using a single laser pulse for both desorption and ionization, an excess of energy is often needed to accomplish both functions, which can lead to extensive fragmentation. Therefore, a particular advantage of the L2MS technique is the independent optimization of the infrared (IR) and ultraviolet (UV) laser pulses for resolving the organic composition of complex samples with minimal fragmentation.

At the core of the L2MS technique are the time-resolved desorption and ionization steps that are independently tunable through the use of delay-separated laser pulses. Previous work has demonstrated that both IR^[8] and UV^[11,16,17] wavelengths can be used in the desorption step to generate a plume of neutral species above the sample surface. The ionization step is selective to certain classes of analyte based on ionization energy, and a UV or VUV ionization wavelength can be selected to introduce a degree of specificity, such as for aromatics.

Here, we describe the demonstration of two-step laser desorption/ionization mass spectrometry in a miniature (20 cm long \times 5 cm diameter), low-voltage (<5 kV) instrument. The goal of miniaturization efforts is a highly capable analytical instrument that can fit within the constrained resource envelope of a future landed mission to a planetary body for regolith or surface analysis. To motivate the development of a dedicated miniature L2MS instrument, we have adapted an existing miniature time-of-flight mass spectrometer to demonstrate two-step operation. The objectives of this work include (1) demonstrating feasibility with ionization occurring within a sample-inlet gap of only a few millimeters in the existing instrument; (2) investigating performance parameters, such as mass resolution, in a miniature instrument; and (3) conducting proof-of-concept measurements using an organic standard, pyrene.

EXPERIMENTAL

The existing LD-TOFMS prototype shown in Fig. 1 employs a cylindrical, curved-field reflectron that has been described fully elsewhere.^[18] The instrument measures approximately

20 cm in length and 5 cm in diameter. It features an asymmetric Einzel lens for ion extraction and focusing, an annular microchannel plate detector (MCP, Hamamatsu; Hamamatsu City, Japan), and a rolled circuit board reflectron. It is housed within a high-vacuum chamber with assorted view ports to allow IR laser transmission down the instrument bore and UV laser transmission parallel to the sample plane. Including the sample probe, the voltage on each element can be tuned for optimal ion transmission and focus. The MCP anode signal is resolved by a digital oscilloscope (LeCroy WaveRunner MXi-A; Chestnut Ridge, NY, USA) and recorded on a PC using a custom LabVIEW (National Instruments, Austin, TX, USA) interface.

For the desorption step of L2MS, the fundamental frequency of a Nd:YAG laser at 1064 nm (Laser 1) was focused at normal incidence on the sample surface to produce a neutral plume from a 275- μ m diameter spot. The pulse width is typically 4–7 ns, and the pulse energy is typically in the range 75–190 μ J. Desorption laser intensities therefore range between 18 and 81 MW/cm². The ionization laser, a frequency-quadrupled Nd:YAG operating at 266 nm (Laser 2), is directed orthogonally to Laser 1, and its focal point is aligned with the inlet of the mass analyzer, as shown in the inset of Fig. 1. A typical UV beam waist diameter is 100 μ m at the intersection with the desorption plume, and the laser energy ranges from 40 to 140 μ J, producing intensities ranging from 77 to 450 MW/cm². The sample is mounted onto a linear motion feedthrough, and the distance of the sample from the instrument inlet and the intersection of the Laser 2 pulse can be easily adjusted. The delay between laser pulses was precisely controlled with a delay generator (DG645; Stanford Research Systems, Sunnyvale, CA, USA) coupled to the external Q-switch triggers of each laser.

In addition to the postionization delay, both laser energies are tuned during the experiment. Operationally, the IR laser is first set to just below the prompt ionization threshold, in the absence of a Laser 2 ionization pulse. To obtain a two-step laser mass spectrum, the delay is then set at an average starting value, typically 1 μ s, and the UV laser energy is increased until a postionization mass spectrum is observed and recorded. The delay is tuned during each experiment to maximize the ion intensity of the species of interest at

