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

Peter Willis

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

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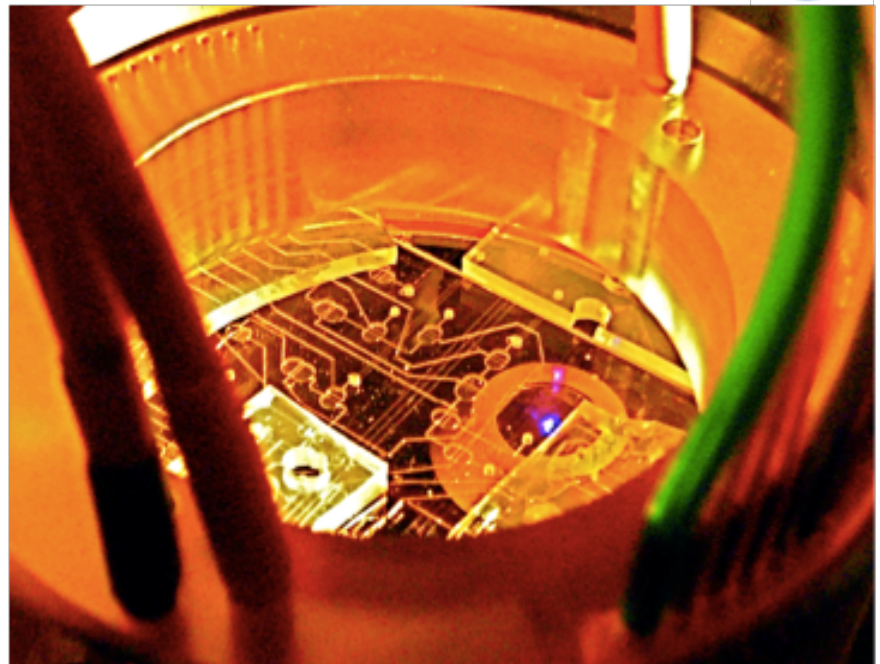
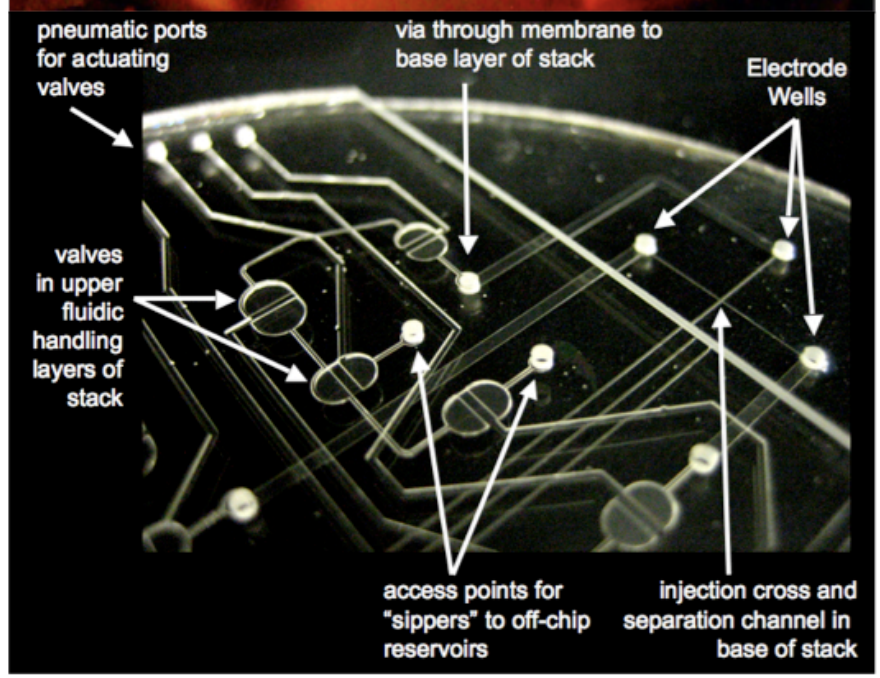




Why choose lab-on-a-chip for spaceflight applications?

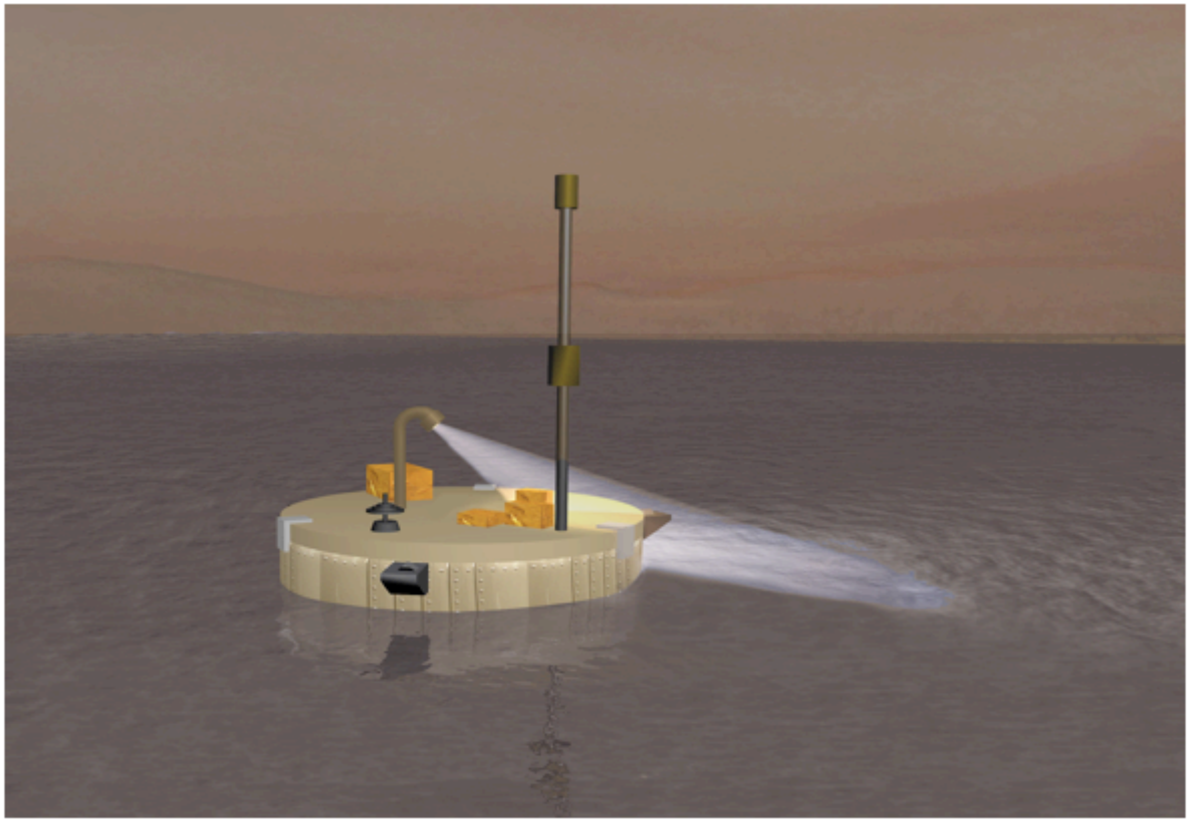
- Low mass, volume, and power requirements (amenable to robotic explorers)
- Fluid motion driven by electric fields or very small pressure differentials (i.e. no pump)
- Extremely sensitive
- Addresses key NASA agency goals
- Requires very little sample (less than a drop)

Key Questions for this workshop:

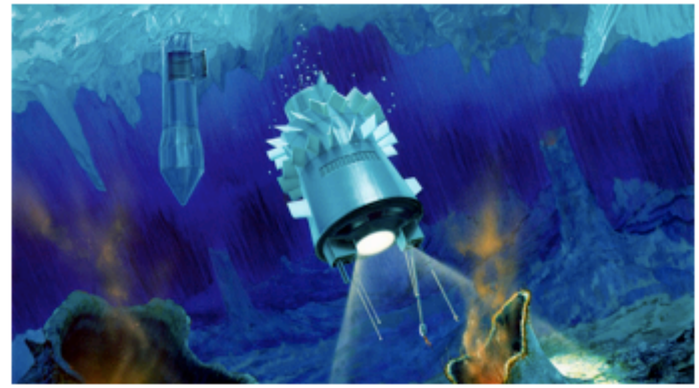
- How is sample handling done on Titan, and how does this affect the sample and analysis protocol?
- What are the specific science goals?

- **lab-on-a-chip instruments** could be designed to function autonomously on the surface of other planets.

