

Sensitive Amino Acid Composition and Chirality  
Analysis in the Martian Regolith with a  
Microfabricated *in situ* Analyzer

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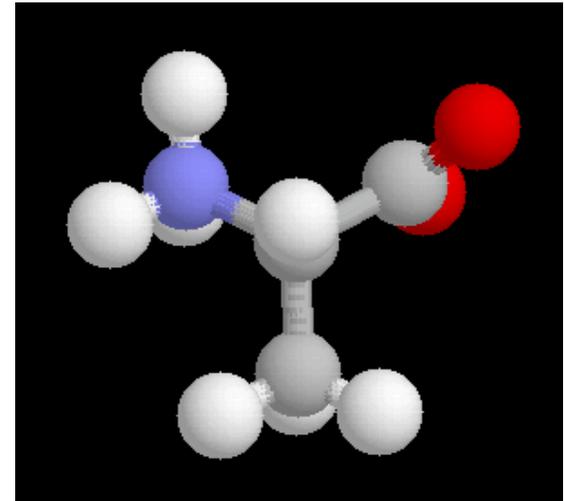
# Why *in situ* Amino Acid Composition and Chirality Analysis?

## Potential Bioorganic signatures:

- Large biomolecules likely degraded by oxidizing surface environment of Mars
- Amino acids have a longer lifetimes in dry, harsh conditions
- Amino acids have been found in Martian meteorites
- Amino acid chirality is indicative of origin:
  - Racemic mixture – abiotic origin
  - Non-racemic mixture – biological origin

## Why *in situ* analysis:

- Significant contamination of Meteorites found on earth by terrestrial sources of life
- Sample return missions are more technologically challenging, costly and time consuming



L-alanine



Allan Hills Meteorite

# Composition and Chirality Analysis through CE

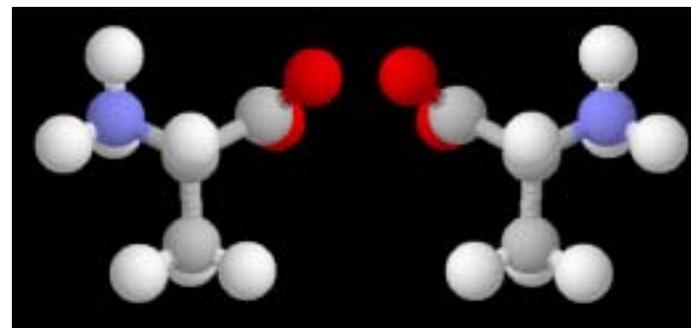
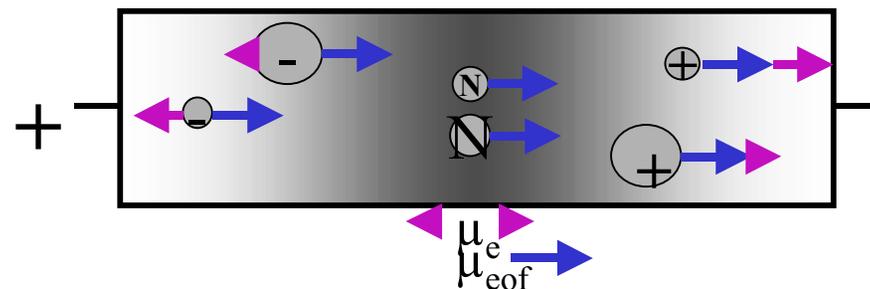
•Electroosmotic flow (EOF) sweeps all molecules to the cathode

•CE separates amino acids based on charge/size ratio

•Cyclodextrins included in running buffer provide enantiomeric resolution of amino acids :

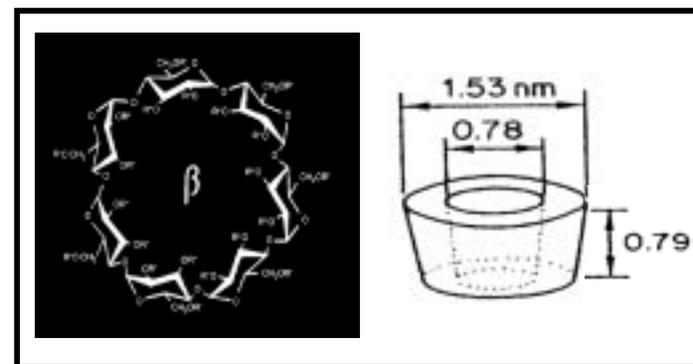


$$K_L \cong K_D$$



L-alanine

D-alanine



$\beta$ -cyclodextrin

# Composition and Chirality Analysis through CE

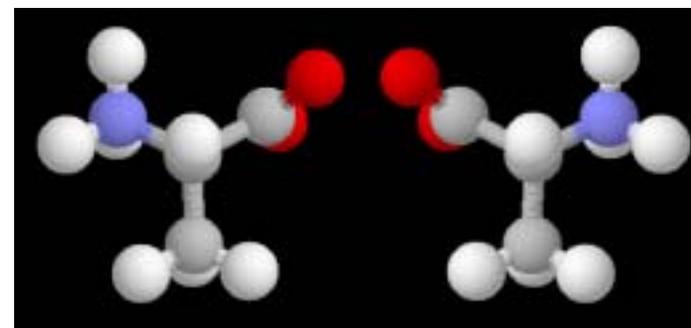
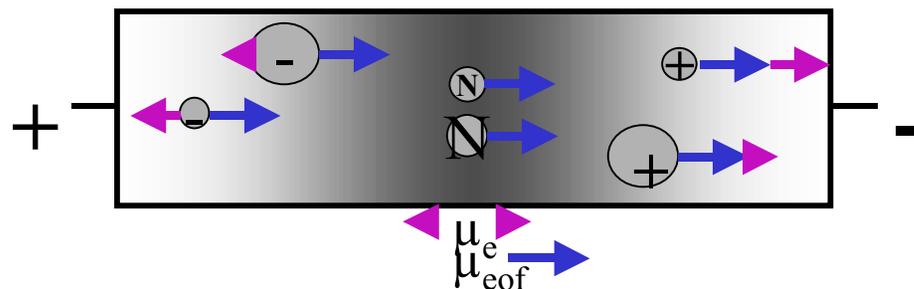
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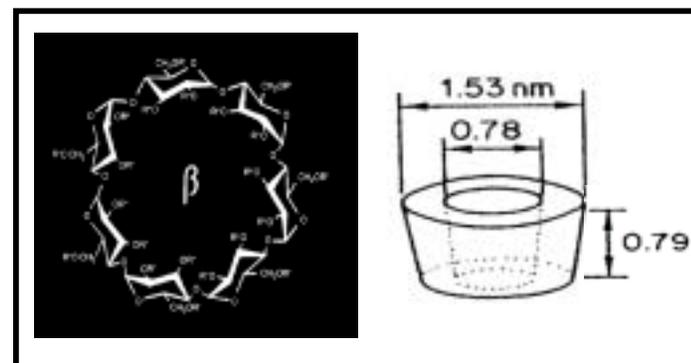


