LIBS DETECTION OF ORGANIC BIOSIGNATURES IN DOPED SUBSTRATES UNDER A MARS SIMULATED ATMOSPHERE.

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Introduction: This work continues previous studies carried out in a Mars-simulated environment, characterizing by LIBS new organic molecules precursors or derived from organic biosignatures.

LIBS is an optical emission spectroscopic technique with specific characteristics that make it advantageous over other analytical methods for several applications, such as rapid elemental analysis, minimal sample preparation and simultaneous multi-elemental detection. These characteristics make LIBS an attractive tool for application in geochemistry and astrobiology.

Life detection within planetary exploration has always been an inspiring challenge that needs essential support from laboratory simulation studies. The possibility of simulating planetary environmental conditions provides key information on the processing of organic biomarkers as they can be experimented on other planets and help in instrument development and landing site selection focused on increasing the probability of detection of specific chemical compounds. Mars is a prime target for future space mission detections of life. Indeed, the recent discovery of the preservation of small organic compounds in harsh conditions on the surface of Mars, along with the presence of organic compounds from meteorites, is particularly encouraging for life detection [1-5].

Limits of detection (LOD) were estimated in conditions similar to those used in the SuperCam module of the Perseverance rover. For LIBS analysis, two types of inorganic matrices were used as substrates (present on the Martian surface and whose formation could be associated with a past biogenic origin). However, these matrices interfered with the molecular signals, making detecting organic signals an analytical challenge. This study analyzed organic compounds of interest in astrobiology in association with carbonates and sulphates under laboratory simulations of Martian conditions.

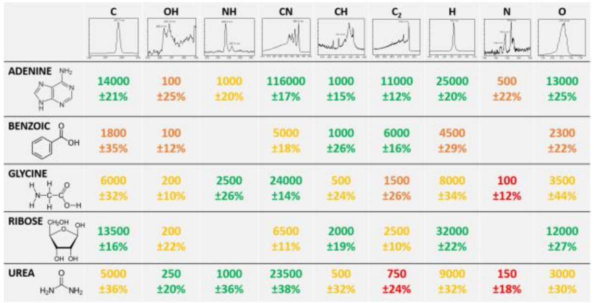
Samples: In this work, organic compounds, including adenine, benzoic acid, glycine, d-ribose, and urea, were analyzed under Mars conditions. The inorganic matrices calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$) were doped with the above-mentioned organic compounds. Prepared samples with specific concentrations of organic dopant homogenized in the matrix substrate were introduced into a vacuum chamber at a pressure of 7 mbar. The gas mixture emulating the composition of the Martian atmosphere was circulated in a dynamic regime.

Goal: This work's main aim is to detect organic biosignatures in doped substrates under Martian-like atmosphere. The results presented here attempted to demonstrate the capability of LIBS as a valuable technique for detecting and interpreting past life evidence in organic biosignatures for future space missions.

Finally, in order to identify and classify groups with similar organic structures and a priori, the same spectral fingerprint, a chemometric study was achieved using discriminant function analysis (DFA). From LIBS spectra, atomic and molecular signals were used for DFA analysis (functions were generated with the statistical weight of each variable).

Results and Discussion: Preliminary LIBS interpretation indicated that all the organic molecules presented a common spectral fingerprint, with the main differences residing in their molecular emissions. Thus, molecules with the presence of aromatic cycles are characterized by a large C_2 band emission, while for aliphatic molecules this contribution was residual and attributable to the influence of the surrounding atmosphere. In the case of molecules containing nitrogen, the emission of the CN species (generated by recombination processes in the plasma plume) dominated LIBS spectrum, being residual for the rest of molecules.

The presence of molecular bands other than CN and C_2, it is also useful in identifying organic compounds. Thus, the OH, NH and CH bands were notably higher in the spectra for urea, glycine and ribose, respectively. This spectral information was summarized in Figure 1.



	C	OH	NH	CN	CH	C_2	H	N	O
ADENINE	14000 ±21%	100 ±25%	1000 ±20%	116000 ±17%	1000 ±15%	11000 ±12%	25000 ±20%	500 ±22%	13000 ±25%
BENZOIC	1800 ±35%	100 ±12%		5000 ±18%	1000 ±26%	6000 ±16%	4500 ±29%		2300 ±22%
GLYCINE	6000 ±32%	200 ±10%	2500 ±26%	24000 ±14%	500 ±24%	1500 ±26%	8000 ±34%	100 ±12%	3500 ±44%
RIBOSE	13500 ±16%	200 ±22%		6500 ±11%	2000 ±19%	2500 ±10%	32000 ±22%		12000 ±27%
UREA	5000 ±36%	250 ±20%	1000 ±36%	23500 ±38%	500 ±32%	750 ±24%	9000 ±32%	150 ±18%	3000 ±30%

Figure 1. Mean intensities of organic emission signals detected for each analyzed molecule. An example type spectrum of each atomic line/molecular band is also shown.

Concerning the calculation of LODs, the presence of the inorganic matrix meant a considerable spectral interference that prevented the detection of the minority molecular emission signals (OH, NH and CH). In the case of calcium carbonate, calculation was only possible for the H(I), CN and C(I) species. In contrast, for calcium sulfate matrix, it was reduced to the CN and C_2 signals due to the presence of humidity in the matrix. In the case of the C(I) and O(I) atomic lines, as the concentration of organic dopant was reduced, the emission response of these species increased due to the changes in the laser-matter interaction, which resulted in a higher ablation rate and the greater contribution of the atmosphere in the plasma chemistry.

The values of Limit of detection, expressed in %wt, for the five organic compounds in both matrices are summarized in Table 1.

Table 1. LODs obtained for the emission species calculated in both inorganic matrices with varying organic sample content. The measurements were performed under Martian atmospheric conditions, and with a laser fluence regime of 43.6 J/cm^2. A=adenine, B= benzoic acid, G= glycine, R= ribose, U= urea

	$CaCO_3$ (%wt)					$CaSO_4$ (%wt)				
	A	B	G	R	U	A	B	G	R	U
CN	2.3		12.8		8.1	2.3		6.7		4.0
C_2	6.4	4.2				16.2	12.8			
H_α	4.9	5.3	1.9	3.2	7.6					

In order to identify and differentiate organic-based compounds, a discriminant function analysis was performed. In this sense, potential of LIBS technology might be significantly enhanced by the use of statistical tools. In the case of pure dopants, the percentage of cases correctly classified was 100%, including the differentiation between glycine and urea with high structural similarity, thus demonstrating the discrimination capacity of the technique in such an application.

The discrimination results achieved for the analyses performed at different dopant concentrations are summarized in Table 2. As seen, for the lowest concentration level in weight, the classification percentage was approximately 70%.

Table 2. Summary of DFA selected variables and classification percentages for the different organic concentration levels.

Dopant Content(%wt)	Input variables for DFA	Event correctly classified (%)	
		$CaCO_3$	$CaSO_4$
2.5	C,CN,C_2,H,O	70.8	71.7
5	C,CN,C_2,H,O	85.8	85.8
10	C,CN,C_2,H,O	92.5	90.8
20	C,CN,C_2,H,O	95	90.8
50	C,CN,C_2,H,O	99.2	100
100	C,CN,C_2,NH,OH,CH,H,O	100	100

Conclusions: Results may contribute to establishing the optimal experimental conditions for the observation of organic carbon species in laser-induced plasmas and the basis for the subsequent detection of carbon biosignatures in geological samples of interest as potential Mars analogues.

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