ENHANCED RESOLUTION OF CHIRAL AMINO ACIDS WITH CAPILLARY ELECTROPHORESIS FOR BIOSIGNATURE DETECTION IN EXTRATERRESTRIAL SAMPLES. J. C. Creamer[1], M. F. Mora[1], F. Kehl[1], and P. A. Willis[1], [1]NASA Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Dr. Pasadena, CA 91109

Introduction: Amino acids are the fundamental building blocks of all of the proteins needed for life on Earth. However, they are also a common byproduct of abiotic chemical reactions. The distribution of amino acids can be indicative of extinct or extant life on other worlds, but in order to use amino acids as biomarkers we need to be able to distinguish between those generated from abiotic and biotic reactions. By targeting detection of a small subset of 17 amino acids found in high abundance in terrestrial life (biotic) and meteorites (abiotic) it is possible to look for three distinct patterns, namely: 1) which amino acids are present; 2) the relative abundance of those amino acids to glycine; 3) the presence of an enantiomeric excess.

However, the in situ analysis of amino acids in extraterrestrial environments remains a challenge. Because of the low expected abundances of organics in planetary samples (amino acids in terrestrial soil can be as low as parts-per-billion) in situ sampling techniques are preferable over remote optical ones because they provide increased sensitivity [1].

Capillary electrophoresis (CE) is an extremely promising analytical technique for polar organic molecules in environments where water is present. Since CE is a liquid-based technique, all sample preparation can be done without leaving the aqueous phase. CE can be coupled to a wide variety of detection methods including laser induced fluorescence detection (LIF) to achieve selective and sensitive detection. Moreover, CE-LIF has been used for many decades for chiral amino acid analysis.

Here, we present two CE methods capable of resolving 17 amino acids labeled with 5-carboxyfluorescein succinimidyl ester. These 17 amino acids (seven enantiomer pairs L/D-Ala, -Asp, -Glu, -His, -Leu, -Ser, -Val and plus the achiral Gly, β-Ala, and GABA) represent the amino acids found in the highest abundance in biotic and abiotic samples. Resolution of the neutral amino acids was achieved using cyclodextrin (CD) mediated MEKC, with dual chiral selectors sodium taurocholate and γ-CD (Figure 1A). The acidic amino acids were resolved by CZE, using γ-CD alone (Figure 1B).

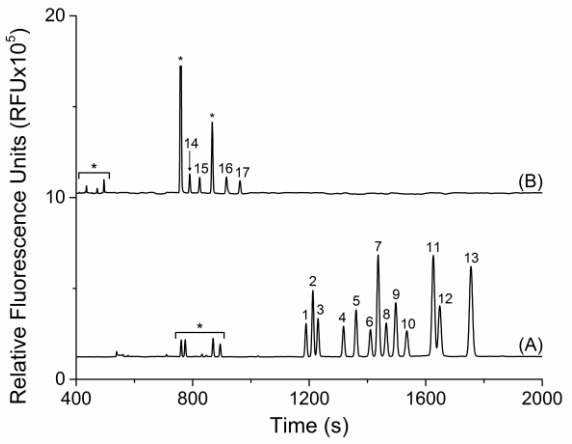

Figure 1: Electropherograms of the two optimized separations for the analysis of 17 amino acids found in high abundance in abiotic and biotic samples. A) The 13 neutral amino acids were resolved with a BGE composed of 80 mM sodium tetraborate, 30 mM γ-CD, 30 mM STC, and 5% v/v CAN. B) The 4 acidic amino acids were resolved with a BGE of 80 mM sodium tetraborate, 30 mM g-CD. Both separations were done on a 40 cm effective length capillary (50 cm total) with a 25 kV separation voltage. Peaks: 1. D-His; 2. D-Leu; 3. D-Val; 4. L-His; 5. L-Leu; 6. D-Ser; 7. GABA; 8. L-Val; 9. D-Ala; 10. L-Ser; 11. β-Ala; 12. L-Ala; 13. Gly; 14. D-Glu; 15. D-Asp; 16. L-Glu; 17. L-Asp; *Dye side products

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References:

[1] Willis, P.A., Creamer, J.S., Mora, M.F. (2015) ABC, 23, 6939-6963.