

Rapid Assessment of High Value Samples: A Miniature AOTF-LDTOF Spectrometer Suite for Cave Environments.

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We discuss the development of a miniature near-infrared point spectrometer, operating between 1.6–3.5 μm region, and based on acousto-optic tunable filter (AOTF) technology. This instrument may be used to screen and corroborate analyses of samples containing organic biomarkers or mineralogical signatures suggestive of extant or extinct organic material collected *in situ* from cave environments. The AOTF point spectrometer will be paired with a laser desorption time-of-flight (LDTOF) mass spectrometer and will prescreen samples for evidence of volatile or refractory organics before the laser desorption and subsequent mass spectrometer measurement. We present laboratory analysis of geological samples of known astrobiological importance, with and without organic biomarkers.

Introduction In cave environments, both on Earth and elsewhere in our solar system, robust sample screening and selection are essential for achieving the maximum scientific benefit with limited payload resources. For both *in situ* analyses and those conducted with samples that have been cached and returned to a laboratory, a central goal of astrobiology in cave settings is to understand the relationship between organic molecules and prebiotic chemistry and habitable environments.

The samples selected for sophisticated laboratory analysis must be carefully vetted by analytical tools that provide the greatest assurance of science value. A cave environment poses additional navigational challenges, thus having a high value down-select process for samples to be retrieved robotically is especially critical. One approach is the identification of key organic functional groups by a spectroscopic prescreening tool, followed by organic compound analysis with one or more mass spectrometric methods of increasing complexity.

The addition of an AOTF spectrometer to an existing LDTOF instrument will enable significant diagnostic capability without exceeding the resources of a small mobile laboratory, and this instrument suite will result in a powerful tool for astrobiological exploration of cave environments in our solar system.

Technology Development AOTF systems provide great flexibility, being very compact, electronically programmable, with time-averaged power requirements of

a few watts or less. They can provide arbitrary spectral selection over a wide tuning range by utilizing a birefringent TeO_2 crystal, which acts as a diffraction grating when compressed using RF waves. With broadband light as an input, orthogonally polarized, spectrally narrow beams are diffracted within the crystal and can be separately re-imaged at the output. The AOTF material, TeO_2 , is inherently rugged and radiation hard. Furthermore, these devices have no moving parts, making them an attractive option for space flight. Our group has a demonstrated history of developing and using AOTF imaging spectrometers for planetary science applications [1, 2, 3, 4, 5].

The LDTOF mass spectrometer provides pulsed-laser desorption and analysis of refractory organic compounds up to $>5,000$ Da on a spatial scale of 50-100 μm determined by the laser spot size at the target. At higher laser power, it also measures major, minor, and trace elements with parts-per-million sensitivity. The LDTOF employs a pulsed 355 nm Nd:YAG laser to desorb and ionize analyte from a solid surface. It collects laser-desorbed ions by drawing them from the sample surface into the ion extraction lens. The ions are focused into a time-of-flight analyzer and terminate at a microchannel plate detector and anode. The voltage pulses are then acquired as a function of time on an oscilloscope. This instrument has been described in detail previously [6].

The AOTF and LDTOF spectrometers have similar requirements for precise positioning of sensor elements near the sample surface. Using a shared optomechanical design, we realized significant savings in instrument mass and complexity. The design phase of the integrated AOTF-LDTOF spectrometer suite is nearing completion. The IR spectrometer components are integrated onto a compact optical deck, the geometry of which is optimized for the shape of the LDTOF MS vacuum shroud.

Laboratory Measurements Spectral detection of biological materials on mineral surfaces first requires a thorough characterization of the uninhabited host minerals, measured using the same instrument. We acquired near-IR spectra of a collection of field samples using both the AOTF spectrometer breadboard and the LDTOF spectrometer. The sample suite includes evaporites (sulfates, carbonates), clays, and iron oxides, all of which can be

linked to aqueous environments and are therefore of high astrobiological interest.

We also used both instruments to record the spectrum of a black desert varnish coating on a fractured sample of weathered rock obtained at the Luis Lopez mine site near Socorro, NM. The uncoated side appeared to have been fractured from a larger rock, and thus has shorter exposure age. The dark color of the desert varnish layers results from a high concentration of oxidized manganese, which can result from either biotic or abiotic processes. However, strong evidence suggests that oxidized Mn in rock varnish is produced by mixotrophic microorganisms in locations that lack abundant organic acids [7].

Finally, we used both the AOTF and LDTOF instruments to measure basalt samples that were both “neat” and doped with pyrene, a polycyclic aromatic hydrocarbon, in order to determine whether we could detect the presence of hydrocarbons in the rock. We see differences in the spectra between the neat and doped basalts, which we are investigating further.

Summary and Conclusions Our instrument development efforts to date have focused on two parallel efforts: the assembly, characterization and demonstration of the compact AOTF spectrometer, and the modifications to the LDTOF chamber in order to accommodate it. The design challenges associated with both aspects of this effort are being successfully addressed, and both the AOTF and the LDTOF are now being used to measure reference samples in the laboratory.

The AOTF measurements of sample reference spectra show that the wavelength calibration of the instrument is very accurate, permitting the identification of known spectral features. The LDTOF mass spectrometer measurements show the expected major and minor elements present in Mars analog samples that have been independently verified with an x-ray diffraction instrument. A comparison between the AOTF and LDTOF measurements of dolomitic samples reveals the complementary nature of the two data sets. The LDTOF identifies the Ca and Mg elemental constituents deriving from the dolomite component of the rock sample. Independently, on a mineralogically related (but not identical) sample, the AOTF spectrometer clearly reveals carbonate peaks. Together, these data sets are consistent with the presence of dolomite. In the near term, we plan to conduct LDTOF measurements on the same sample set used in AOTF studies to fully characterize a common set of minerals. To this, we will add a complement of astrobiologically relevant biosignatures from a variety of geomicrobial study sites well characterized in our previous

work [8, 9, 10, 11, 12, 13]. These include desert varnish on volcanic, sedimentary, and igneous bedrock, gypsum weathering rind and evaporite communities, travertines and tufas, and a spectrum of biofabrics and biominerals from cave deposits and surfaces.

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