Titan



Europa

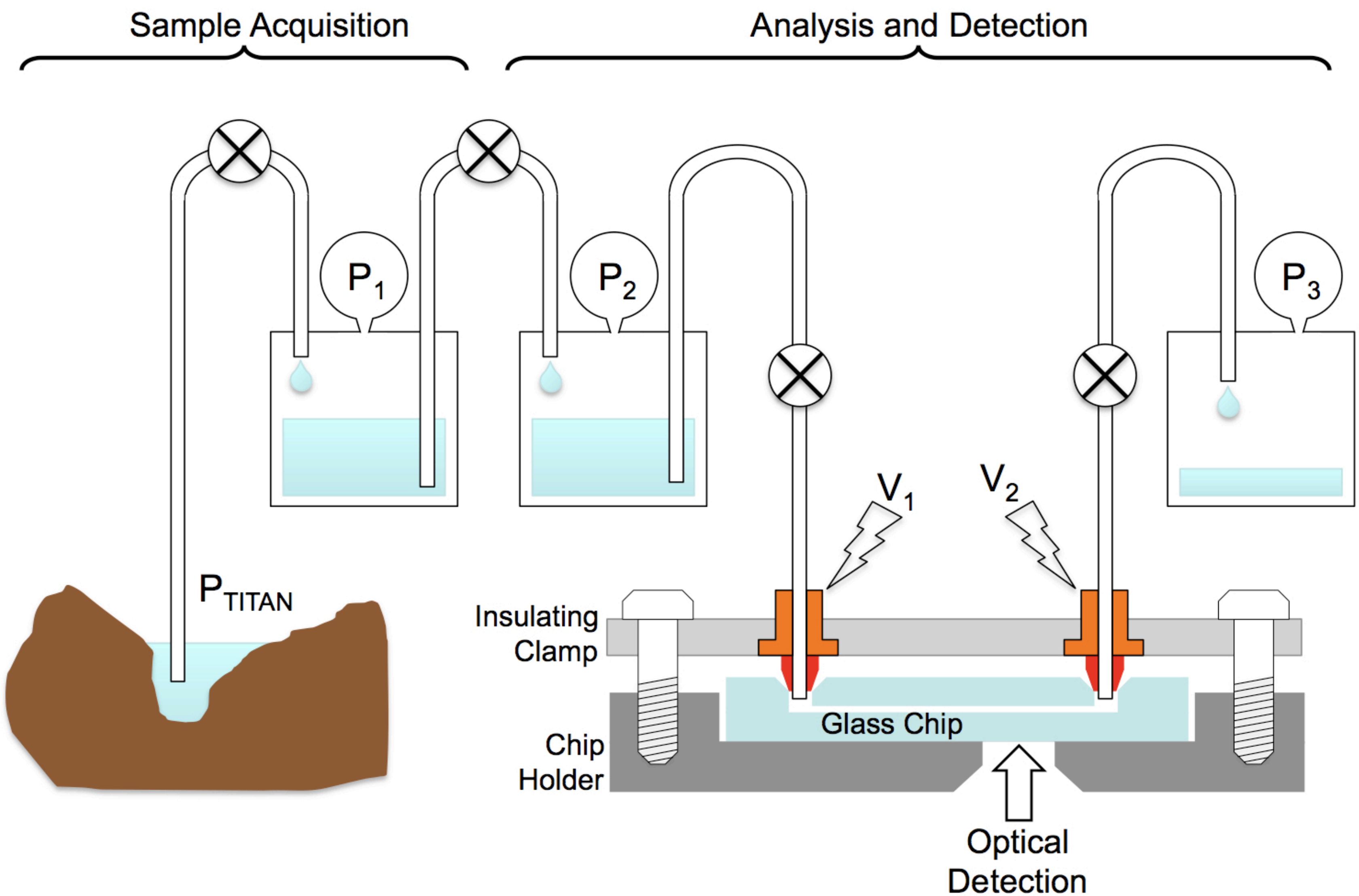


Mars

- For Titan deployment, liquid could be sipped directly from lakes or processed from sediment and analyzed on-chip

Figure 1. of (Successful) ASTID Proposal

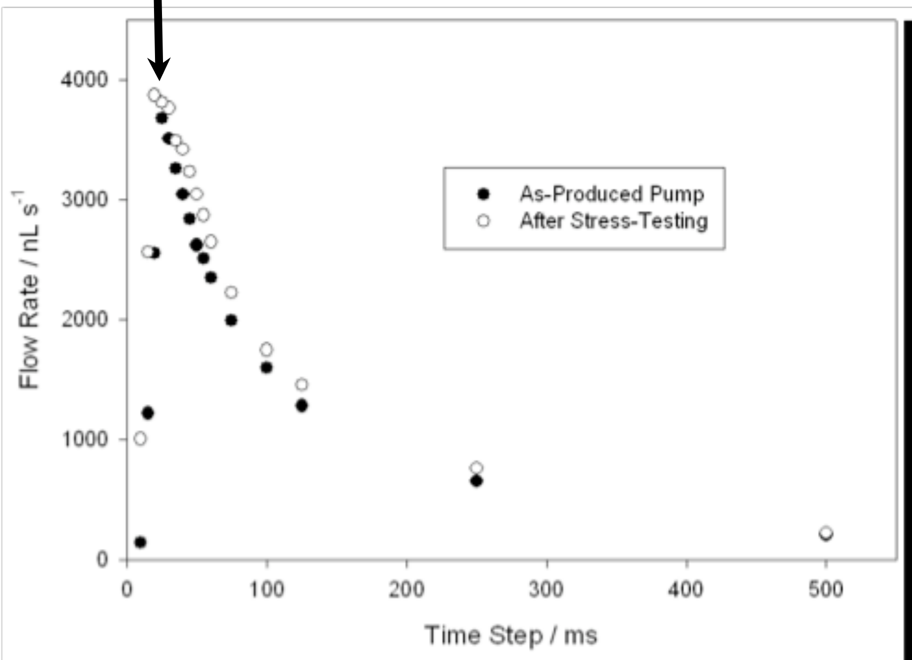
"Lab-on-a-Chip System Development for Titan Exploration"

