DETECTING ORGANICS *IN SITU* USING LUMINESCENCE SPECTROSCOPY N.E. Bramall[1], C.R. Stoker[1], P.B. Price[2], L.J, Allamandola[1], [1]NASA Ames Research Center, MS245-3, Moffett Field, CA 94089, nebramall@gmail.com, Carol.R.Stoker@nasa.gov, Louis.J.Allamandola@nasa.gov, [2]U.C. Berkeley Dept. of Physics, 366 LeConte Hall, Berkeley CA 94720, bprice@berkeley.edu

Introduction: In searching for life, a strategy to locate biomolecules and organics is needed. For a large class of organic molecules, luminescence spectroscopy is well-suited to this task because the technique requires no consumables, requires no sample handling/acquition, no sample modification (e.g. heating), is very rapid, and is very sensitive[1]. Furthermore, the method is remarkably sensitive to many organic molecules including polycyclic aromatic hydrocarbons (PAHs), aromatic amino acids & proteins, porphyrins, F420, NADH, and siderophores.

PAHs are of particular interest as they have been identified in carbonacaceous chrondrites, interplanetary dust, and Martian meteorites [2-12]. Being among the most ubiquitous organic compounds in the universe [12], any study of extraterrestrial organic chemistry and prebiotic chemistry would greatly benefit from understanding the distribution and presence of PAHs in the solar system. Also, though abiotic in nature, extraterrestrial PAHs may have fueled the emergence of life on Earth [11,12,8] and similar delivery mechanisms may have led to their affecting the development of life on other planets and moons in the solar system-- so understanding them also has implications for the search for life.

Because PAHs often have very high luminescence cross-sections, luminescence spectroscopy is a particularly good method to detect them and detection levels approacting 10 ppt in complicated matrices have been reported (e.g. [13]).

Previously Developed Instruments: In the past, we have developed several borehole logging instruments tuned to detect the protein, NADH, chlorophyll, and F420 biosignatures of microorganisms [1]. Our most recent development, developed with Photon Systems (Covina, CA), is the Miniature Biospectral Logger (mBSL), which is only 5.1 cm in diameter and ~1.3 m long but is capable of detecting the presence of a single bacterium against a clay mineral background with a single 100 microsecond-long laser pulse [1]. Figure 1 shows the mBSL depicted in a borehole and its optical layout. At the heart of the mBSL is a quasi-CW 224 nm hollow cathode HeAg laser (Photon Systems) (A) which serves as the excitation source. Long-pass dichroics (B) act to remove plasma lines from the laser and a photodiode (C) measures the power output of the laser. Mirror (D) redirects the beam to a long-pass dichroic (E) which redirects it to an off-axis parabolic mirror (F) that focuses the beam through a quartz

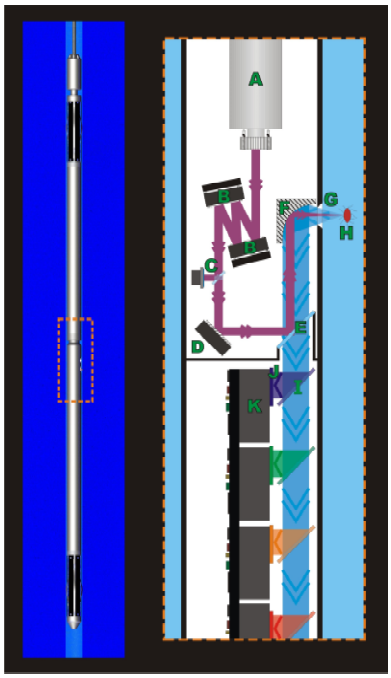

Figure 1. The current mBSL shown in a borehole (left) and its optical layout (right). The key is as follows:

