DETECTION LIMITS FOR CHIRAL AMINO ACIDS USING A POLARIZATION CAMERA. C. W. Cook[1], D. Viola[2], S. Byrne[1], C. Drouet d'Aubigny[1], [1]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721 (clairec@email.arizona.edu), [2]NASA Ames Research Center, Mountain View, CA 94035)

Introduction: The detection of biosignatures on a planetary surface is of high scientific interest and high enantiomeric excesses are one such signature. Enantiomers are each of the two non-superimposable mirror image configurations of chiral molecules. In biological materials on Earth, the ratio of the L enantiomer to the D enantiomer of amino acids is high, while in abiotic materials, the two are found in approximately equal amounts [1].

High enantiomeric excesses in samples can be detected by their polarizing effects on transmitted light. The optical rotation of a molecule is the angle by which plane-polarized light is rotated when it passes through a sample of the molecule in solution. The two enantiomers of a chiral molecule will have optical rotations with equal magnitude and opposite sign. For abiotic mixtures of two enantiomers, the optical rotations will roughly cancel out. However, in biogenic samples, a net change in optical rotation may be imparted. Polarimetry has thus been proposed as a biosignature detection method [2-4] .

Europa is a moon of Jupiter which hosts a liquid water ocean beneath its ice shell [5] and is a target in the search for life elsewhere in the solar system. NASA has released a report delineating requirements for a Europa lander which includes determining the enantiomeric ratios of amino acids present [6]. In development work for the Cold Lightweight Imagers for Europa (C-LIFE) microscopic imager we assess the potential of polarization measurements to quantify enantiomeric excesses and report our results here.

Methods: The experimental set-up is shown in Figure 1. An LED light source is collimated and directed through a polarizer to create plane-polarized light, followed by a cuvette holding the sample, and the collimated beam is analyzed by a polarization camera (4D Technology's PolarCam Snapshot Micropolarizer Camera).

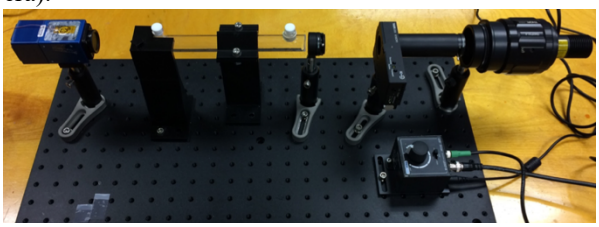

Figure 1: From left to right: PolarCam, cuvette, polarizer, LED.

PolarCam uses a wiregrid polarizer array which contains a pattern of polarizers with 0, 45, 90, and 135 degree polarizations that together form a super pixel which is repeated over the array (Figure 2).

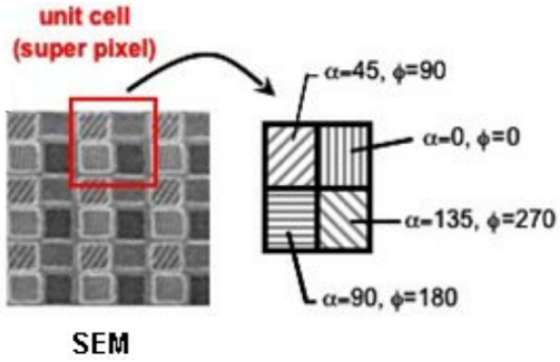

Figure 2: SEM image of the array and the arrangement of the polarizer array for a single super pixel [7].

We investigated two amino acids: serine (with a specific optical rotation at 590 nm of -6.83° [8]) and phenylalanine (with a specific optical rotation at 590 nm of -35.1° [9]). At shorter wavelengths, the specific optical rotation is higher, so in order to determine the effect of wavelength on the detection limit, we measured the optical rotation at 490 nm in addition to 590 nm. Solutions of a single amino acid were measured for a range of enantiomeric excesses. In addition, some measurements were made with mixtures of serine and phenylalanine, with varying enantiomeric excess ratios. To determine the effect of salts on the optical rotation, measurements were also made with sodium chloride (NaCl) or magnesium sulfate heptahydrate (MgSO4 • 7H2O) added to the amino acids. In each case, the stock solution with the amino acid(s) dissolved in water was serially diluted to produce solutions for a range of concentrations. Control measurements of pure water were taken before and after sample measurements.

For each sample and control measurement, we find the Angle of Linear Polarization (AoLP) by combining elements of each super pixel, then the average AoLP over all super pixels on the detector. To find the optical rotation, the AoLP for the sample must be subtracted from the AoLP for the control. We mitigate systematic errors which cause the AoLP to drift over time, by linearly interpolating between the AoLP for the controls taken before and after the sample measurement to find what the control AoLP would be at the time the sample measurement was taken. We then subtract the AoLP of the sample from this control AoLP to get the optical rotation of the sample. Figure 3 shows an example of the optical rotations obtained in this way for phenylalanine.