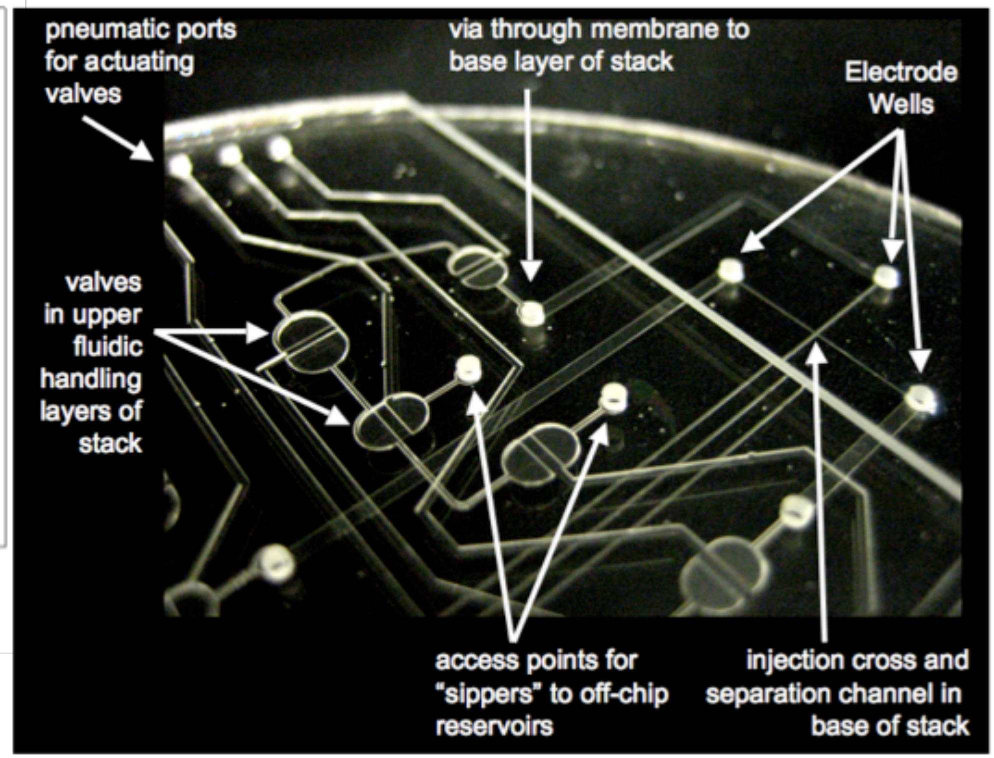


Fluorocur PFPE Pumps

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

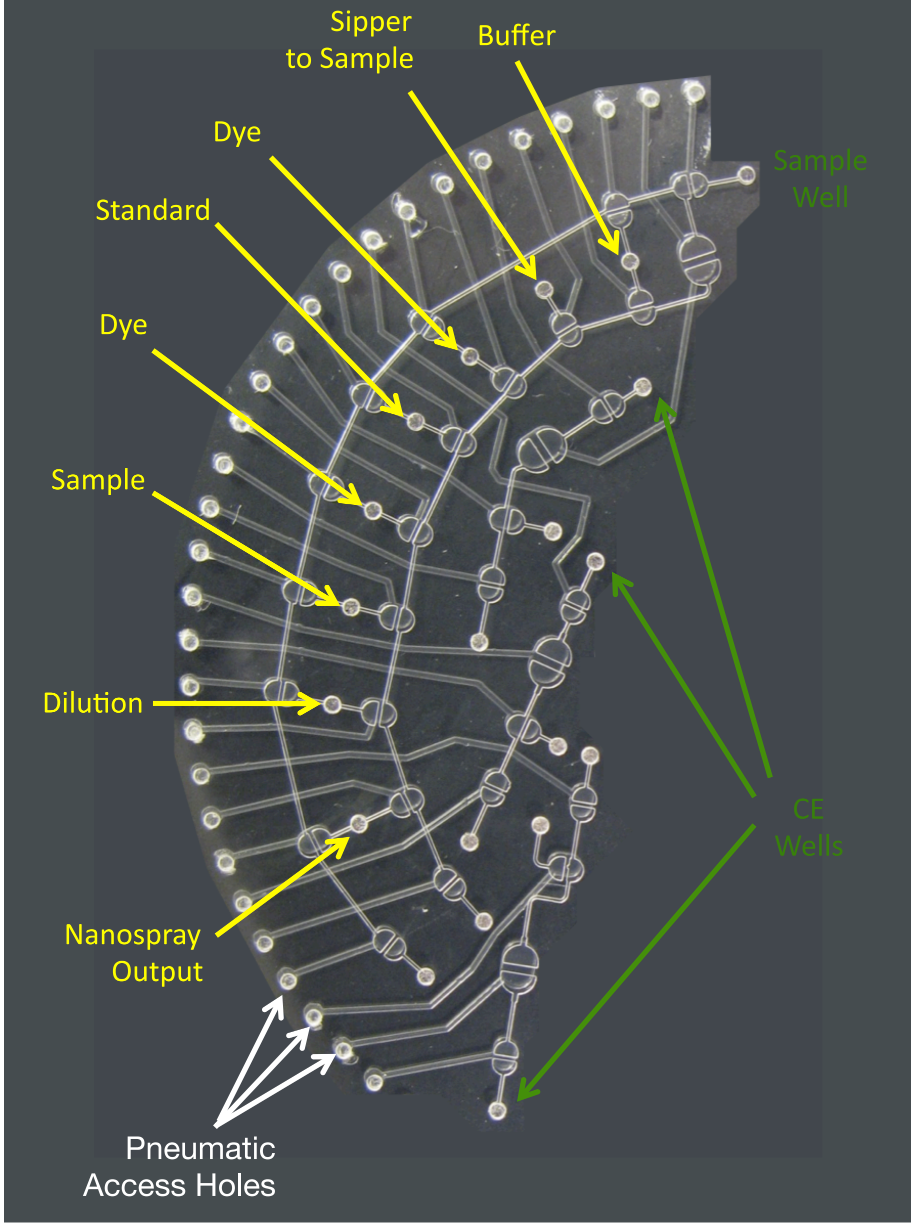
Time to fill an Electrode Well (20 µL) is 5 sec

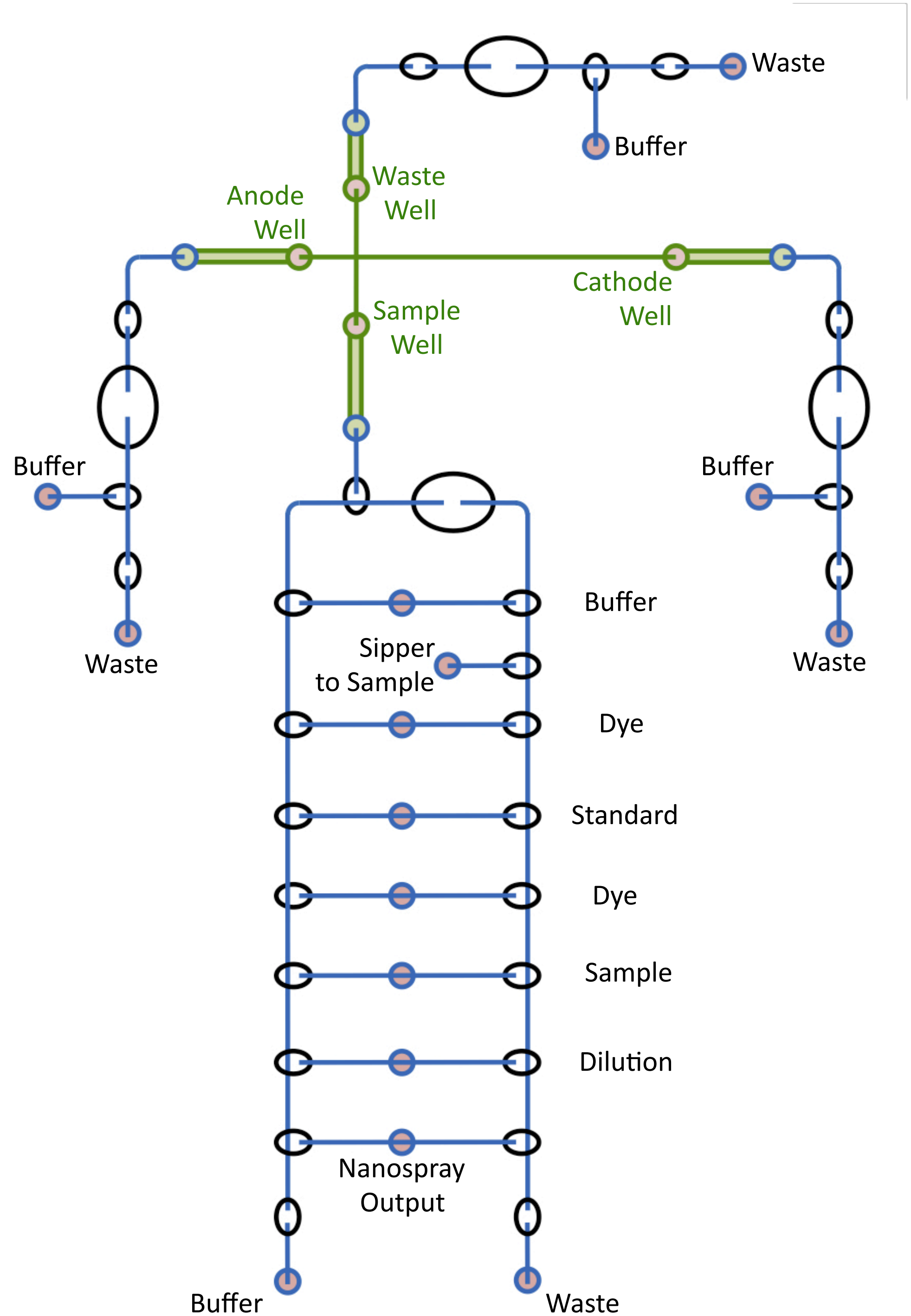




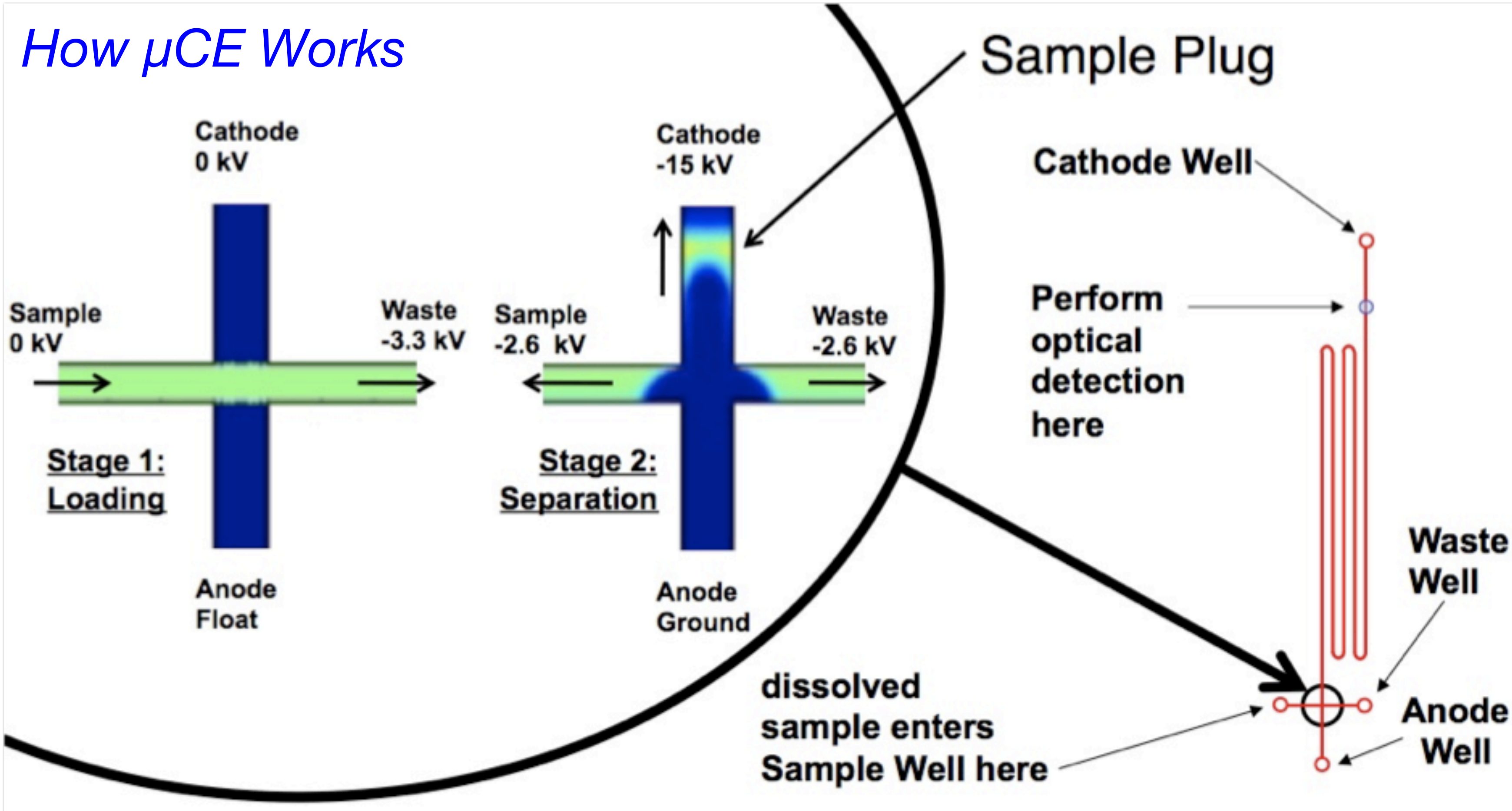
shown above are measured pumping rates
before and after
one million actuations
and
thirty temperature cycles
from -50C to +50C

