ELEMENTAL ESTIMATION OF ORGANICS THROUGH UV TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY: IMPLICATIONS FOR PLANETARY EXPLORATION.

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Introduction: For sample return missions such as OSIRIX-REx and the Mars Sample Return mission, prioritization of analyses of returned samples will be more important component of the mission's scientific success. This is particularly true as many of the analyses contemplated for returned samples are at least partially destructive [1-4].

In the specific case of Mars, the Perseverance Rover is equipped with 43 canisters, some of which will be filled with geologically relevant samples from the Jezero Crater. Subsequently, the samples will be retrieved to Earth in a future joint ESA-NASA mission. Given the limited samples scheduled to be returned from missions and the pristineness of such samples, it is important to consider suitable non-destructive alternatives where possible.

Laser-induced Fluorescence spectroscopy (LIF) is a minimally destructive laser-based technique in which the excitation of molecules by the absorption of photons yields spontaneous emission of light [1] which can be used to detect organics and minerals in geological samples. In addition, by sequentially increasing the gate delay of acquired LIF spectra, it is possible to obtain time-resolved LIF spectra (TR-LIF), thereby allowing for the fingerprinting of organics based on the fluorescence lifetimes at specific band regions. While these capabilities are impactful in themselves, we sought to determine whether TR-LIF could be used as a minimally-destructive technique for the estimation of other properties.

The objective of this work is to investigate the application of TR-LIF as a non-destructive technique for estimating elemental abundance in samples relevant to planetary exploration.

Methods:

Experimental setup. Nine pure amino acid samples (glycine, b-alanine L-alanine, 2-aminoisobutyric acid, D/L 2-aminobutyric acid, L-aspartic acid, L-glutamic acid, L-proline, and L-phenylalanine) were obtained from Sigma Aldrich in powdered form. About 0.5 g of each sample was pelletized with a Pike Technology pellet presser. Isopropanol was used to clean the pellet presser between uses to avoid cross-contamination. Pellets consisted only of the amino acid (i.e., no substrate).

Samples were analyzed using UV time-resolved laser-induced fluorescence spectroscopy (TR-LIF) using a 266 nm Q-passive puled laser. The setup included a spot size of 50 mm, laser power of 0.1 mW, and a repletion rate of 5 KHz (see [2] for full optical setup details). The TR-LIF spectra were measured using a gate step of 0.1 ns over a 20 ns period, a gate width of 3 ns, and 1200 accumulations per spectrum. TR-LIF imaging was conducted using an Andor iStar DH334t gated iCCD.

Decay rate calculation. Band regions corresponding to specific amino acids under consideration were identified in the LIF spectra. Subsequently, the fluorescence lifetime (decay rate) was calculated for each TR-LIF spectrum. This was done using a previously defined methodology [2]. Briefly, given f_{obs}, f_{laser}, f_{decay}, and f_{gate} corresponding to the observed rate of decay (from the TR-LIF spectra), profile of the laser pulse, true lifetime, and profile of the detector, respectively, the objective is to find f_{decay} using the expression

$$f_{obs} = f_{laser} * f_{decay} * f_{gate}$$

where ($*$) is the convolution operator. To solve for f_{decay}, we:

1. Simulate a gaussian function for the laser profile and rectangular function for the laser and detector profiles, respectively
2. An exponential function is fit to the empirical decay curve
3. The three curves from (1-2) are transformed into the frequency domain using a fast Fourier transform (FFT) thereby yielding f_{obs}, f_{laser}, and f_{gate}
4. A deconvolution, the inverse of (eq. 1) is then used to solve for f_{decay}
5. f_{decay} is then transformed back to the time domain through an inverse FFT
6. An exponential function is fit to the results of step 5 and the coefficient yield the decay rate

This process was conducted for each of the 9 samples. An additional 8 decay rates were obtained from the literature [5-7].

