Lab-on-a-Chip System Development for In Situ Exploration of Titan

Peter Willis
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

KISS Workshop, Caltech
May 25, 2010
Why choose lab-on-a-chip for spaceflight applications?

- Low mass, volume, and power requirements (amenable to robotic explorers)
- Fluid motion driven by electric fields or very small pressure differentials (i.e. no pump)
- Extremely sensitive
- Addresses key NASA agency goals
- Requires very little sample (less than a drop)

Key Questions for this workshop:
- How is sample handling done on Titan, and how does this affect the sample and analysis protocol?
- What are the specific science goals?
- **lab-on-a-chip instruments** could be designed to function autonomously on the surface of other planets.

- For Titan deployment, liquid could be sipped directly from lakes or processed from sediment and analyzed on-chip.
Figure 1. of (Successful) ASTID Proposal
“Lab-on-a-Chip System Development for Titan Exploration”
**Fluorocur PFPE Pumps**

Max abs. rate: 4 µL/sec
4mL / 1000sec
40mL / 10,000 sec
40mL / 2.8 hours

Time to fill an Electrode Well (20 µL) is 5 sec

shown above are measured pumping rates before and after one million actuations and thirty temperature cycles from -50C to +50C
How μCE Works

Three Mechanisms at play:
*Diffusion, Electrophoresis, and Electroosmosis*

\[
\frac{dc}{dt} + \nabla \cdot \left[ D \nabla c z_i \mu_i Fc \nabla V + cu \right] = 0
\]

*this is what separates a charged mixture into its components*
Laser Induced Fluorescence Detection of Labeled Amino Acids

5 mM Borate pH = 8.5
5 amino acids mixture - $E_{\text{SEP}} = 5$ kV

Intensity vs. Time (sec)

- 20 nM
- 10 nM
Micro-capillary electrochromatography (μCEC) enables separations of neutral species through surface interactions with solid phase filling channels.
Where we are going: \( \mu \)CEC of PAHs

And CHIRAL resolution of amino acids

And Sending Everything into a Mass Spectrometer

N.B. Phase II SBIR with LGR to add spectroscopic second dimension and package portable unit

Extra Slides
Interfacing Lab-on-a-Chip With Mass Spectrometry

Label-free detection/identification of analytes

Electrospray Process

- Taylor Cone
- High Voltage Power Supply
- REACTION

PicoTip™ commercial product

300nL/min
30/70 water/acetonitrile
or 50/50 water/methanol
1.4-3.0 kV bias

m/z of MH⁺ Ions Displayed

Valine 118
Glutamic Acid 148

Glycine 76
Serine 106
Aspartic Acid 134

Mass spectrum of five amino acids produced via nanoelectrospray ionization of methanol/water solution
New LC-MS system
Note: all sprays so far have been driven by mechanical or pneumatic pressure, and have been pure samples.
Extra Slides: Mars Analyses
Field Testing in the Atacama Desert, Chile

demonstrated prototype operation in Mars analog relevant environment

differentiated between high and low concentration organic samples

**Phoenix Analogue Experiment**

### RESULTS FROM PHOENIX MARS LANDER

Measured concentrations of ionic species in Rosy Red soil sample. Assumes delivery of a 1cm³ sample with density of 1g/cm³.

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>Concentration in Cell, mM</th>
<th>Est %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺</td>
<td>2.9 (±1)</td>
<td>?</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.6 (±0.3)</td>
<td>3-5*</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.4 (±0.5)</td>
<td>0.10</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.4 (±0.2)</td>
<td>0.03</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>2.6 (±1)</td>
<td>0.75</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.6 (±0.2)</td>
<td>0.04</td>
</tr>
<tr>
<td>pH</td>
<td>7.7 (±0.3)</td>
<td></td>
</tr>
</tbody>
</table>

*From TEGA Analysis

### MARTIAN ANALOGUE SAMPLE

We prepared a sample containing the soluble salts reported by the Phoenix Lander. We also included an ionic sulfate species**. Sample was spiked with 1µM Trp amino acid (200 ppb).

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>Concentration in Analogue, mM</th>
<th>Ion Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺</td>
<td>2.9</td>
<td>MgSO₄</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.6</td>
<td>CaCl₂</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.6</td>
<td>NaClO₄</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.4</td>
<td>KCl</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>2.6</td>
<td>NaClO₄</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.6</td>
<td>KCl, CaCl₂</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.9</td>
<td>MgSO₄</td>
</tr>
<tr>
<td>Total</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

**Presence of sulfates in the Martian regolith has been reported by analysis of data from MOC, OMEGA, MER Opportunity, and MSG TES instruments.
Phoenix Analogue Experiment
(Preliminary Data)

Significant finding: electrospray MS tolerated mM salt concentration in buffer -- Tryptophan was detectable even at the parent ion mass/charge.


We need to do MS-MS analysis underway to determine what these peaks are.