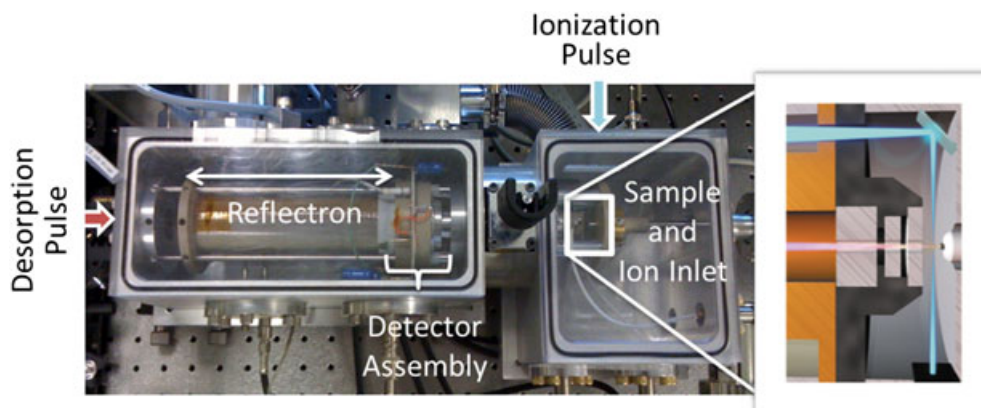


Figure 1. The L2MS experimental hardware employs a high-vacuum chamber that houses the time-of-flight analyzer. The desorption laser pulse passes through a quartz viewport, to transmit down the bore of the analyzer to the sample surface. After a delay, the ionization laser pulse passes through a side view port to intersect the desorbed plume. The sample is held on a linear motion feedthrough to adjust the position with respect to the instrument inlet.

the detector (discussed further below), to account for small changes in geometry and position between samples. Delays ranged between 0.3 and 2 μ s.

Sample preparation

Samples are mounted on the end of a 6 mm diameter cylindrical stainless steel probe. Liquid samples, including slurry suspensions of powder, are deposited from solution or suspension directly onto the probe surface using an Eppendorf pipette and subsequently dried prior to introduction into the vacuum chamber. The sample volume used is typically 2–3 μ L.

Pyrene, a model polycyclic aromatic hydrocarbon (PAH), was selected to demonstrate and characterize the L2MS technique in the miniature instrument described above. The pyrene standard (98% pure) was purchased in powder form from Sigma-Aldrich (St. Louis, MO, USA) and dissolved in dichloromethane at a concentration of 1000 ppm. The source solution was stored in a freezer when not in use.

RESULTS

The experiments reported here focused on measurements needed for our three objectives: feasibility, performance, and proof-of-concept.

Successful L2MS measurements have been conducted for pyrene, a model PAH with a molecular ion of m/z 202. Figure 2 shows the evolution of the mass spectrum under various laser energy conditions. Each spectrum is a raw average of 10 individual laser shots. The IR and UV lasers exhibit energy thresholds for desorption and ionization, respectively. Below the IR threshold (Fig. 2(a)) and below the UV threshold (Fig. 2(b)), a negligible ion signal is detected. At UV laser energies just above the ionization threshold, the molecular ion is clearly dominant in the spectrum at m/z 202 (Fig. 2(c)). At UV energies further above the ionization threshold, fragment ions start to become apparent (Fig. 2(d)), and at high UV laser energy, low-mass peaks dominate the spectrum (Fig. 2(e)), indicating nearly complete fragmentation of the molecular ion.

A single-laser shot spectrum is shown in Fig. 3 for a narrow mass range bracketing the molecular ion of pyrene at m/z 202. To determine the mass resolution shown by this spectrum, the peaks in Fig. 4 were fitted to a Gaussian form (using multiple peak fit in Origin 8.1; OriginLab Corporation, Northampton, MA, USA). The full-width at half-maximum was calculated for the m/z 202 peak, and $m/\Delta m$ was found to be \sim 380 at this mass.

An interesting feature of the L2MS technique is the insensitivity to salts, compared with direct LDMS. None of the L2MS spectra in Fig. 2 show evidence for the presence of Na^+ (m/z 23) or K^+ (m/z 39 and 41) ions. These sodium and potassium salt species, ubiquitous in natural samples as well as laboratory standard solutions, are easily ionized and consistently seen in single-laser LDMS. Using identical sample preparation methods to the L2MS study described above, a single 355 nm laser pulse was used to produce one-step desorption and ionization of pyrene. In contrast to the L2MS findings, the single-laser desorption/ionization spectrum shown in Fig. 4 is dominated by low-mass Na^+ and K^+ salt ions. In addition to the molecular ion at m/z 202, higher mass peaks above m/z 350 may indicate the formation