Fully Automated Fluidic Bus Layout





How μCE Works

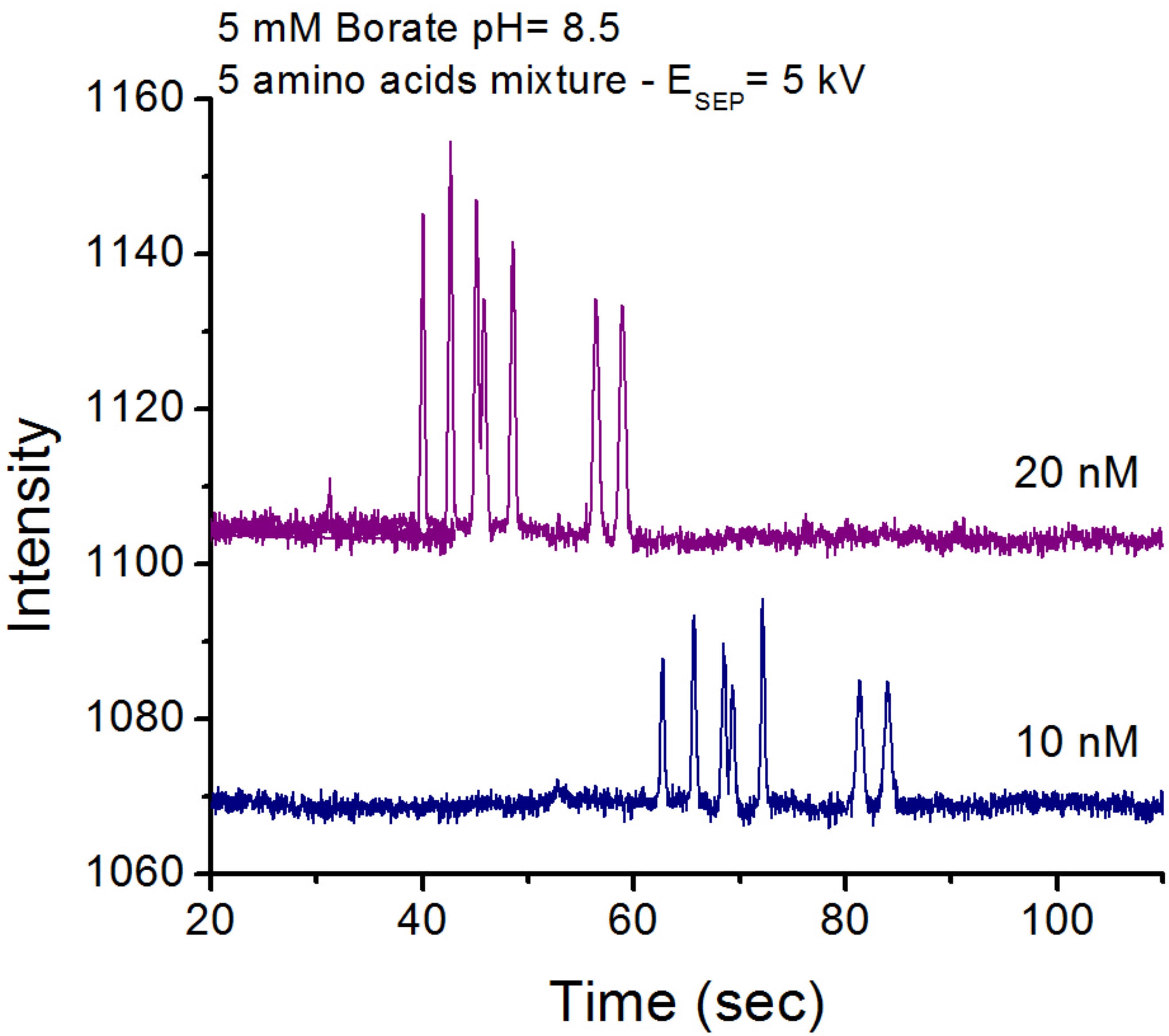


Three Mechanisms at play:
Diffusion, Electrophoresis, and Electroosmosis

$$\frac{dc}{dt} + \nabla \bullet \left[-D\nabla c - z_i \mu_i F c \nabla V + c\bar{u} \right] = 0$$

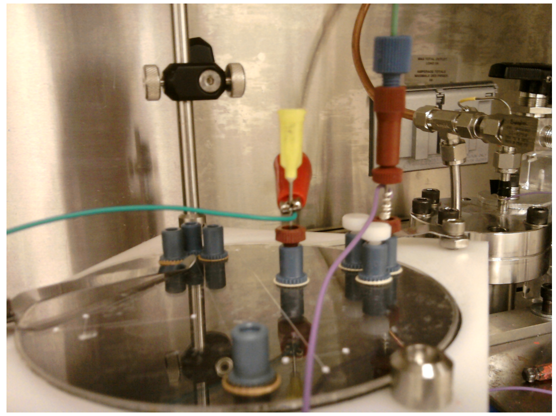
this is what separates a charged mixture into its components

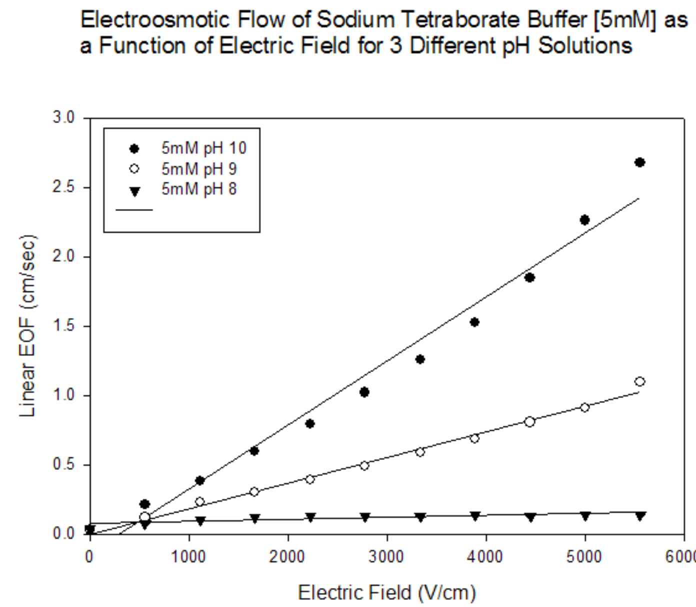
Laser Induced Fluorescence Detection of Labeled Amino Acids