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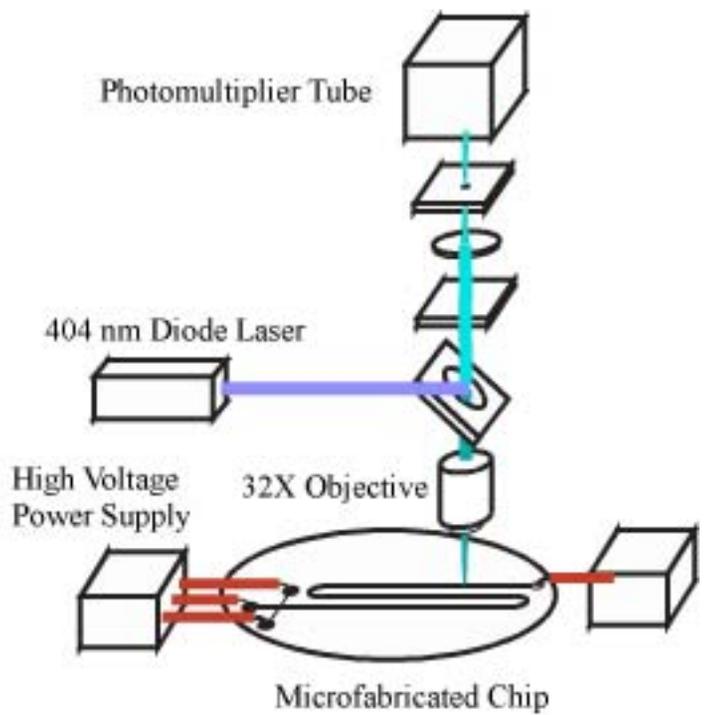
L-alanine

D-alanine

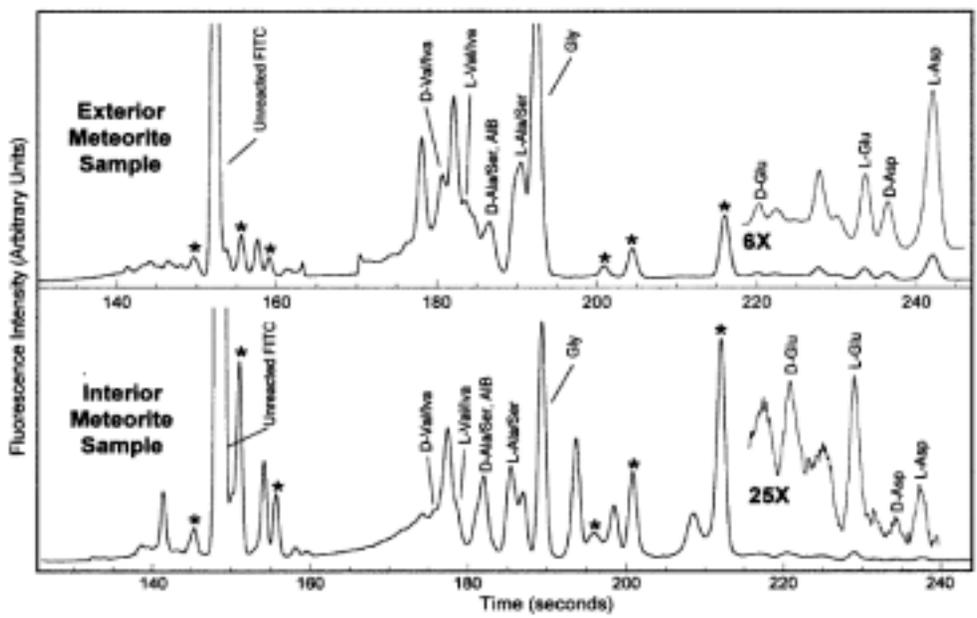


β-cyclodextrin

# Established Separation and Microscope Detection System



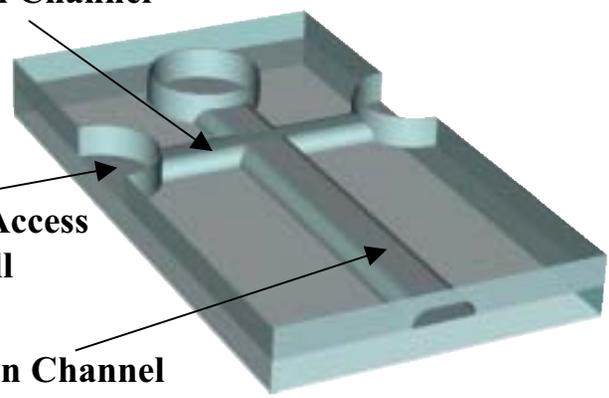
Analysis of Fluorescein-labeled Amino Acids