Elemental estimation

To estimate the elemental composition of nitrogen (N) and carbon (C), we conducted a univariable linear regression between the decay rates and the elemental composition of N and C (determined through the stoichiometry of the amino acids); this was assumed to be a valid estimate of the true composition given the high purity of the amino acid samples (the literature samples also had a comparable degree of purity). The significance of the linear relationship was assessed by the p-value of the corresponding F-test and mean squared error (MSE).

Results: At the $\alpha = 0.05$ level of significance, we found that the decay rate from the TR-LIF spectra is a statistically significant predictor of nitrogen (p <0.025; MSE = $5.29 * 10^{-4}$); see Figure 1. Similarly, we observe that the decay rate from the TR-LIF spectra is a statistically significant predictor of carbon (p <0.025; MSE = $8.7 * 10^{-4}$); see Figure 2.
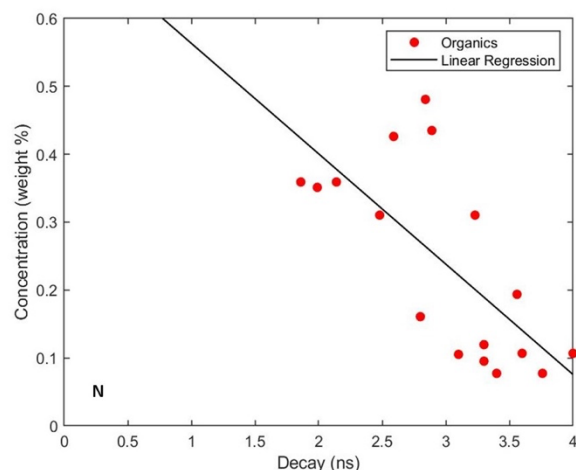

Figure 1. Illustrates the linear relationship between the decay rate and the elemental abundance of nitrogen.
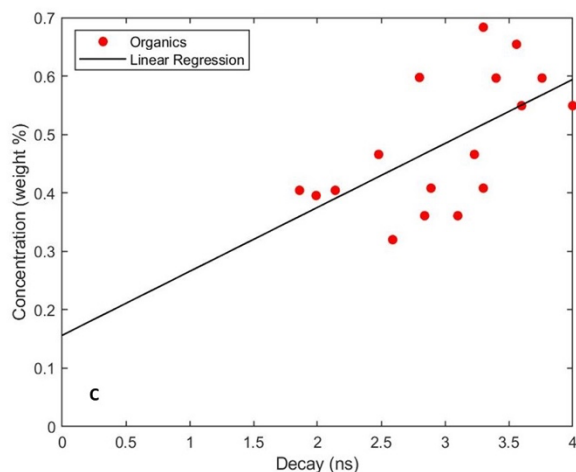

Figure 2. Illustrates the linear relationship between the decay rate and the elemental abundance of carbon.

Discussion: While TR-LIF has historically been used as a non-destructive technique for mineralogical and biological fingerprinting, there is a paucity of evidence to support the method as a technique for elemental estimation. However, the present results suggest that TR-LIF may in-fact be used as a technique for non-destructive elemental estimation. This is particularly important in the context of return sample planetary exploration, where samples are likely to be scarce and non-destructive techniques, correspondingly attractive.

Future work will focus on expanding the suite of samples and range of elements under consideration for the proposed predictive framework.

References: [1] Lalla E. A. et al. (2021) *J. Appl. Spectrosc., 75(9), 1093-1113*. [2] Lymer E. A. et al. (2021) *Astrobiology., 21(11), 1350-1362*. [3] Lalla E. A. et al. (2022) *Astrobiology., 20(11), 1303-1320*. [4] *J. Chemomem., 33(10), e3174*. [5] Chen R. F. et al. (1978) Arch. *Biochem. Biophys., 189, 241-250*. [6] Ross J. B. A. et al. (1992) *Topics of Fluorescence Spectroscopy*. [7] Cote K et al. (2019) *70th International Astronautical Congress (IAC)., IAC-190A3-3B-12*.