We take the detection limit for optical rotation as the lowest measured concentration for which 1) the optical rotation plus or minus its error bars never crosses zero, 2) the optical rotation has the expected sign, and 3)

every higher-concentration measurement satisfies conditions 1 and 2.

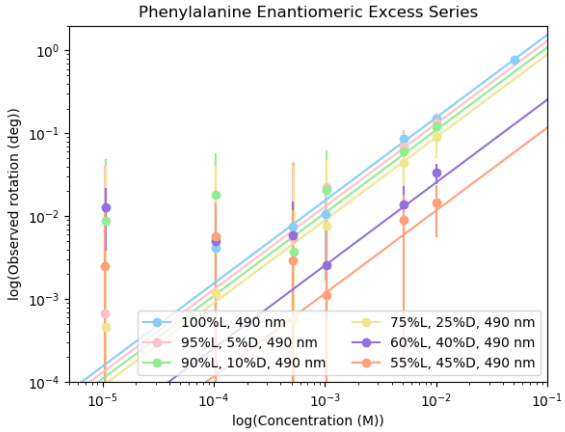

Figure 3: Absolute value of optical rotation of phenylalanine for various enantiomeric excesses (with >50% of L enantiomer) and concentrations. Curves shown are linear fits to the data points, passing through (0,0).

Systematic errors were driven mainly by camera temperature. Given sufficient time to fully warm up results converged to their final values with much smaller error. Before this factor was recognized, some measurements were made without the camera warmed up, leading to larger errors and higher concentration detection limits than measurements taken with the camera warmed up.

Results: For both serine and phenylalanine, as expected, enantiomeric ratios closer to 50:50 result in a smaller optical rotation.

Table 1 shows the concentration detection limits for the optical rotation of serine and phenylalanine at 490 nm over a range of enantiomeric excesses. The detection limits given are the lowest concentration measured at which the conditions described above are satisfied, but detections could potentially occur at concentrations between this concentration and the next lowest investigated concentration that did not satisfy the conditions.

Most detection limits followed expected trends. It was expected that the detection limit for lower enantiomeric excess ratios will be higher, and this appears to be the case for 100%L—60%L serine. As expected, the 40%L serine detection limit is the same as the 60%L detection limit and the 25%L serine detection limit is the same as the 75%L measurement.

In several cases, anomalous results occurred when the camera had not fully warmed up. The detection limit for 60%L serine is lower than for 55%L. Although it would be expected for the 55%L and 45%L serine measurements to have the same detection limit, none of the measurements made for 45% L met the detection limit criteria. The measured 100%D detection limit was larger than the 100%L detection limit (for serine and phenylalanine).

The optical rotations of the mixed amino acids are consistent with a linear combination of the optical rotations of the components. As expected, because phenylalanine has a higher specific optical rotation, the solutions with a higher proportion of phenylalanine have a higher optical rotation and lower detection limit.

In general, the addition of either salt lowered the optical rotation, but did not always raise the detection limit at the resolution of concentrations measured.

NASA's Europa lander report stipulated that enantiomeric excess should be quantified with an accuracy of 5% or better [6]. Using this instrument, solutions with enantiomeric excesses 5% apart are only distinguishable at concentrations higher than 0.5 M for serine and not distinguishable at any measured concentration for phenylalanine, although this might be improved if the measurements were all taken with the camera warmed up. The percent error in the optical rotation is over 5% except in a few cases (100%L serine above 0.1 M, 95%L serine at 0.5 M, and 100%L phenylalanine at 0.05 M).

Amino Acid	Enantiomeric Excess	Concentration Detection Limit (M) (490 nm)
Serine	100%L	0.005
	95%L, 5%D	0.05
	90%L, 10%D	0.05
	75%L, 25%D	0.05
	60%L, 40%D	0.1
	55%L, 45%D	0.05
	45%L, 55%D	none
	40%L, 60%D	0.1
	25%L, 75%D	0.05
	100%D	0.01
Phenylalanine	100%L	0.0005
	95%L, 5%D	0.005
	90%L, 10%D	0.005
	75%L, 25%D	0.005
	60%L, 40%D	0.005
	55%L, 45%D	0.01
	45%L, 55%D	0.01
	40%L, 60%D	0.005
	25%L, 75%D	0.005
	100%D	0.01

Table 1: Detection limits for serine and phenylalanine with varying enantiomeric ratios.

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