Injection Channel

Drilled Access Well

Separation Channel



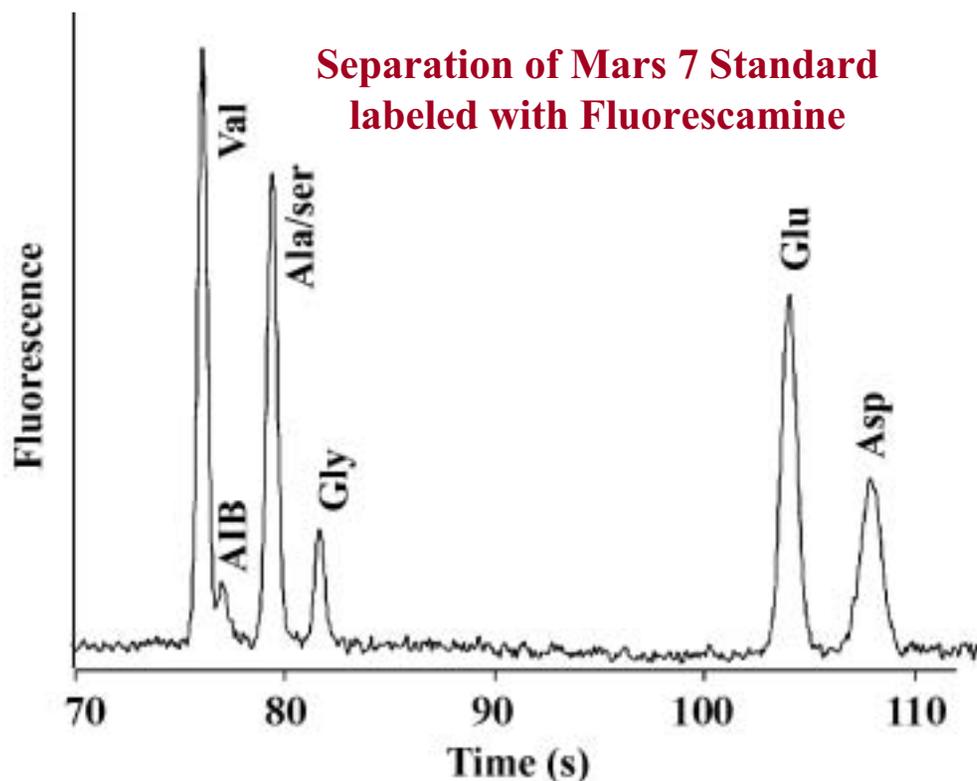
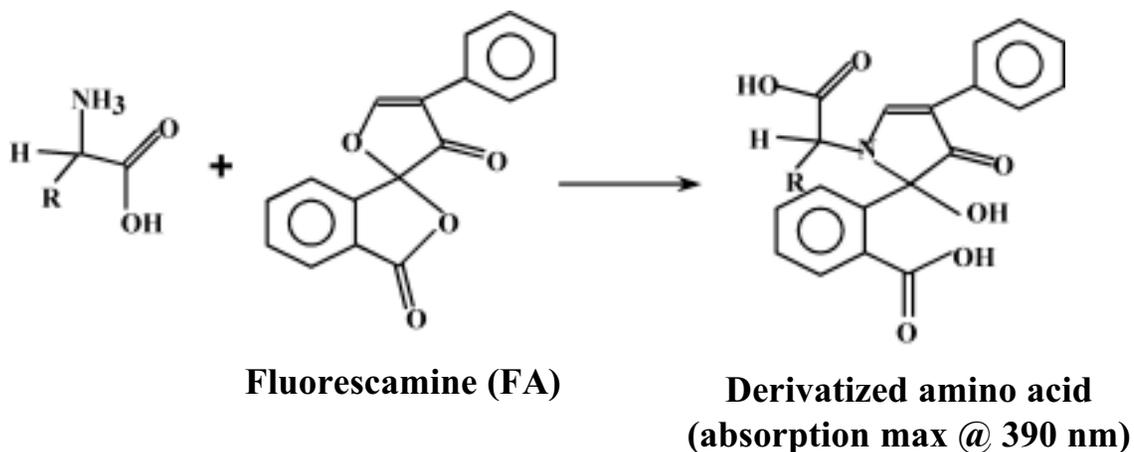
Murchison Meteorite Glu and Asp D/L values

| Amino Acid | HPLC      | Microchip CE |
|------------|-----------|--------------|
| <b>Glu</b> |           |              |
| Exterior   | 0.3 + 0.1 | 0.33 + 0.04  |
| Interior   | 0.7 + 0.1 | 0.65 + 0.07  |
| <b>Asp</b> |           |              |
| Exterior   | 0.3 + 0.1 | 0.21 + 0.03  |
| Interior   | 0.3 + 0.1 | 0.30 + 0.06  |

# Separation of Fluorescamine-labeled Amino Acids

## Benefits of Fluorescamine:

- Fluorogenic reagent
- Reaction time ~1 min
- ~ 50 nM LOD attainable

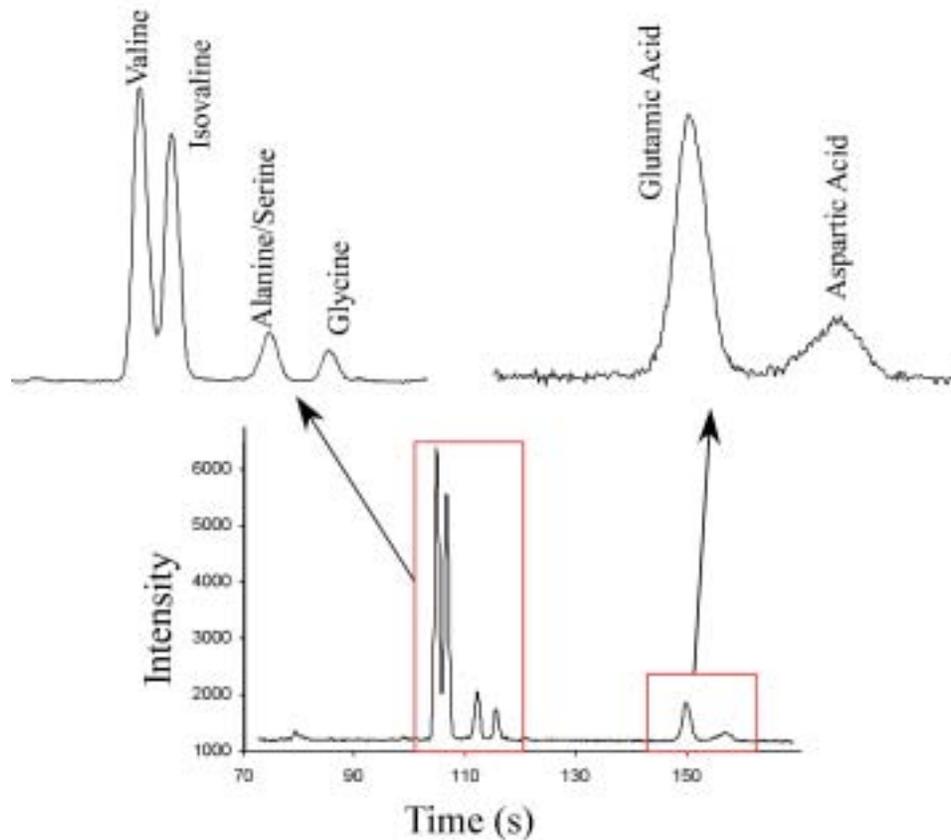


## Run Conditions

Inject 30 seconds @ -200 V/cm  
Run 200 seconds @ -750 V/cm  
10 mM CO<sub>3</sub><sup>2-</sup> pH 9.0, 20°C