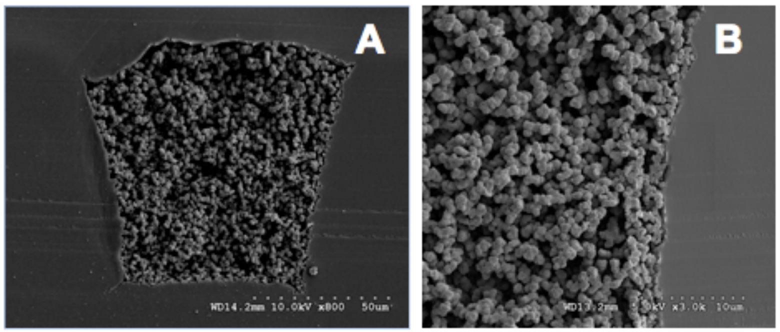


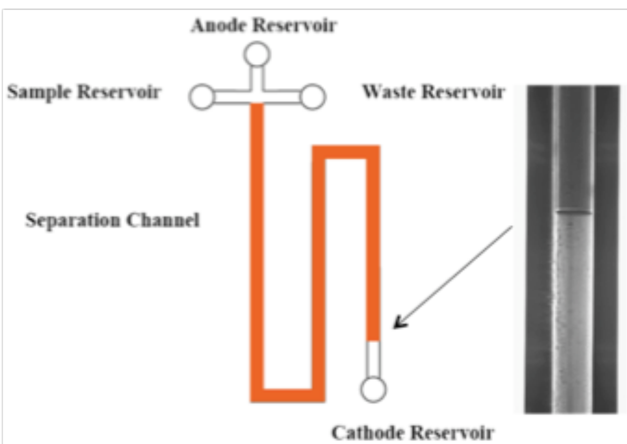
Micro-capillary electrochromatography

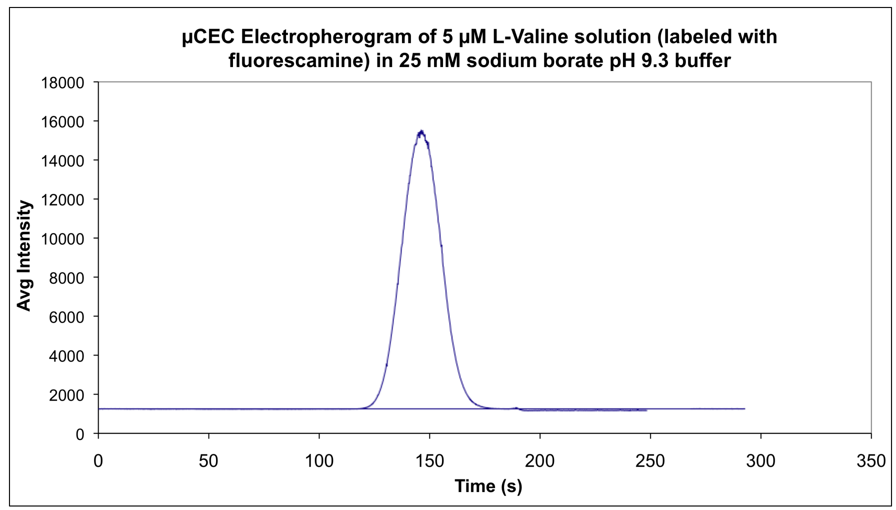
(µCEC)











Surface interactions with solid phase filling channels enables separations of neutral species

Where we are going: μCEC of PAHs

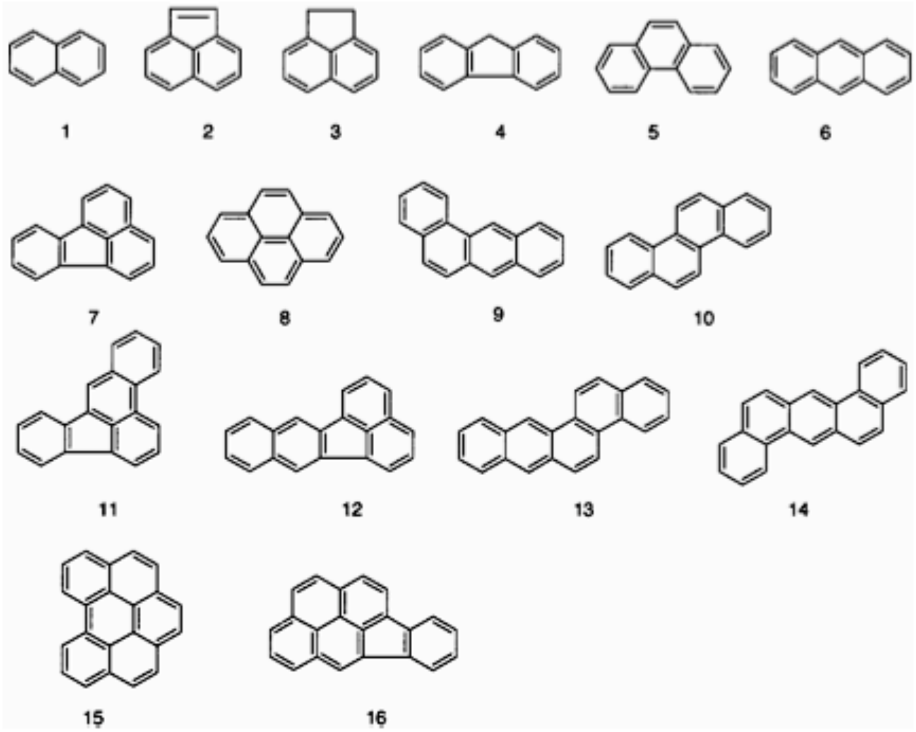


Figure 4. Structures of the PAHs: (1) naphthalene, (2) acenaphthalene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benz[*a*]anthracene, (10) chrysene, (11) benz[*b*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene, (14) dibenz[*a,h*]anthracene, (15) benzo[*ghi*]perylene, and (16) indeno[1,2,3-*cd*]pyrene.

And CHIRAL resolution of amino acids

And Sending Everything into a Mass Spectrometer

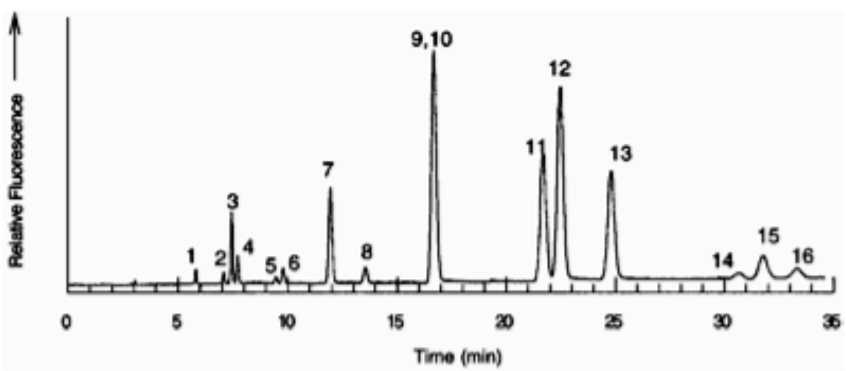


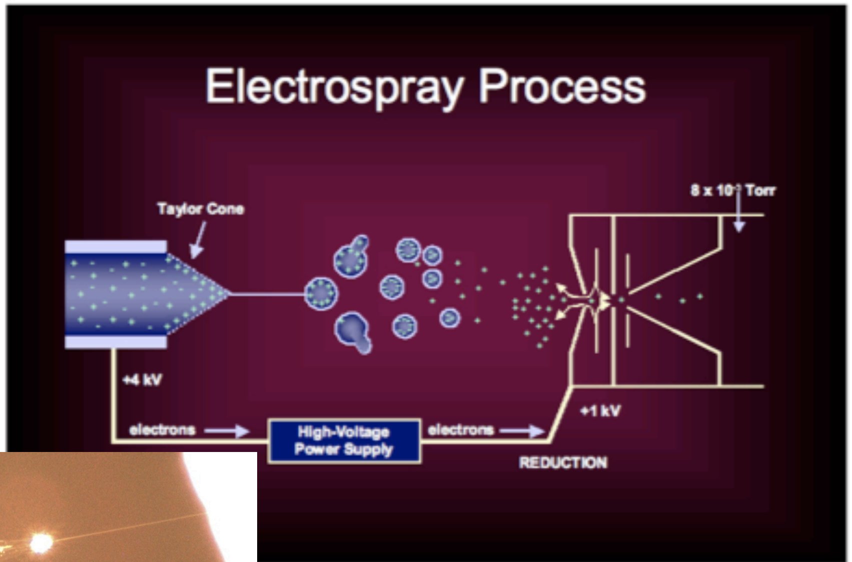
Figure 5. Electrochromatographic separation of 16 PAHs on the butyl stationary phase in 75:25 v/v acetonitrile/5 mM tris, pH 8, at field strength of 833 V/cm.

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

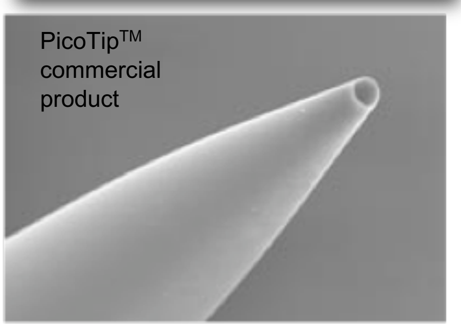
Ngola et al., *Anal. Chem.* 2001, 73(5) pp 849-856.

