

**NATIVE FLUORESCENCE FOR THE DETECTION OF ORGANICS.** N. E. Bramall<sup>1</sup> and L. J. Allamandola<sup>2</sup>, <sup>1</sup>Los Gatos Research ([N.Bramall@lgrinc.com](mailto:N.Bramall@lgrinc.com), 67 East Evelyn Ave. Ste. 3, Mountain View, CA 94041-1518), <sup>2</sup>NASA Ames Research Center (Astrophysics Branch, MS 245-6, Moffett Field, CA 94035-1000)

**Introduction:** A primary goal of the Mars exploration program has been to find life (extant or extinct) and organic material. Whether for sample-return or *in situ* studies, a tool to quickly triage samples based on their likelihood to contain biological material or organics is essential. Such a tool would ideally require little to no sample handling and be highly-sensitive. Spectroscopic techniques are thus especially well-suited for this task. Of the different spectroscopic methods available, fluorescence is by far the most sensitive to large classes of important, stable organic molecules, and it can be performed in a stand-off mode without requiring sample acquisition, does not require reagents of any kind, and a measurement can take much less than a second.

**Fluorescence of Organics:** Many organic molecules are highly-fluorescent. Of the different types, aromatic molecules are generally the most fluorescent. Aromatic compounds are found in abundance in all known forms of life where their complexity ranges from high-level structures (e.g., lignin and chlorophyll) down to the most basic building blocks (e.g., aromatic amino acids). Although extraterrestrial life will undoubtedly be composed of different biomolecules, aromatic structures are so functional that some class of them will likely be a part of any extraterrestrial biochemistry.

Polycyclic Aromatic Hydrocarbons (PAHs) are a very important class of highly-fluorescent aromatic molecules. PAHs are abundant throughout the universe. Within the Solar System, they are present in carbonaceous chondrites, interplanetary dust particles and Martian meteorites, and there is spectroscopic evidence for PAHs frozen in Saturn's rings, Titan's atmosphere and comets. Beyond the Solar System, the tell-tale infra-red emission signature from astronomical PAHs spans the Universe. They are associated with many very different objects within our Galaxy, from the atmospheres of dying stars to regions of star and planet formation. They dominate the emission from galaxies out to redshifts approaching  $z = 6$ , i.e. a few billion years after the Big Bang. Most recently, they have even been detected being ejected from very active, star forming galaxies into intergalactic space. Clearly, PAHs are everywhere and because of their great thermodynamic stabilities, astronomical PAHs are more abundant than all the known interstellar, polyatomic molecules combined. They are now routinely used as tracers of star formation and are being developed into probes of planet formation. Thus, they are

an important component of the materials which rain down on planets. Although a large number of PAH isomers are possible, the more condensed forms are substantially more stable than less condensed forms and are likely to be dominant in the often unforgiving, planetary surface environments. Their ubiquity alone makes their detection important, but it may be that extraterrestrial PAHs even fueled the emergence of life on Earth and perhaps elsewhere (e.g., [1][2]).

Fluorescence spectroscopy is extremely sensitive to aromatic compounds. In the case of aromatic amino acids, detection limits down to  $10^{-8}$  moles have been reported [3] and their detection within living systems can be made to the levels of a single bacterium resting upon a clay mineral [4]. PAHs are extremely fluorescent and their detection has been reported down to parts-per-trillion levels [5]. It has often been observed that for a large class of organics, fluorescence spectroscopy is unmatched in its sensitivity (e.g., [6]).

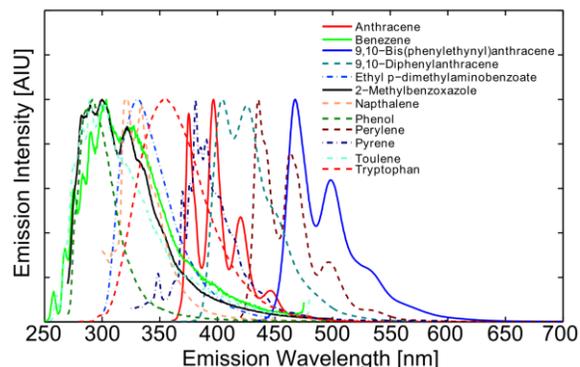


Figure 1: Normalized emission of aromatic organics excited at peak wavelengths shown in Figure 2.

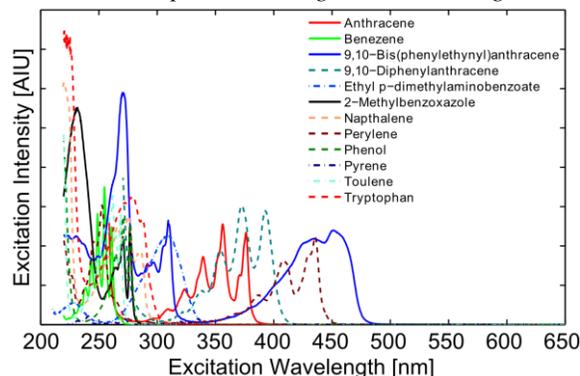


Figure 2: The excitation spectra of some organic molecules.