# Proof of Concept: Sampling from MOD Cold Finger

## Achiral Separation

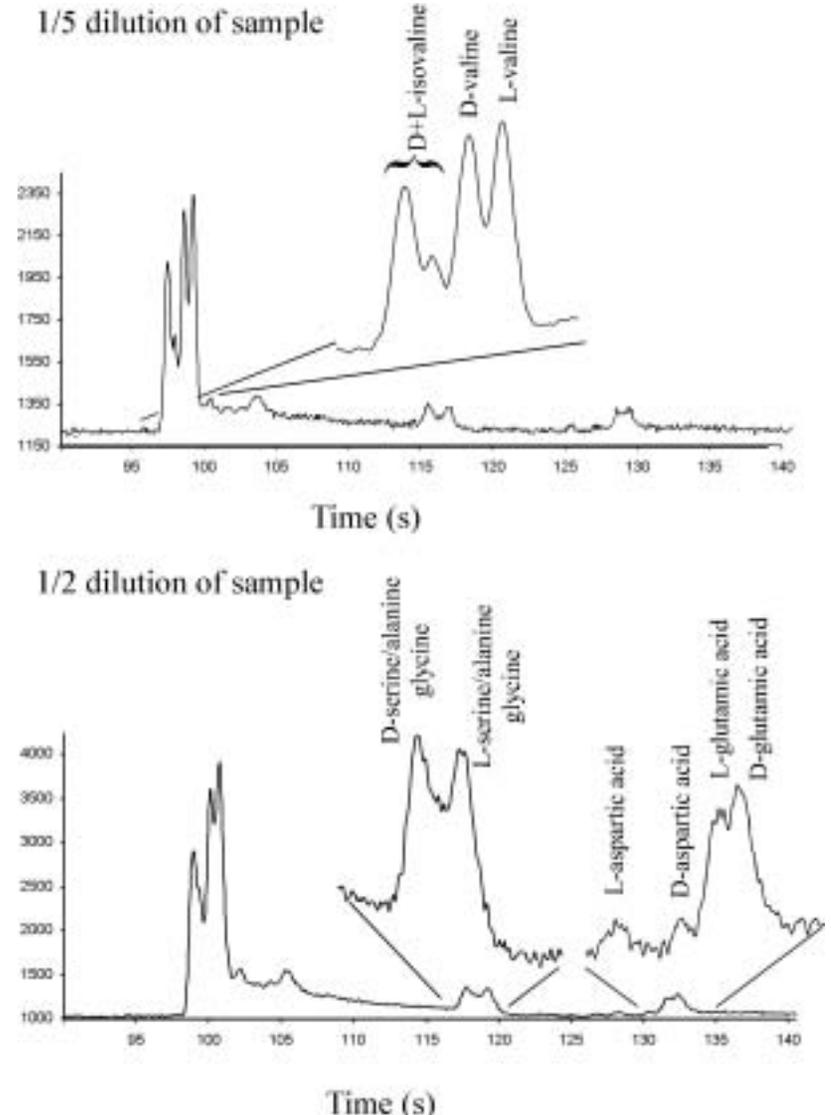


## **Sample preparation:**

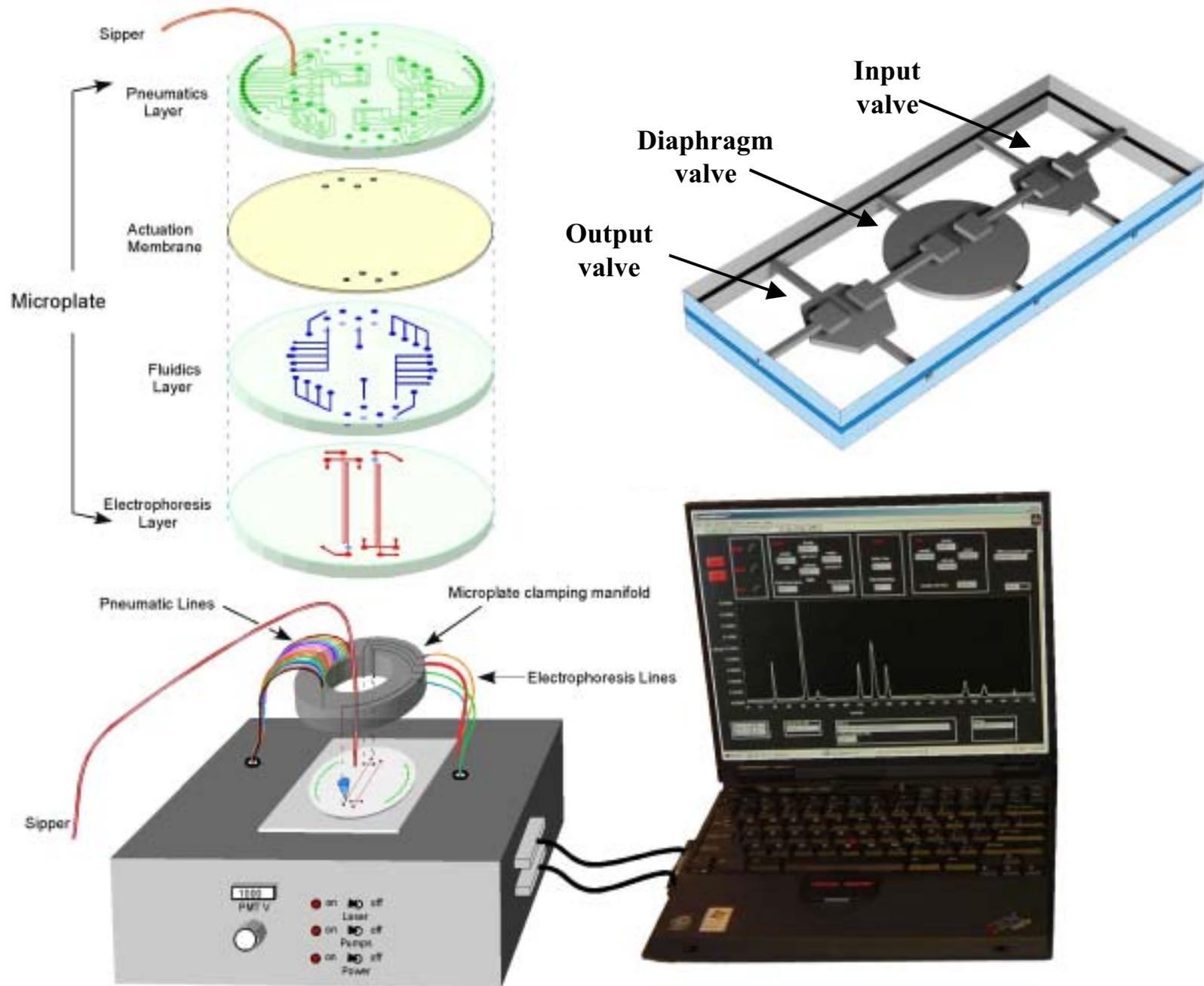
- 1 mL of  $10^{-4}$  M fluorescamine sublimed onto plate
- 1 mL of  $10^{-5}$  M (total aa) sample sublimed onto plate
- 50  $\mu$ L buffer expelled on to chip, collected
- Sample diluted accordingly, loaded into chip

Skelley, A. M.; Mathies, R. A. *J. Chromatogr. A* 2003, 1021, 191-199.