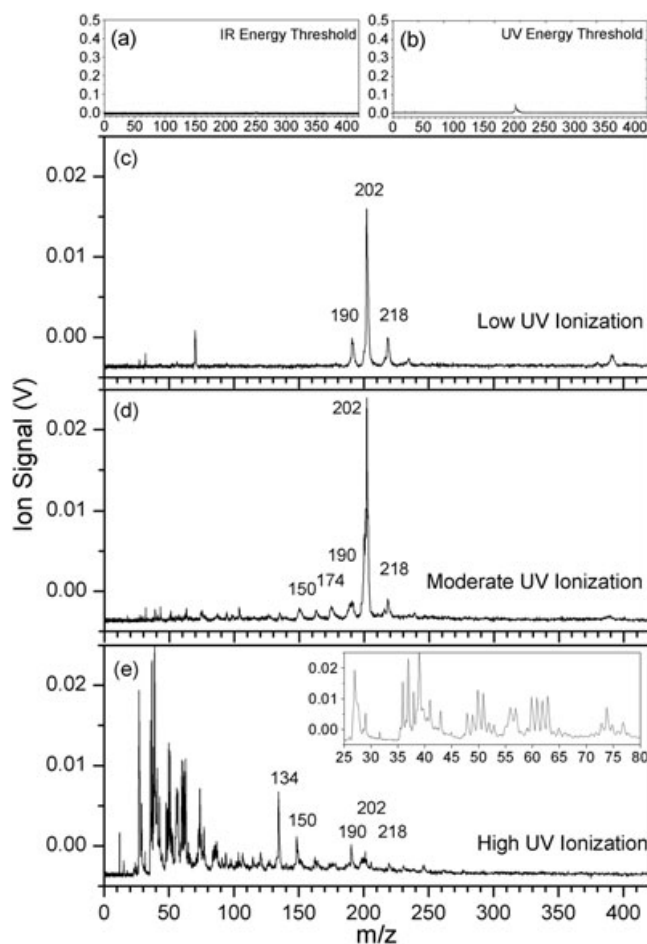


Figure 2. Two-step laser desorption/ionization mass spectra of pyrene. Single laser pulses of (a) the IR laser and (b) the UV laser at fluences below the ionization threshold, as verified by a negligible or incipient ion signal. (c) Above the UV ionization threshold (laser energy \sim 11 μ J), the molecular ion of pyrene is the dominant peak at m/z 202. (d) Moderate UV laser energies (laser energy \sim 55 μ J) reveal the onset of fragmentation. (e) High UV laser energies (laser energy \sim 260 μ J) produce nearly complete fragmentation of the molecular ion.

of dimers, clusters, or salt adducts due to the excess UV laser energy that often accompanies single-laser LDMS. This peak complexity is largely avoided with the use of L2MS, as in Fig. 2, where the molecular ion at m/z 202 is clearly the dominant signature and contributions from salt cations are not present.

The lack of salt peaks in L2MS spectra is perhaps surprising, given the high efficiency with which they are desorbed and ionized in traditional LDMS. One possible explanation for the lack of salt peaks may be elucidated by further consideration of the dependence of plume expansion rate on atomic or molecular weight, during the desorption step. In the regime where laser fluence is held near or just below the ionization threshold, thermal desorption due to local heating is expected to be the dominant mechanism for generating gas-phase neutrals. As a result, these neutrals take the form of a Maxwell-Boltzmann distribution in energy,^[17] and the rate of plume expansion is understood to depend linearly on laser fluence.^[19] Based on IR spot size at the sample surface, measured to be approximately 275 microns in diameter, and

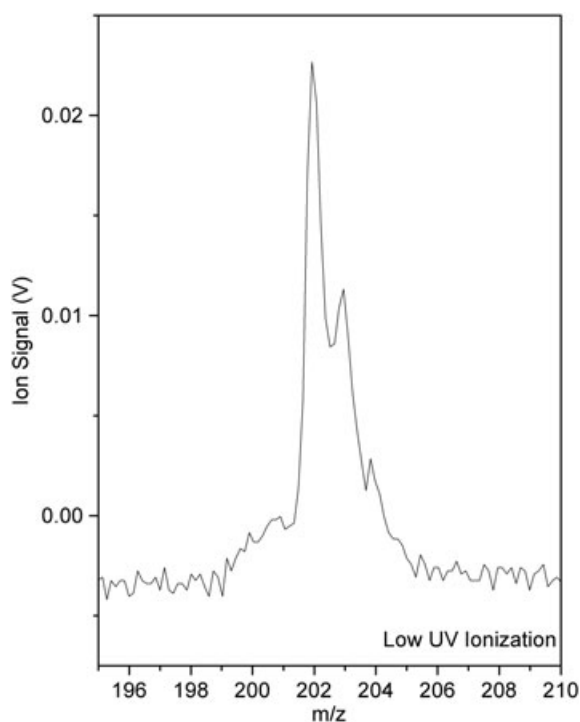


Figure 3. The pyrene molecular ion is shown for a single-shot L2MS spectrum. The UV laser energy was set just above ionization threshold (energy $\sim 11 \mu\text{J}$), as in Fig. 2(c). Mass resolution was calculated to exceed $m/\Delta m$ of 380.

