MULTI-LAYER MICROFLUIDIC DEVICES FOR AMINO ACID ANALYSIS: 
THE MARS ORGANIC ANALYZER

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Requirements for Extraterrestrial Life

1. Liquid Water

- Mars Global Surveyor: Mars Orbital Camera detected gullies\(^1\) \(\rightarrow\) liquid water on Mars in geologically recent past

- Mars Exploration Rover Opportunity: Mössbauer spectrometer detects jarosite\(^2\) \(\rightarrow\) only formed in the presence of liquid water

2. Bioorganic Molecules

- Viking 1 and 2: carried GCMS but no conclusive signs of life detected

- Further experiments by Benner et al. suggest that the Viking GCMS would be unable to detect highly oxidized organics

In situ Biomarker Analysis: What do we look for and how do we do it?

Potential bioorganic signatures:
• Large biomolecules: likely degraded by oxidizing surface environment of Mars
• Amino acids: longer lifetimes in dry, harsh conditions
• Chirality: indicative of origin:
  • Racemic mixture – abiotic origin
  • Non-racemic mixture – biological origin

Amino acid analysis using microchip CE:
• Electroosmotic flow (EOF) all molecules to cathode
• CE separates amino acids based on charge/size ratio
• Cyclodextrins: provide enantiomeric resolution of amino acids:
  
  \[ \text{L-aa} + \text{CD} \rightleftharpoons \text{L-complex} \quad (K_L) \]
  
  \[ \text{D-aa} + \text{CD} \rightleftharpoons \text{D-complex} \quad (K_D) \]
  
  \[ K_L \approx K_D \]

• Microchip platform allows integration of CE and microfluidics
Sample Collection to Analysis: Mars Organic Detector (MOD) and Mars Organic Analyzer (MOA)

Key stages for analysis:

1. Soil sample obtained by MOD, amino acids extracted by sublimation

2. Amino acids labeled on MOD cold finger with fluorescamine

3. Labeled amino acids delivered to CE using microfluidic capabilities of MOA

4. Composition and chirality

Development of Portable CE Instrument: Mars Organic Analyzer (MOA)

- Portable instrument: all electronics, pneumatics, CE power supplies, optics
- Total mass ~ 11 kg, peak power consumption ~ 15 W
- Confocal optics provide excellent imaging of microfabricated channel
- Custom-built objective gives NA ~ 0.9
- 100 um-diameter fiber optic acts as pinhole and passes fluorescence to PMT
Microfabricated device contains 2 separation channels (red)

Each separation channel: microfluidic bus (blue) for sample handling, pumps for filling and emptying separation channel

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• Microfabricated channels formed by bonding 2 glass layers together
• Microfabricated pumps formed by combining 2 glass layers with a PDMS membrane
Lab-Based Characterization of MOA

- Microfabricated CE analyzer has demonstrated pM and parts-per-trillion sensitivity

Injection Style | LOD  | ppb (1 g soil) |
---|---|---|
Cross Injection | 13.3 nM | 0.50 |
2 s Direct Injection | 1.33 nM | 0.050 |
10 s Direct Injection | 133 pM | 0.0050 |

A.M. Skelley et al., submitted.
Lab-Based Analysis of Atacama Samples using MOA

- The Atacama Desert, Chile is one of the driest sites on Earth (<0.5 mm H₂O/year) and provides an ideal location for testing biomarker detection instruments.

- Aqueous amino acid extracts of soil samples were analyzed by the MOA in the laboratory.

The MOA successfully analyzed amino acids from soil samples at the dry limit of microbial life.

**MOA analysis of Atacama extracts**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amino Acid</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT01-12</td>
<td>Ala/Ser</td>
<td>0.009 ± 0.006</td>
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<tr>
<td>24.1°S</td>
<td>Gly</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Glu</td>
<td>&lt; blank</td>
</tr>
<tr>
<td></td>
<td>Asp</td>
<td>0.01 ± 0.01</td>
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<tr>
<td>AT01-17</td>
<td>Ala/Ser</td>
<td>0.01 ± 0.02</td>
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<tr>
<td>25.8°S</td>
<td>Gly</td>
<td>0.02 ± 0.04</td>
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<tr>
<td></td>
<td>Glu</td>
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</tr>
<tr>
<td></td>
<td>Asp</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>AT01-22</td>
<td>Val/γ-ABA</td>
<td>0.56 ± 0.04</td>
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<tr>
<td>28.2°S</td>
<td>Ala/Ser</td>
<td>0.17 ± 0.02</td>
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<tr>
<td></td>
<td>Gly</td>
<td>0.32 ± 0.07</td>
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<tr>
<td></td>
<td>Glu</td>
<td>0.36 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>Asp</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>

All values are blank corrected.


2) A.M. Skelley et al., submitted.
Field Testing of MOD-MOA on Mars-Like Samples

• Field testing of the MOD-MOA instrument was performed in the Panoche Valley, CA.

• The Panoche Valley has high levels of jarosite, a mineral recently detected on Mars that indicates the planet was once wet.

• Samples were ground, sublimed by MOD, transferred to the MOA using the sipper and microfabricated pumps, and analyzed for amino acid composition in the field.

• MOD-MOA combination successfully analyzed amino acids from jarosite in the field.

• Significant amino acid biomarkers are found in acidic jarosite soils.

A.M. Skelley et al., submitted.
The fully integrated MAP has been selected for the 2009 ExoMars (ESA) missions and is in competition for the Mars Science Lander (MSL - NASA) mission.
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For more info:
http://astrobiology.berkeley.edu