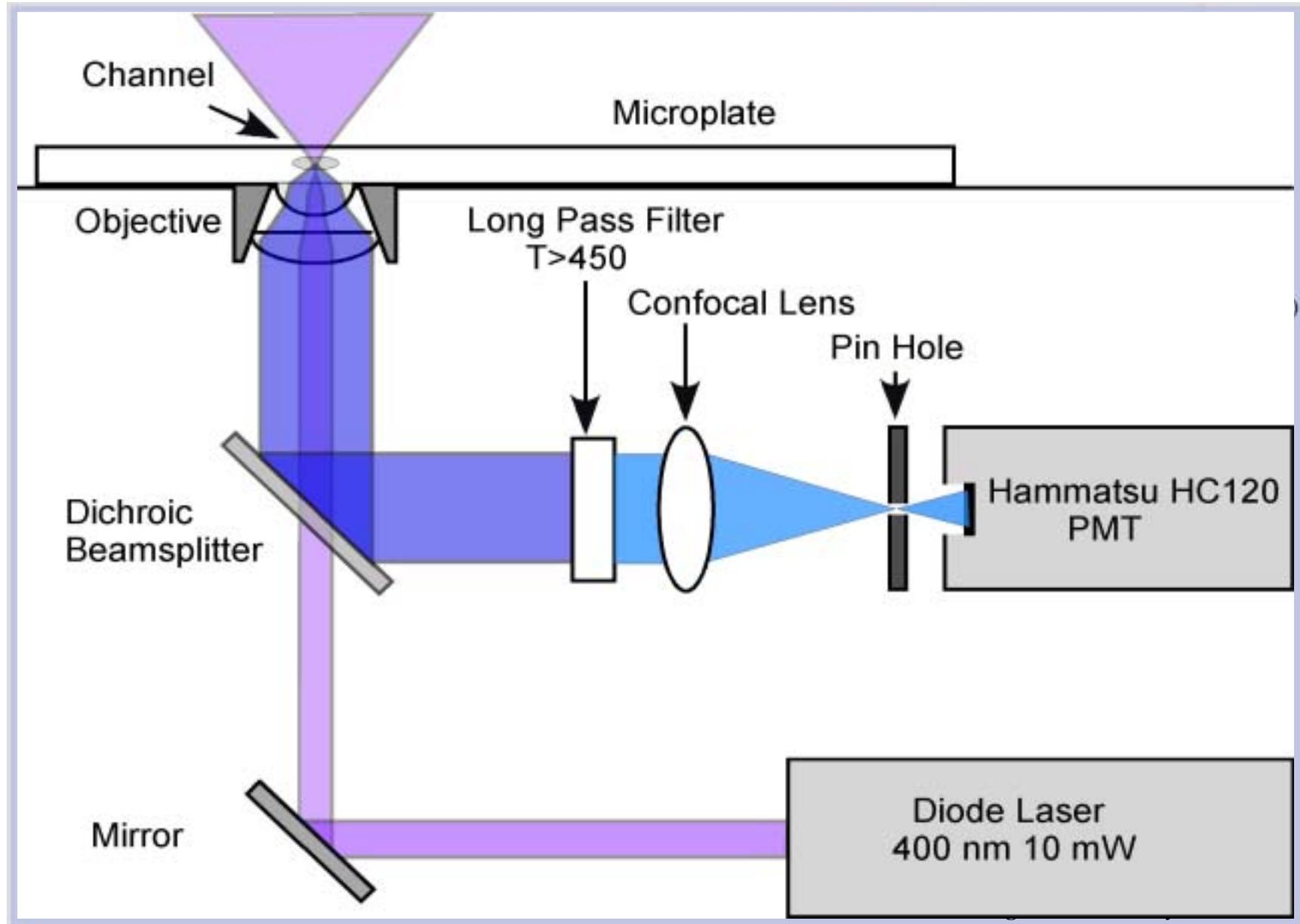
## Chiral Separation



# Mars Organic Analyzer - Schematic

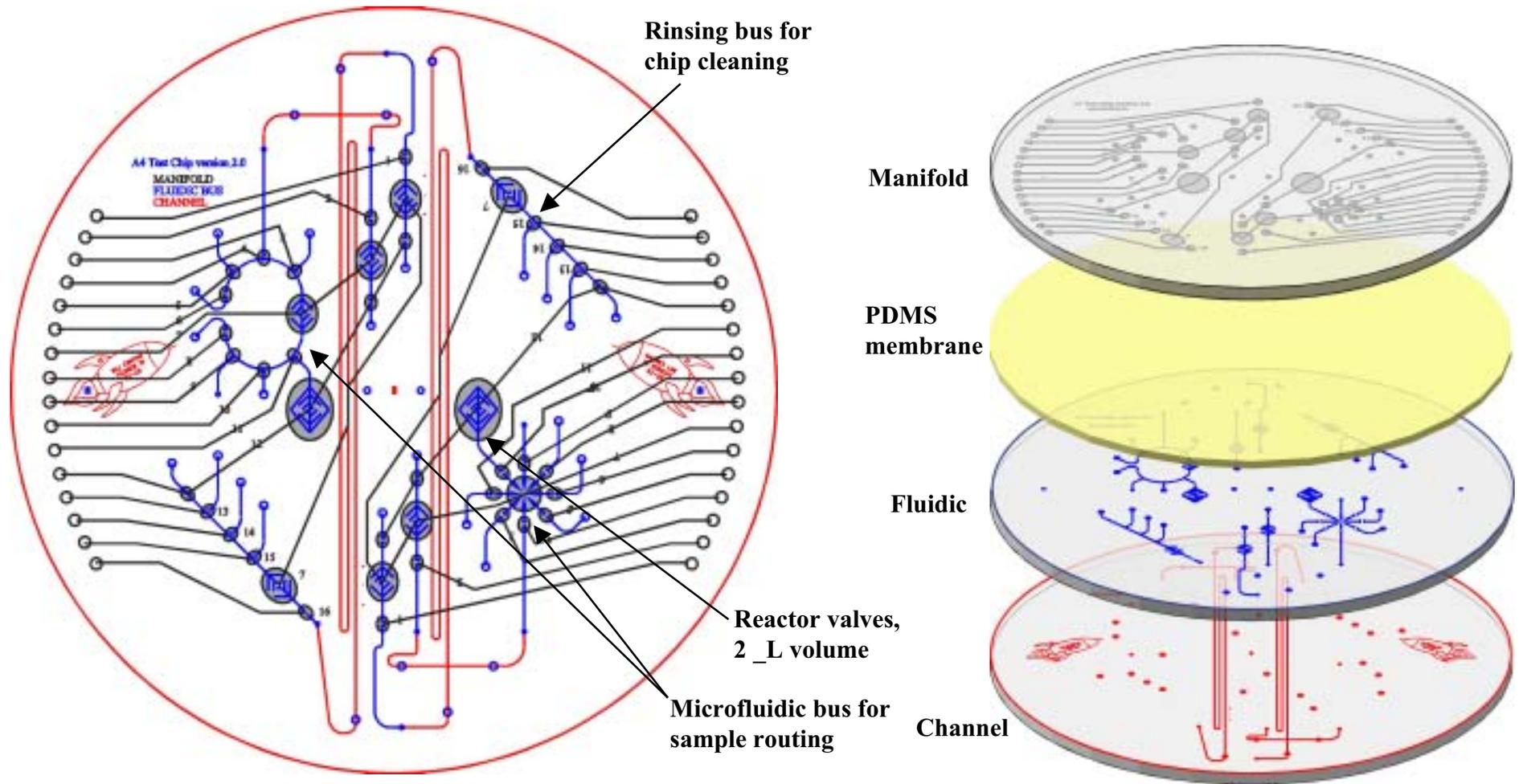


# Mars Organic Analyzer (MOA)



• Portable analyzer for determination of amino acid composition and chirality