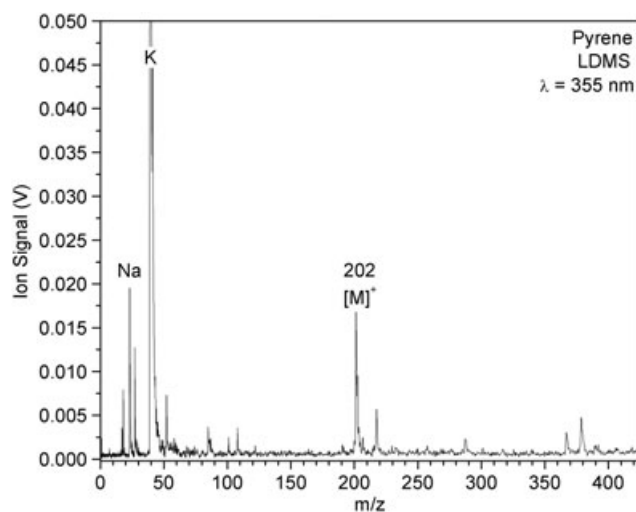


Figure 4. A single-step laser mass spectrum shows inorganic salt peaks (Na^+ at m/z 23 and K^+ isotopes at m/z 39 and 41) with higher intensities than the pyrene molecular ion at m/z 202. L2MS is observed to be insensitive to these ubiquitous elemental interferents.

maximum IR laser energy of $190 \mu\text{J}$, we can calculate the approximate laser fluence, or the energy deposited at the sample surface per unit area. A typical desorption laser fluence value for these experiments was found to be $320 \text{ mJ}/\text{cm}^2$. This fluence is higher than that reported for XeCl excimer laser desorption experiments,^[17] but the discrepancy may be accounted for, in part, by the 3-fold lower energy of the 1064 nm photons used in this work.

Based on dimensions of the instrument and the typical pulse delay used for optimized postionization signal, we can calculate the plume expansion rate for pyrene to be approximately 500 m/s. This value is consistent with literature values.^[19] It is important to note, however, that the plume expansion rate follows an inverse-square root-dependence on molecular weight. This corresponds to an expansion rate that is a factor of 2.7 higher for Na, than for pyrene. We recall that the UV ionization laser pulse delay is set to maximize ion signal at the detector, but this may have the effect of selecting a cross-section of the expanding plume that is characterized by some distribution of molecular weights. Similar mass-dependent velocity dispersion has been observed for fullerenes and metal ions.^[17,20] In practice, therefore, an ionization pulse delay that is optimized for pyrene may not be simultaneously optimized for the lower mass salts, serving effectively as a high-pass filter and allowing low-mass neutrals to travel out of the ionization volume before the second laser pulse is triggered.

The appearance of low-mass pyrene fragments at high ionization laser fluence is consistent with this model. Fragmentation of the molecular ion, in this case, is a result of the ionization pulse and is independent of the desorption process. The scalar velocity distribution of neutrals of different masses arises from the thermal energy imparted during the desorption pulse; the masses selected by ionization timing are contained within this distribution. The fragment ions, as a result, are generated from the temporal 'slice' of the neutral plume containing the molecular ion, and those fragment ions are readily analyzed and detected by the instrument. Follow-on experiments to document the dependence of the delay required for a particular mass range are planned to corroborate these findings.

CONCLUSIONS

Successful demonstration of two-step laser desorption/ionization has been shown using a miniature time-of-flight mass spectrometer prototype, measuring approximately 20 cm in length. Optimized studies of a model PAH, pyrene, has shown that unit mass resolution can be achieved at m/z values of several hundred, even for the mm-scale ionization source, low extraction voltages ($< 5000 \text{ V}$), and 100 micron-scale effective ionization volume described here. This performance holds promise for implementing advanced LD-TOFMS approaches on a future *in situ* landed planetary mission. We have estimated that such an instrument could weigh only 5–6 kg, making it a compelling instrument package for detecting and characterizing classes of organics in complex planetary samples on a small mission payload. The selectivity of L2MS would be especially enabling for distinguishing between inorganic clusters that point to surface mineralogy and aromatic species that are likely to be present on differentiated planets (e.g., Mars), primitive bodies (e.g., comets and asteroids), and the icy satellites of the outer solar system. In future work, the sensitivity and selectivity of the L2MS technique will be quantified on the miniature instrument using a systematic suite of standards, mixtures, and analogs of varying compositional complexity.

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