Extra Slides

Interfacing Lab-on-a-Chip With Mass Spectrometry



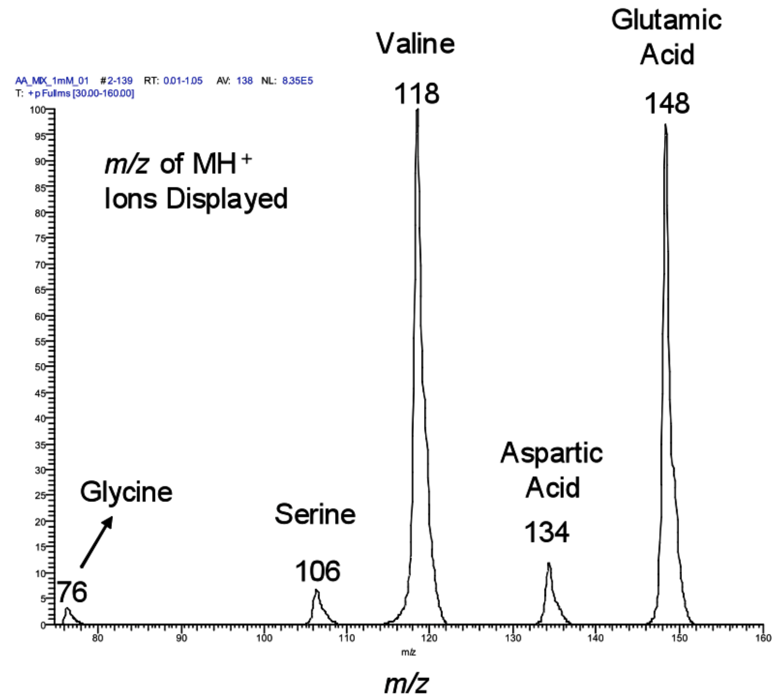
Pulled Capillary



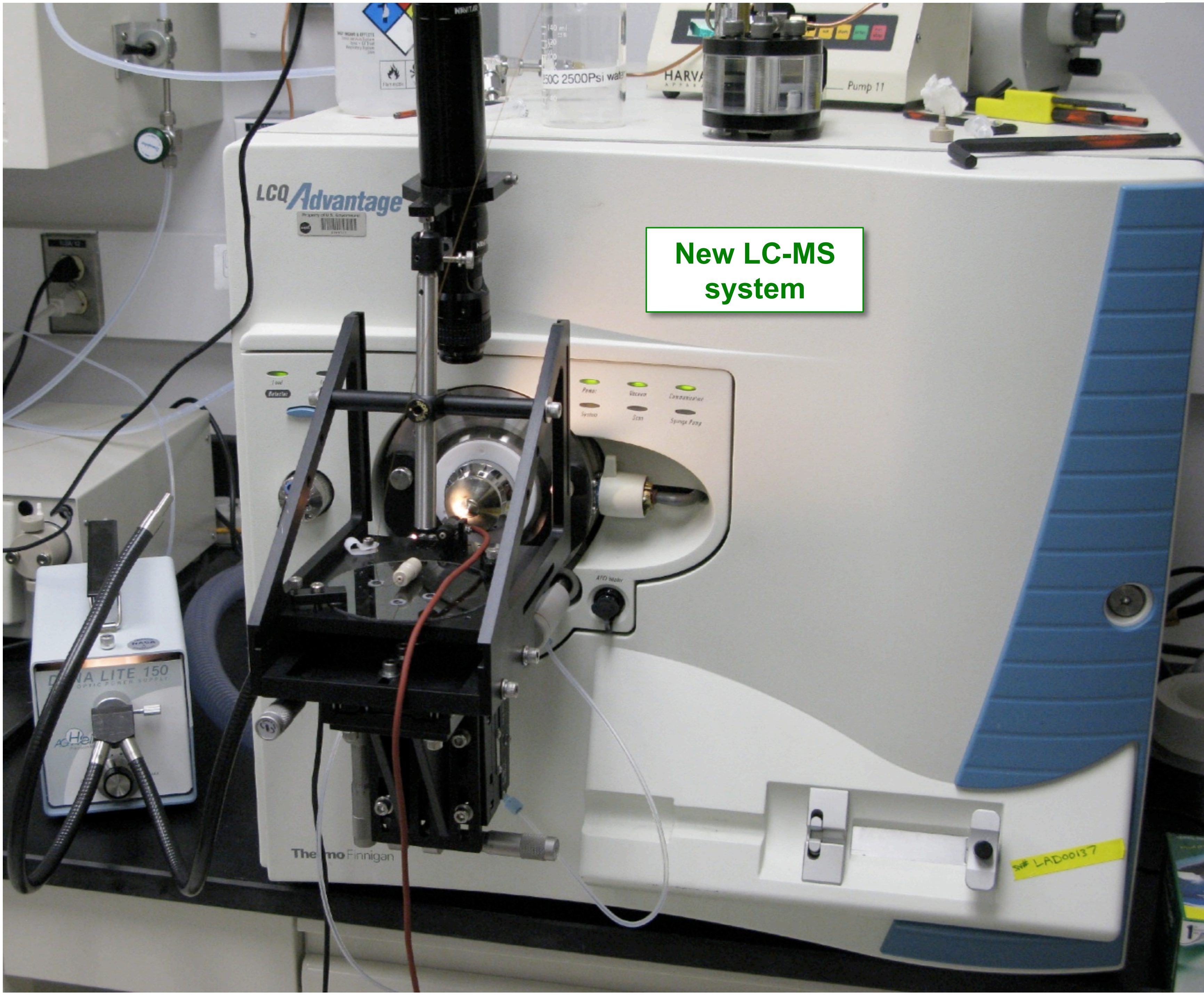
From "Electrospray Ionization Mass Spectrometry: Fundamentals, Instrumentation, and Applications", John Wiley & Sons, Inc., New York

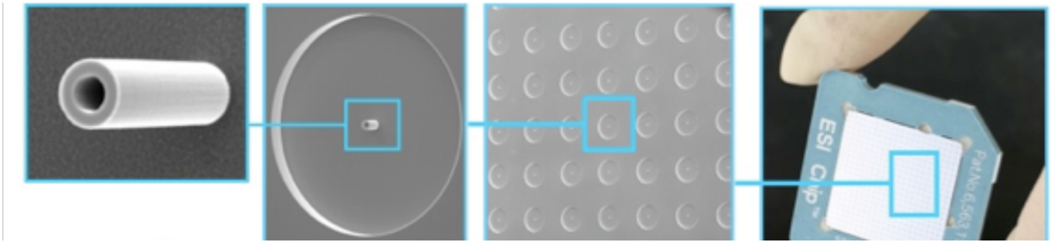
300nL/min
30/70 water/acetonitrile
or 50/50 water/methanol
1.4-3.0 kV bias

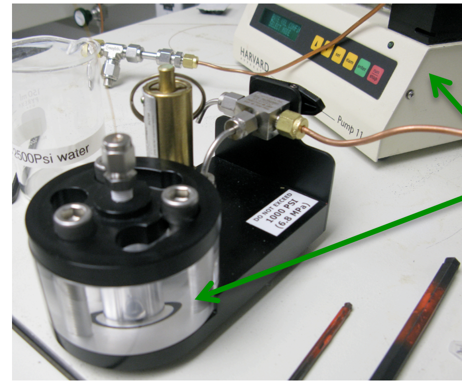
- Label-free detection/identification of analytes



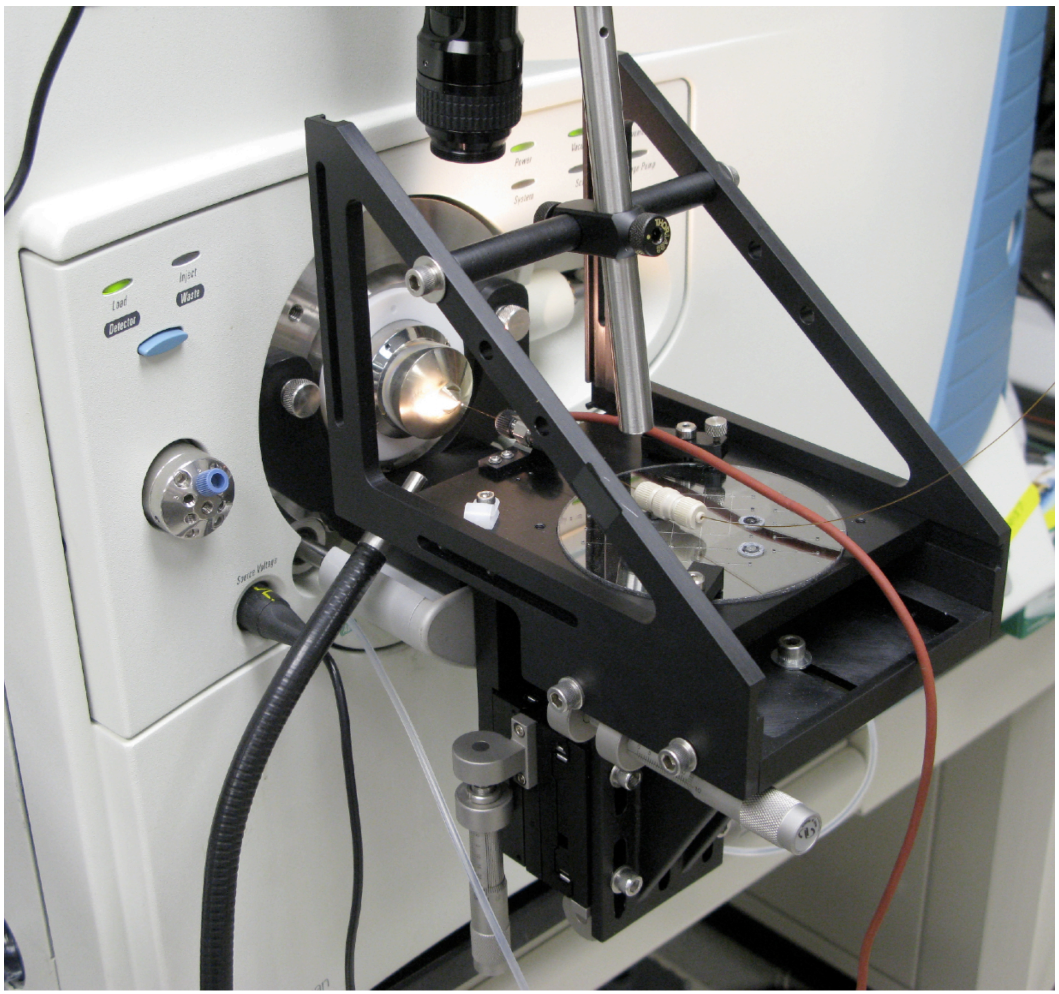
Mass spectrum of five amino acids produced via nanoelectrospray ionization of methanol/water solution