# Microfabricated Device



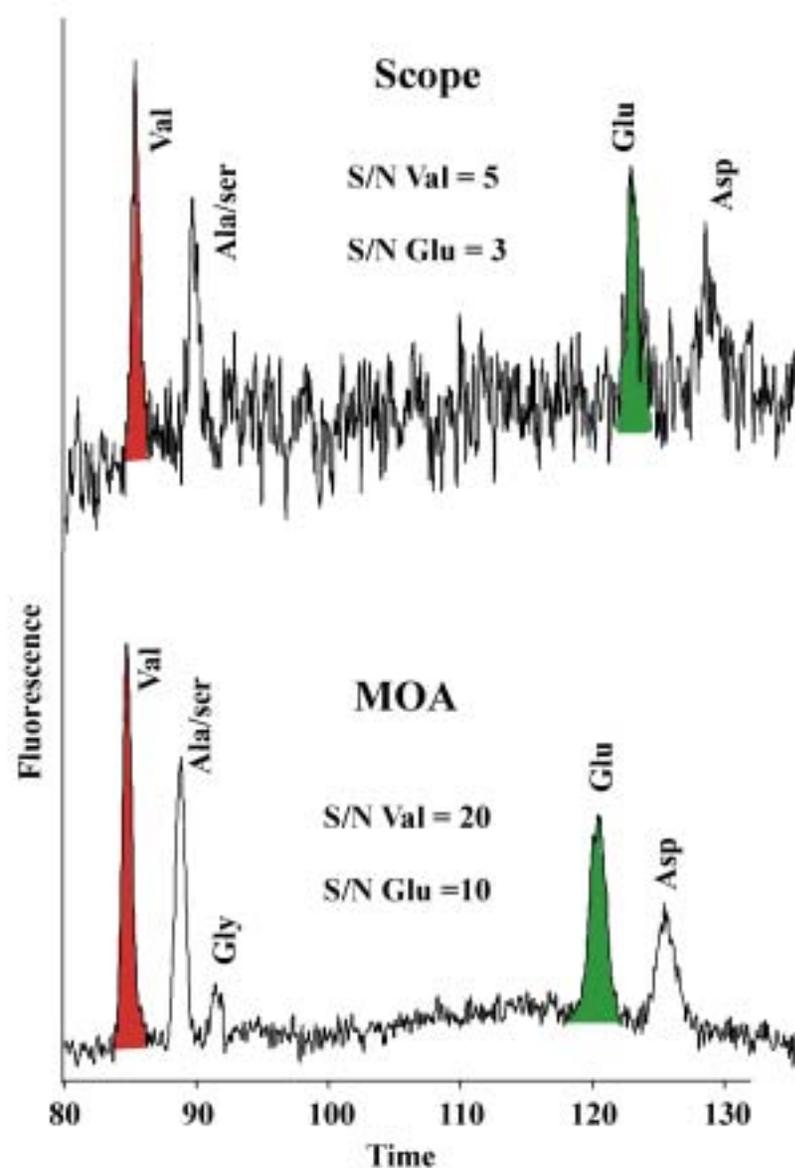
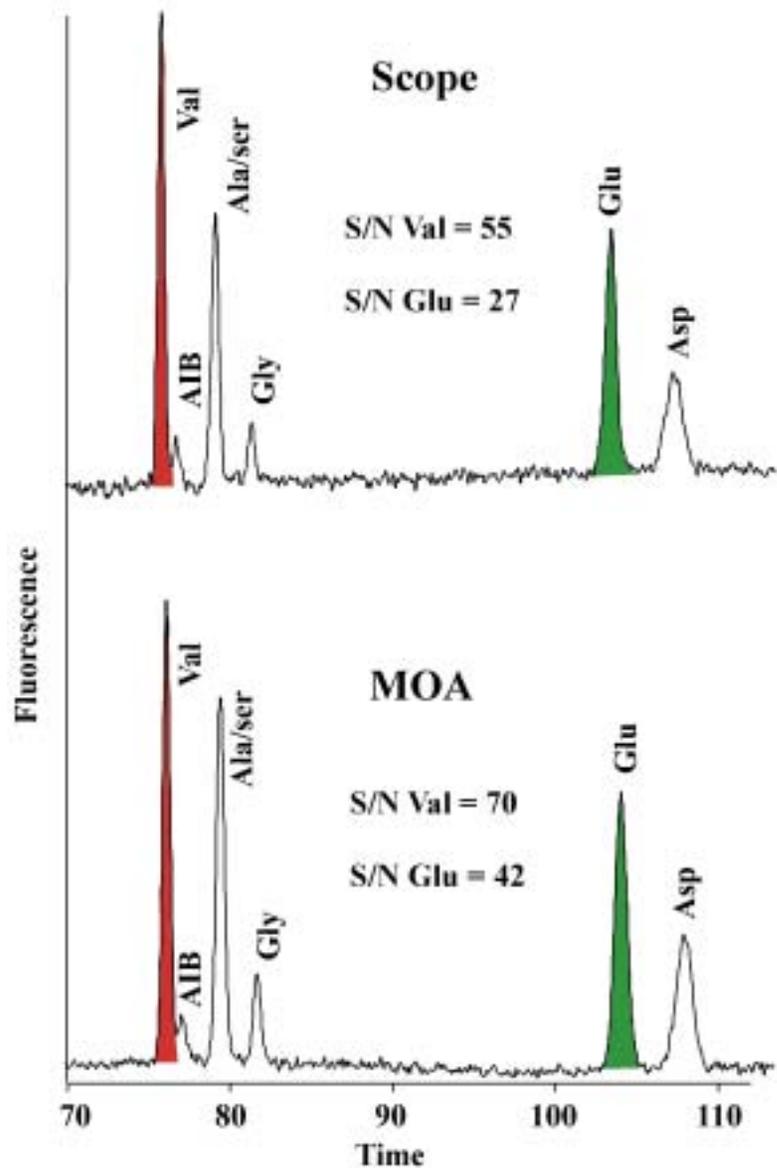
- 4-layer structure, < 4 mm thick
- Diaphragm pumps deliver ~ 1 uL per actuation
- Input/output valves can actuate in under 100 ms
- Flow rates up to 350 nL/s are obtained