A	224 nm HeAg Laser (quasi-CW)
B	Long-pass dichroics to clean plasma lines from the beam
C	A pick-off and photodiode to monitor the laser power
D	Plane mirror
E	Long-pass dichroic
F	Off-axis parabolic mirror
G	Sapphire Window
H	Target
I	Long-pass detector dichroics
J	Band-pass filter
K	Photomultiplier tube (PMT)

window (G) onto the target (H), covering an elliptical spot with semi-major and minor radii of 100 and 65 microns respectively at a distance of roughly 13 mm from the outside wall of the instrument with a depth of field of 3 mm. Luminescence is collected and collimated by the same off-axis parabolic mirror and passes through the dichoric (E) into the detector chain consisting of a series of six long-pass dichroics (I) that split up the collected light into six different spectral bands and re-direct them to corresponding bandpass-filtered (J) photomultiplier tubes (PMTs) (K). An electronics board (L) integrates the current produced by the PMTs, digitizes it, and sends it to a central computer which

parses and saves the data. In essence, the mBSL is a very sensitive, six-channel fluorimeter.

In addition to the version that targets proteins, a second mBSL has been made that targets chlorophyll and F420, using a 405 nm diode laser.

The components used in the mBSL have either been tested to TRL6 or better or have COTS alternatives which have been.

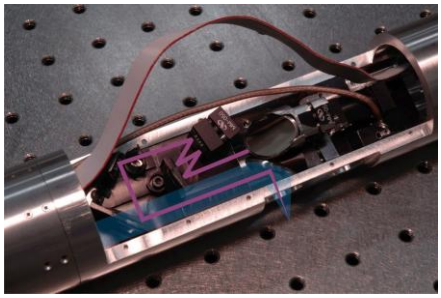

Figure 2. The optical path overlain on a photo of the mBSL.

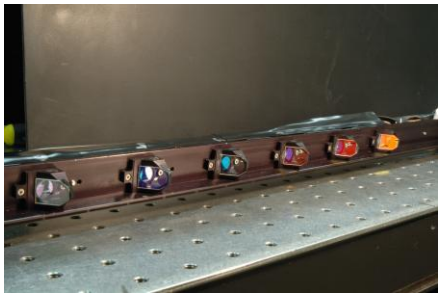

Figure 3. The dichroics chain.

Future Directions: There is still much work to be done in order to fully express the utility of luminescence for detecting organics. There are three different aspects to a substance's luminescence: (1) its emission spectrum, (2) its excitation spectrum, and (3) its characteristic luminescence lifetime(s). The mBSL currenly only targets compounds excited at a particular wavelenth and records only their emission spectra.

Multiwavelength excitation. In order to be as useful as posible, a luminescence detection instrument needs to be able to identify more than one or two different types of organics. Different molecules have different emission and excitation spectra. By using multiple wavlengths to excite luminescence in a target, many more species can be detected. In addition, doing so would also probe their excitation spectra so that different species could be better separated from one-another in the event that their emission spectra overlap.

Time-gated Detection: Different compounds have different luminescence lifetimes. By using a short laser pulse, and gating the detectors to integrate only during the expected luminescence of the compound of interest, individual fluorophores may be detected against rather large backgrounds.

Time Correlated Single Photon Counting (TCSPC). TCSPC is a powerful way to measure the luminescence lifetime of a sample. By using an array of high-speed photon counting detectors, the arrival times of individual fluoresced photons can be determined. In this way, the luminescence lifetime(s) of a target material may be measured in correlation with its emission spectrum and excitation spectrum, providing a complete luminescence characterization of a sample.

Summary: Luminescence spectroscopy is a very powerful tool in the search for organic molecules. Because it is a rapid technique with very high sensitivity and requires no reagents, sample acquisition, or sample modification (e.g. heating, grinding), luminescence spectroscopy would be a powerful tool for planetary exploration. It could be used as a triage instrument in conjunction with highly-definitive but limited-run techniques, or help in sample selection and collection for sample-return missions.

Luminescence detection instruments may take many forms, including borehole logging instruments (possibly integrated into drill strings), surface scanning instruments, and even remote detection.

By expanding on current instrumentation by adding multiple excitation sources and luminescence lifetime detection/gating techniques, a system could be made that is highly sensitive to and definitive of a large class of organic molecules, including many biomarkers such as porphyrins, proteins and aromatic amino acids, and other aromatic biomolecules.

We will present work we have done to to implement luminescence techniques for planetary exploration as well as environmental data that we have recovered with past prototypes

References:

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