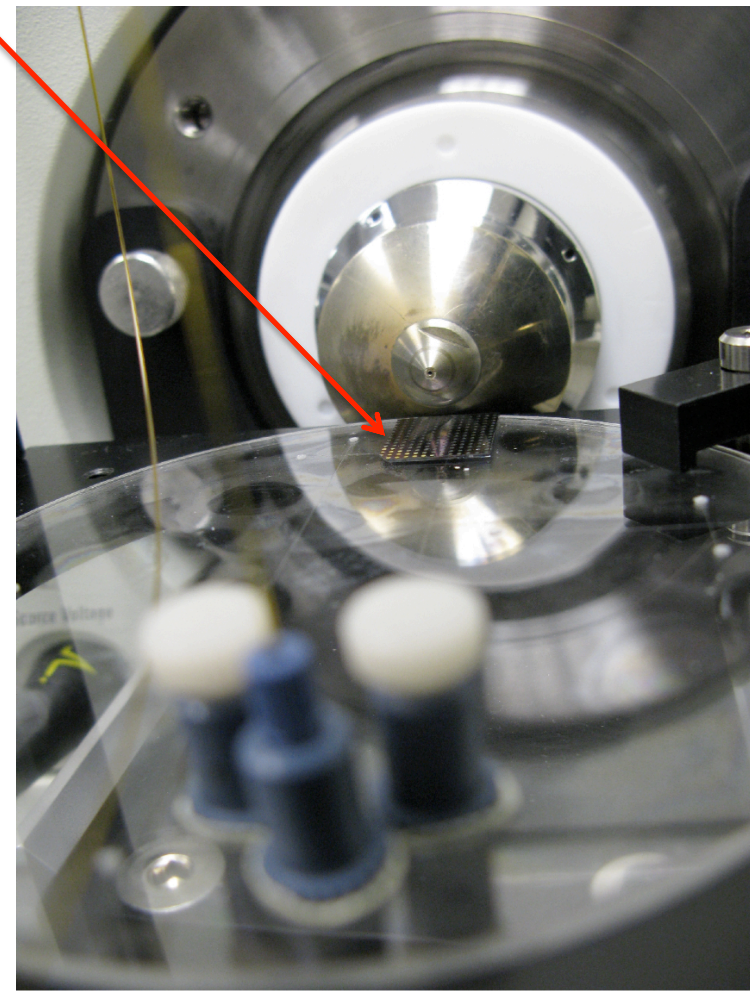

New LC-MS system
LCQ Advantage
Pump 11

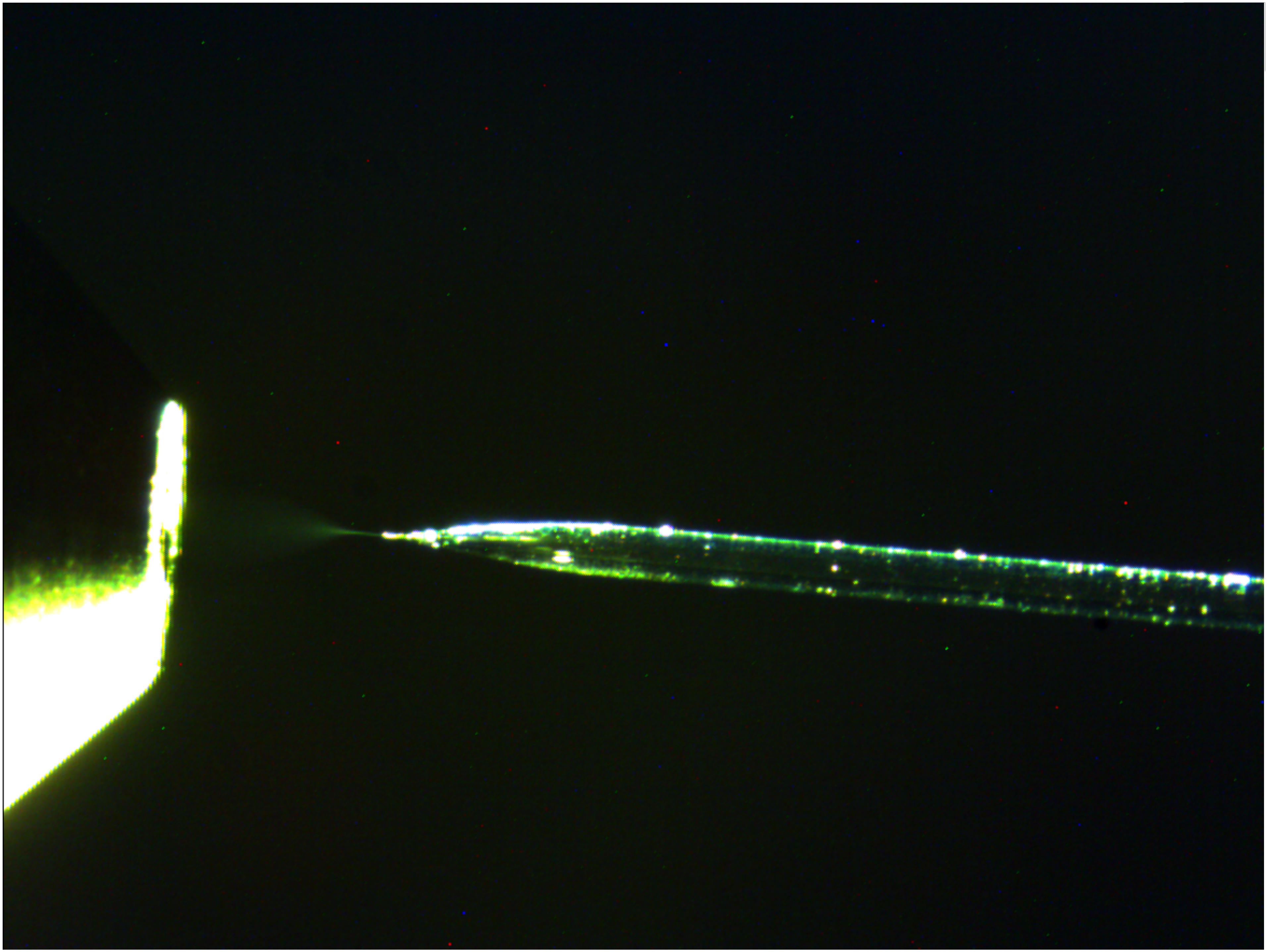




Note: all sprays so far have been driven by mechanical or pneumatic pressure, and have been pure samples