- Microfluidic bus has 5 reservoirs for buffer, water, labeling dye, waste, etc., reactor valve and sipper
- Rinsing bus allows device to be used for multiple samples
- 2 separation channels, 21 cm long

# Comparison of Microscope and MOA Systems

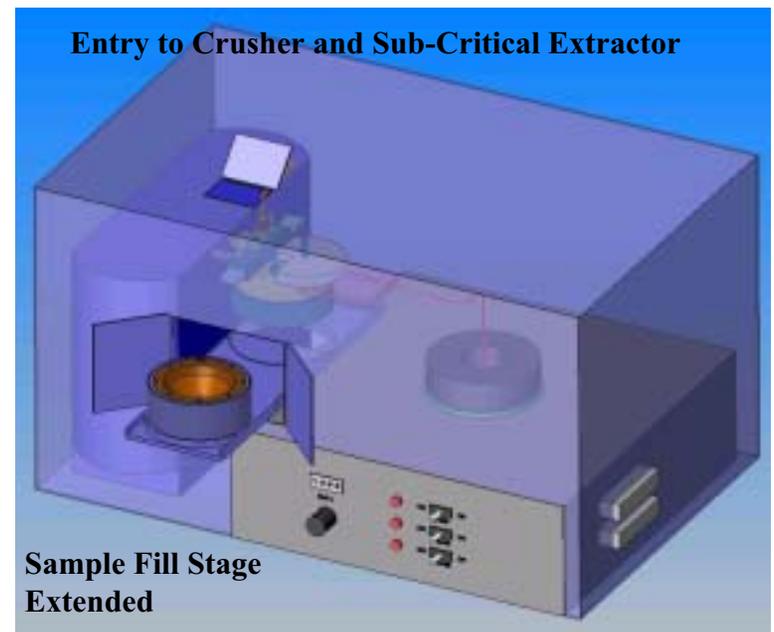
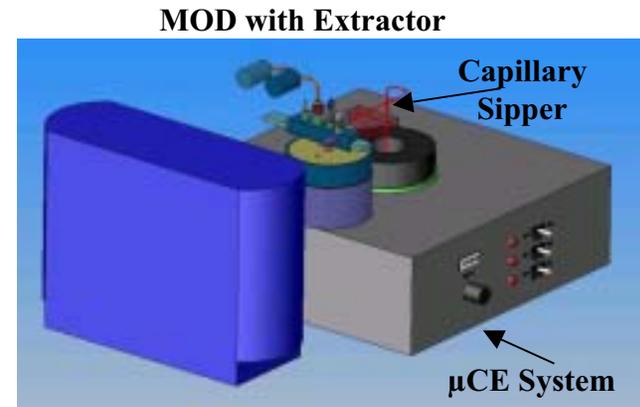
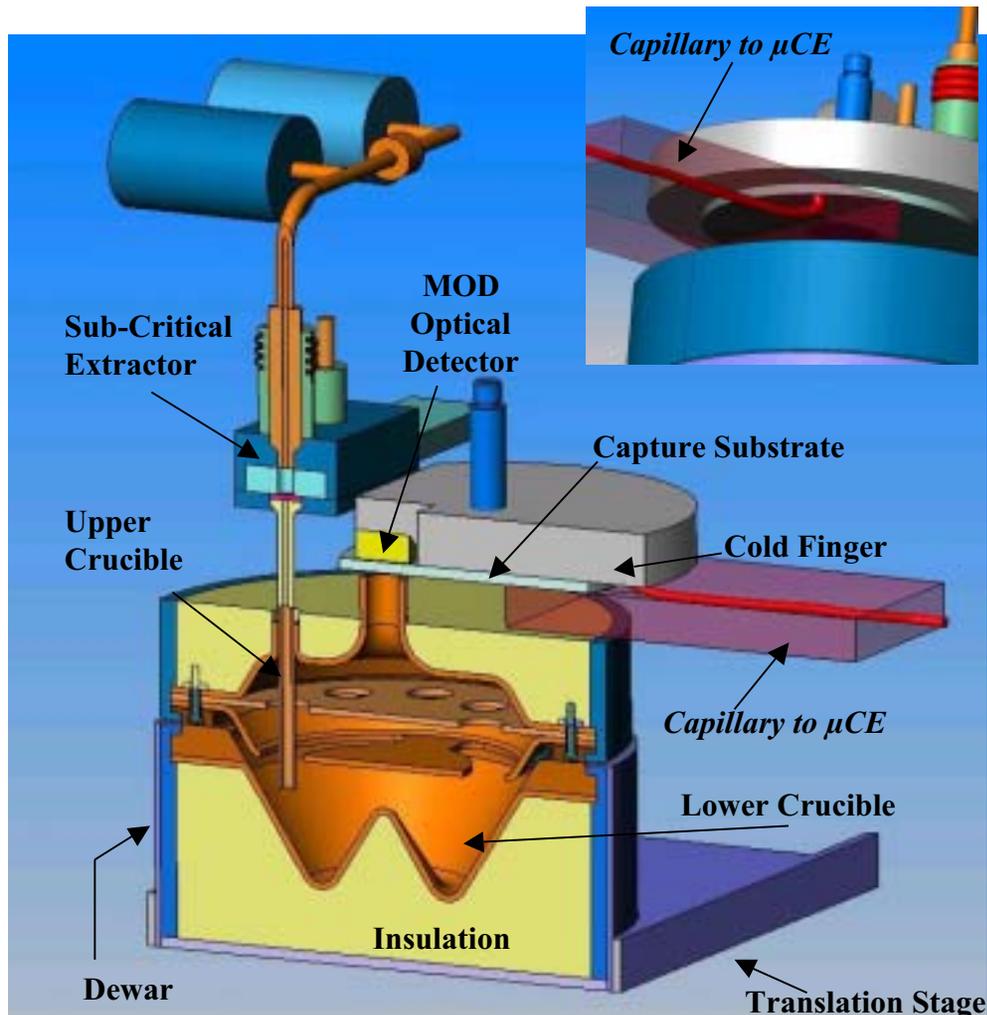
Concentration Val, Glu Injected = 667 nM