**Stability of Aromatic Organics:** Any organics (or class of organics) on or near the Martian surface or frozen in its polar caps must be unusually stable to survive the harsh radiation environment. As a class, aromatic molecules are much more thermodynamically stable than all other organics due to electron delocalization in their molecular orbitals. Because of this, the organic population sampled by landers and rovers will likely be dominated by aromatic-rich species such as PAHs. Among the aromatics there is a sub-class called superaromatics which, because of allowing electron delocalization to a larger extent, are even more stable. For any given number of rings, the most stable PAHs are those with the most condensed structures such as pyrene, coronene, ovalene, circumcoronene, etc. It is this inherent stability of aromaticity that allows PAHs and PAH-related species to withstand the radiative cauldron associated with astronomical objects spanning the Universe, environments which weed out and convert the bulk of all other polyatomic species into PAHs.

**Requirements for Fluorescence Instruments on Mars:** Any instrument sent to detect organics on Mars should be sensitive to a very large class of molecules, especially PAHs, and not specific molecules as it is difficult to predict exactly what organic molecules may be present.

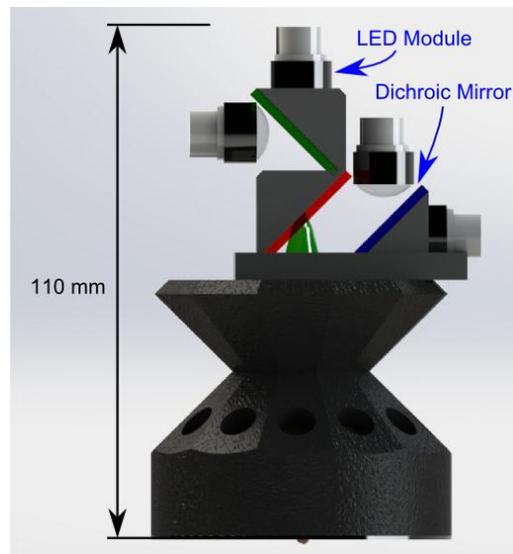
This requires that the instrument excite fluorescence at a number of different wavelengths (see *Figure 2*), collect emission over a broad range of wavelengths (*Figure 1*) and, ideally, measure the fluorescent lifetime of each emission band at each excitation wavelength. Lifetime measurements are especially useful in distinguishing organic molecules from minerals. This three-fold approach extracts as much information as possible from the target.

**FLEXEMS:** The Fluorescence Lifetime Excitation Emission Spectrometer (FLEXEMS), shown in *Figure 3*, is a miniature stand-off fluorescence spectrometer capable of measuring both the emission and fluorescence lifetime of a target at four different excitation wavelengths (light-emitting diodes (LEDs)) ranging from 255 nm to 405 nm. By using a configuration of dichroic mirrors, each excitation wavelength can be used without requiring any moving parts.

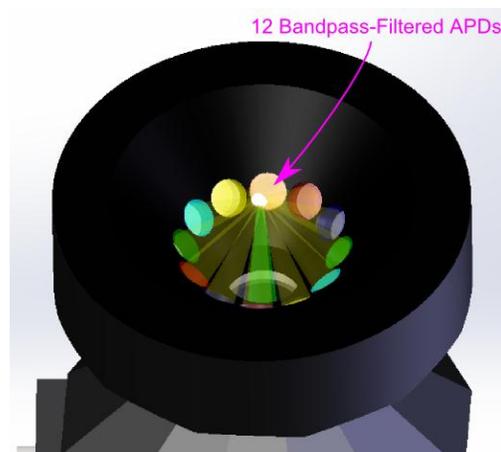
During a measurement, excitation light is focused down onto a target causing it to fluoresce (*Figure 4*). The emitted light is filtered by a series of bandpass filters each of which covers a lens that focuses the filtered light onto an avalanche photodiode (APD). Time-Correlated Single Photon Counting (TCSPC) is used in each channel to record the emission and fluorescence lifetime of the target with extreme sensitivity.

FLEXEMS requires no reagents, sample handling, and acquires *in-situ* readings in under a second. All of

the elements used in FLEXEMS are intrinsically small, rugged, and require low power, allowing the instrument to be very attractive for space flight.



**Figure 3:** Side view of FLEXEMS with the top removed to show the excitation LED configuration.



**Figure 4:** A view of FLEXEMS measuring the fluorescence from a small target. Twelve emission channels record the emitted fluorescence.

**References.** [1] Shimoyama and Katsumata (2001), *Chem. Lett.*, 30, 292-203. [2] Llorca (2004), *Int. Microbio.*, 7, 239-248. [3] Zhang and Sweedler (2001), *Anal. Chem.*, 73, 5620-5624. [4] Bramall (2007), PhD thesis. [5] Taylor (1993), *Anal. Instrum.*, 21, 141-162. [6] McDonald *et al.* (2004), *Icarus*, 132,170-175.