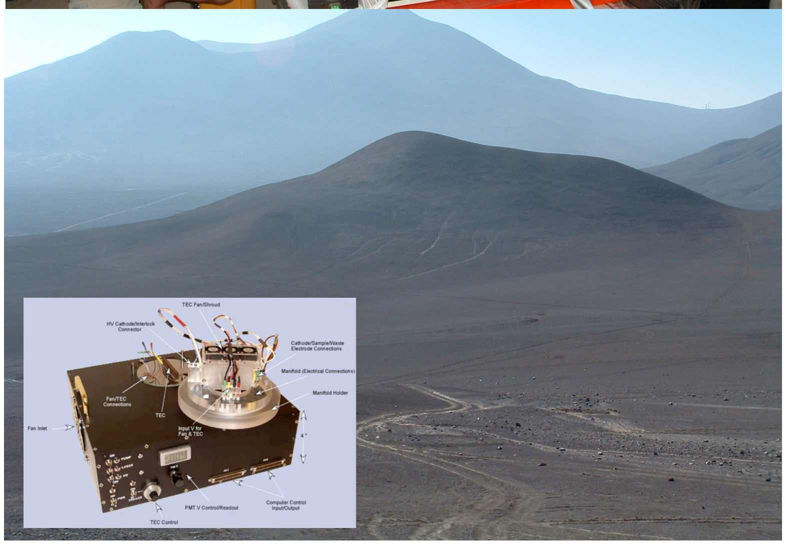


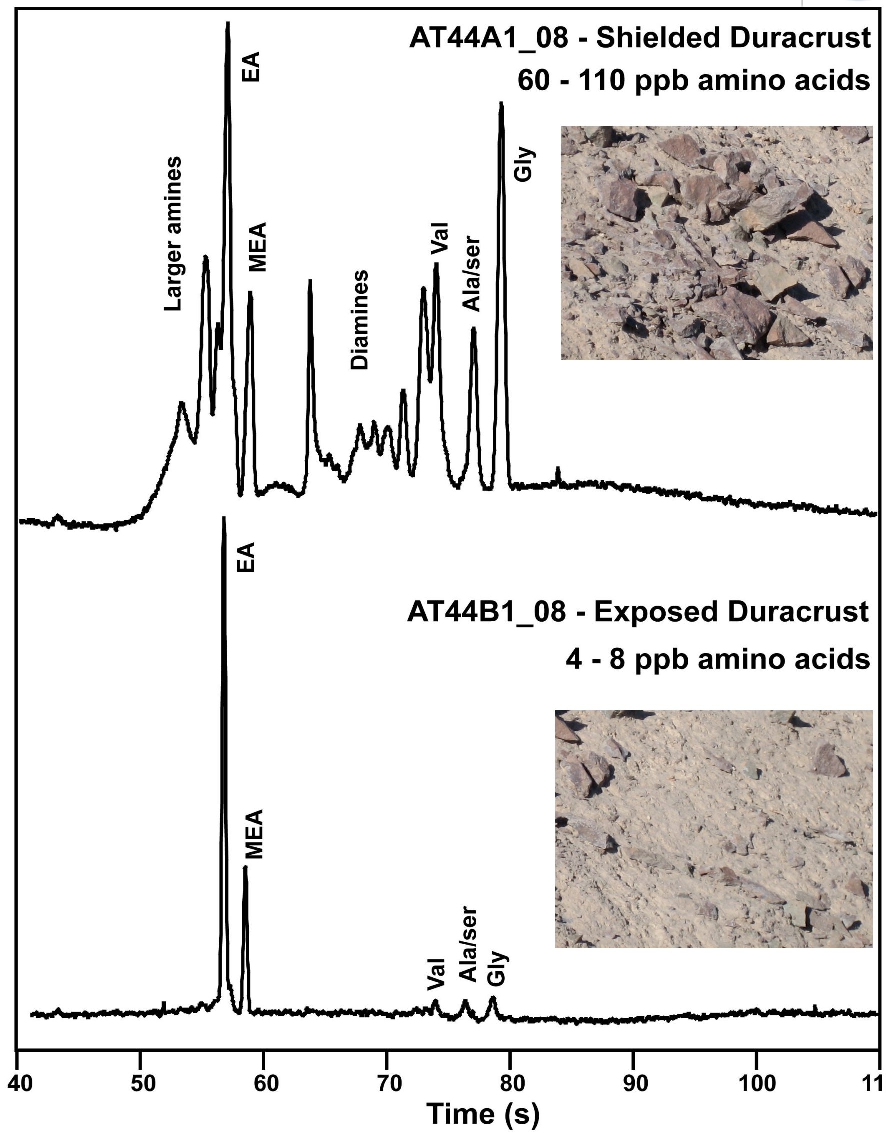




Extra Slides: Mars Analyses

Field Testing in the Atacama Desert, Chile

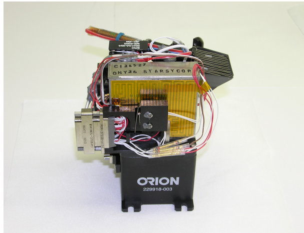




demonstrated prototype operation in Mars analog relevant environment

differentiated between high and low concentration organic samples

A.M. Skelley, A.D. Aubrey, P.A. Willis, X. Amashukeli, P. Ehrenfreund, J.L. Bada, F.J. Grunthaner, and R.A. Mathies, *J. Geophys. Res.*, 2007, **112**, G04S11, DOI: 10.1029/2006JG000329



Phoenix Analogue Experiment

RESULTS FROM PHOENIX MARS LANDER

Measured concentrations of ionic species in Rosy Red soil sample. Assumes delivery of a 1cm^3 sample with density of 1g/cm^3.

Ionic Species	Concentration in Cell, mM	Est %wt
Mg^{2+}	2.9 (±1)	?
Ca^{2+}	0.6 (±0.3)	3-5*
Na^{+}	1.4 (±0.5)	0.10
K^{+}	0.4 (±0.2)	0.03
ClO_4^-	2.6 (±1)	0.75
Cl^-	0.6 (±0.2)	0.04
pH	7.7 (±0.3)	

* From TEGA Analysis

MARTIAN ANALOGUE SAMPLE

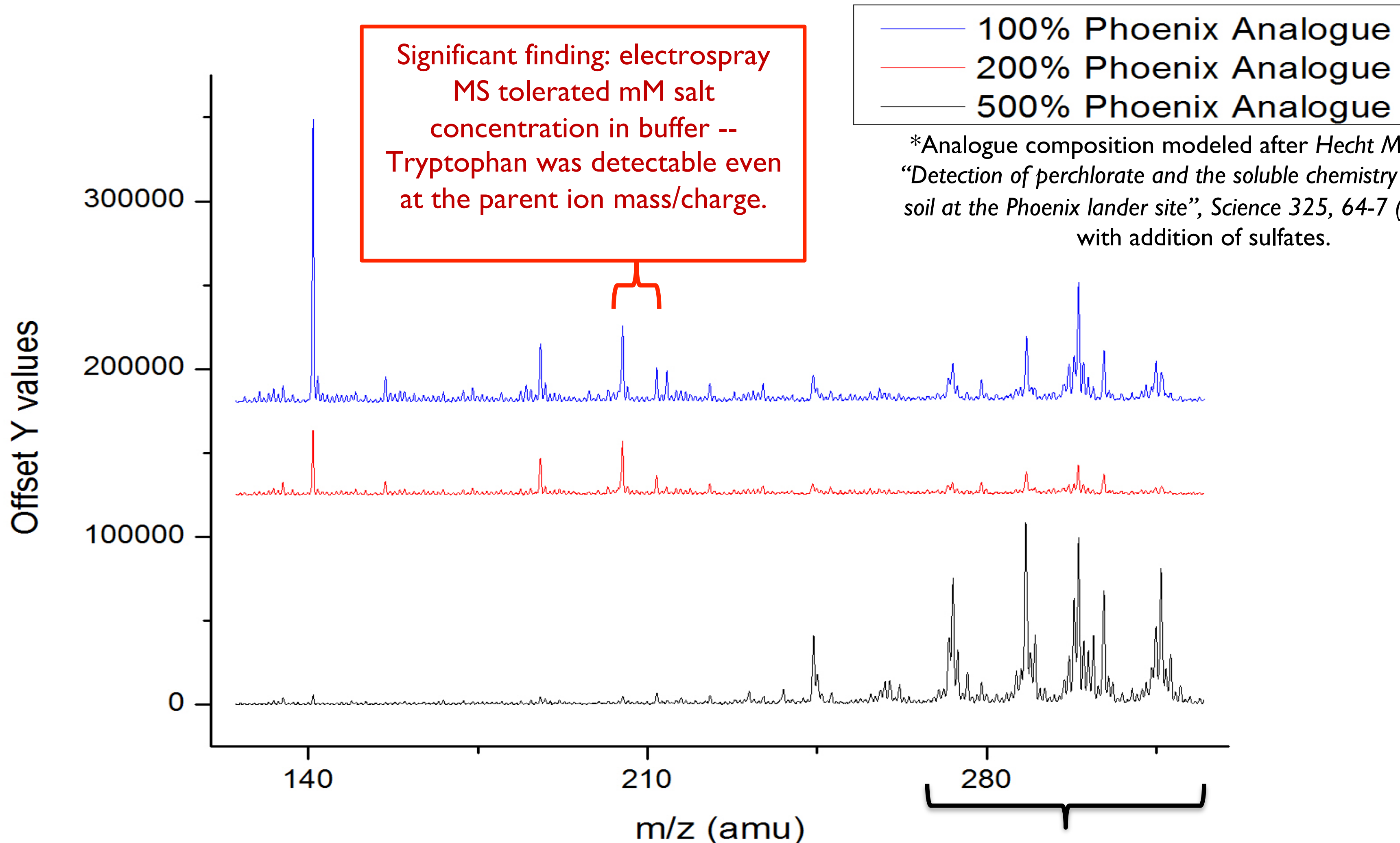
We prepared a sample containing the soluble salts reported by the Phoenix Lander. We also included an ionic sulfate species**. Sample was spiked with 1µM Trp amino acid (200 ppb).

Ionic Species	Concentration in Analogue, mM	Ion Source
Mg^{2+}	2.9	$MgSO_4$
Ca^{2+}	0.6	$CaCl_2$
Na^{+}	2.6	$NaClO_4$
K^{+}	0.4	KCl
ClO_4^-	2.6	$NaClO_4$
Cl^-	1.6	KCl, $CaCl_2$
SO_4^{2-}	2.9	$MgSO_4$
Total	6.5	

**Presence of sulfates in the Martian regolith has been reported by analysis of data from MOC, OMEGA, MER Opportunity , MSG TES instruments

Phoenix Analogue Experiment

(Preliminary Data)



*Analogue composition modeled after *Hecht M. H., et al. "Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix lander site", Science 325, 64-7 (July 2009)* with addition of sulfates.

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

May 25, 2010