Concentration Val, Glu Injected = 133 nM



•MOA system shows superior sensitivity compared to microscope; separation efficiency is maintained

# Integration of MOA and MOD



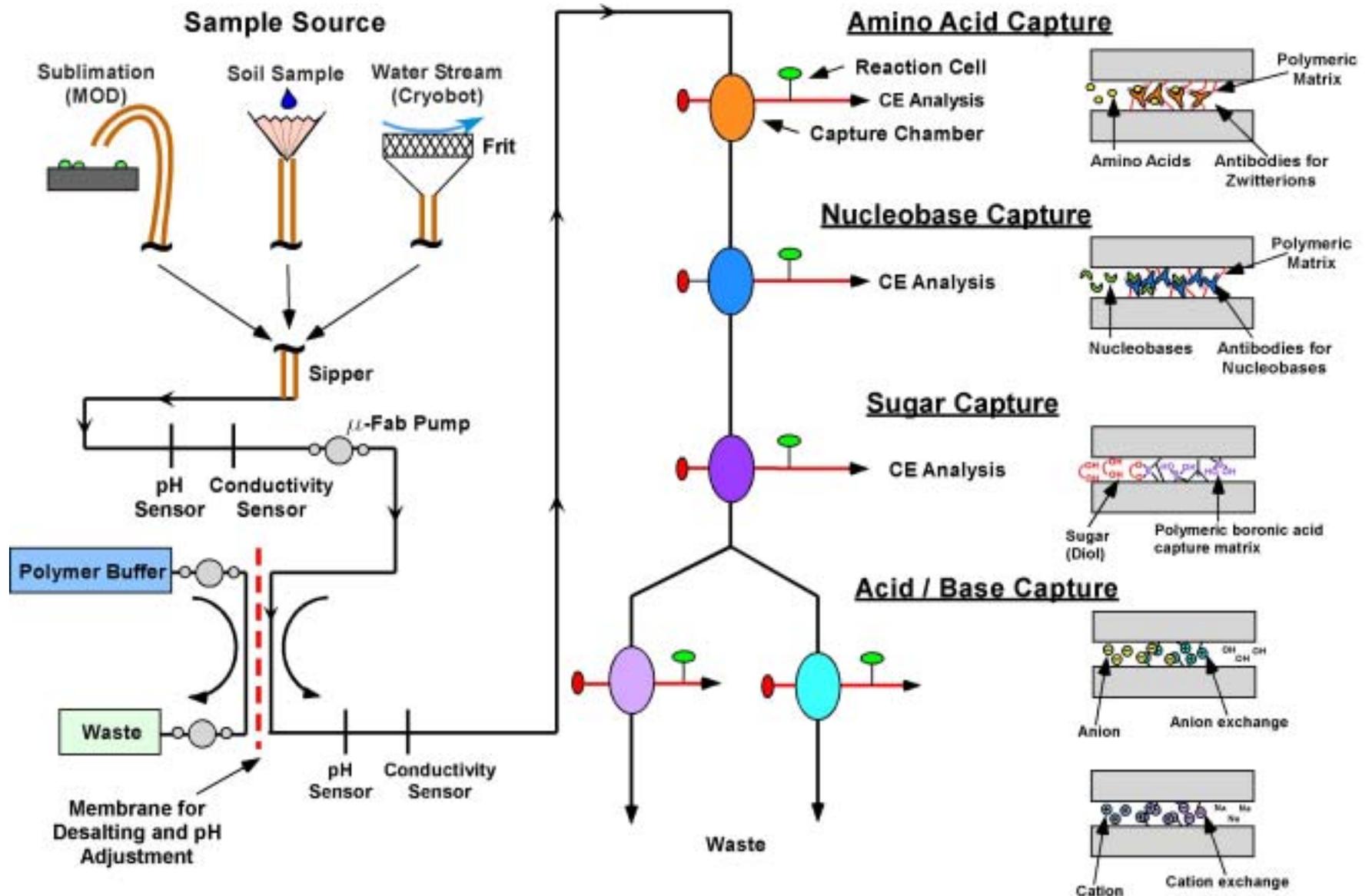
- Field testing of MOA and MOD devices to take place January 2004 in Mojave Desert, CA and February 2004 in Atacama Desert, Chile

# Summary

- **Amino acid composition and chirality is an ideal means for detecting extinct or extant Life on Mars.**
- **Microfabricated CE instrument provides means for sensitive analysis of amino acid composition and chirality.**
- **Portable CE instrument called the Mars Organic Analyzer has shown identical separation efficiency and greater sensitivity than standard lab systems.**
- **Combining microfabricated CE instrument with proven sample extraction efficiency of MOD will provide sensitive analysis of amino acids in Martian soil.**
- **Field tests in Mojave and Atacama Deserts are under way as a critical test of technology readiness and analysis capabilities.**
- **Future work on the development of the Mars Organic Laboratory will target a full suite of bioorganic molecules.**

Funded by NASA, NSERC  
Microfabrication done in UC Berkeley Microlab

# Next Stage – Complete Bio-organic Analysis



# Instrument Overview

