Advancements in Analytical Methods for Determining VOCs in Water

OTCO Water Laboratory Analyst Workshop

May 14th, 2015

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Founder, CTO VGC Chromatography

My Background – Analytical Chemist, Chromatographer

- BS (ACS) Chemistry Miami University (Go Redskins/hawks)
- MS, PhD Analytical Chemistry Univ. Michigan (Go Buckeyes!)
- 2 Yrs at Schlumberger
- 5 years at Miami Univ./IDCAST (CBRNE sensors, microGC)
- 2 years (and counting) Founder/CTO VGC Chromatography

- Gas/vapor sensing
- Gas chromatography, GCxGC
- Sorptive Microsensors
- MicroGC, Portable GC, Microanalytical Systems
- Electrochemistry, IC, ICP-MS, HPLC, LC/MS,

Outline

- Background, theoretical on VOC (in water) methodologies
  - Gas Chromatography, Differential Migration
  - Mass Spectrometry
  - Headspace
  - Solid Phase Extraction
  - Purge and Trap

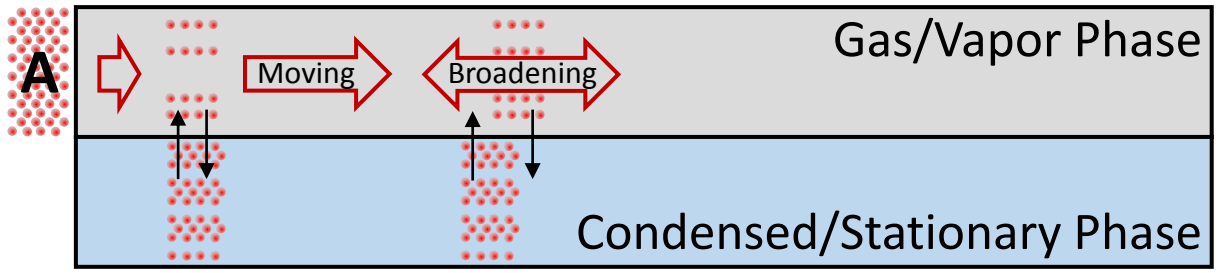
- Highlights of recent advances in GC
- New applications for GC and water
- Automated VOC monitoring in the field

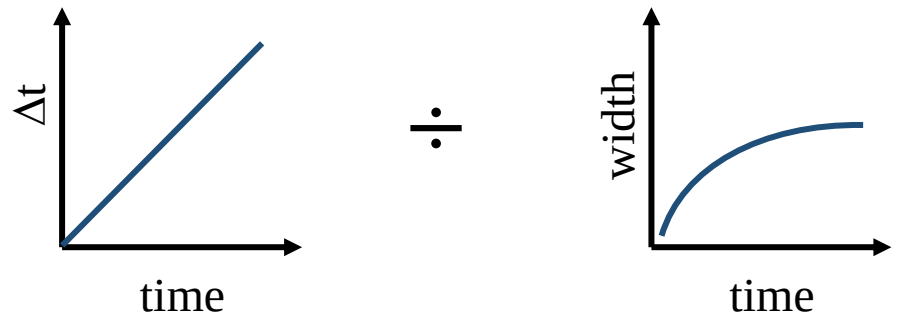
This is a Workshop…

…Please Interrupt/Interact

Gas Chromatography (GC); Differential Migration

Physical separation by disturbance of equilibrium by flowing carrier gas through a column



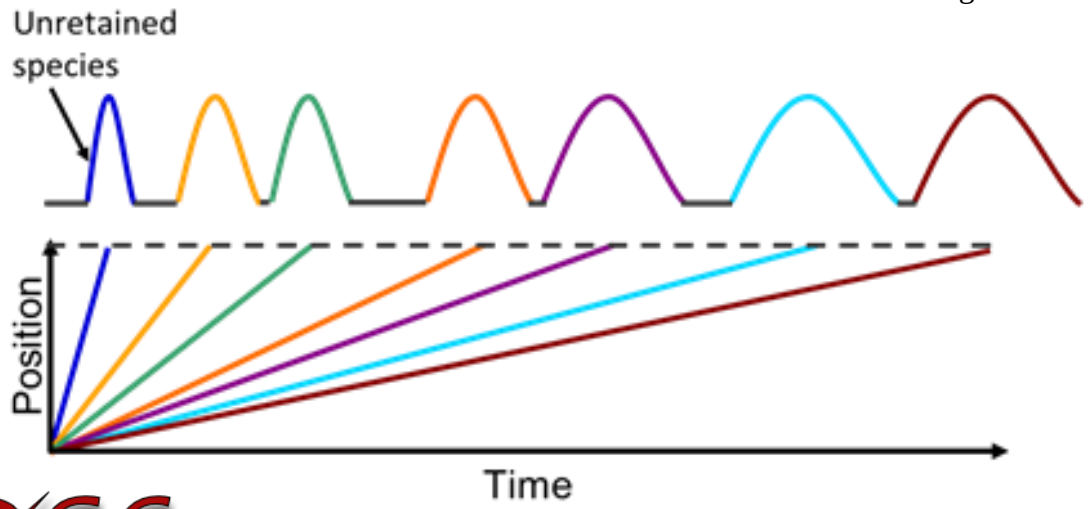


Attempted Equilibrium (never achieved)

$$[A]_g \rightleftharpoons [A]_s$$

Partition Coefficient = $K = k_e/k_c = [A]_s / [A]_g$

Distribution Coefficient = $D = \text{mass } A_s / \text{mass } A_g$



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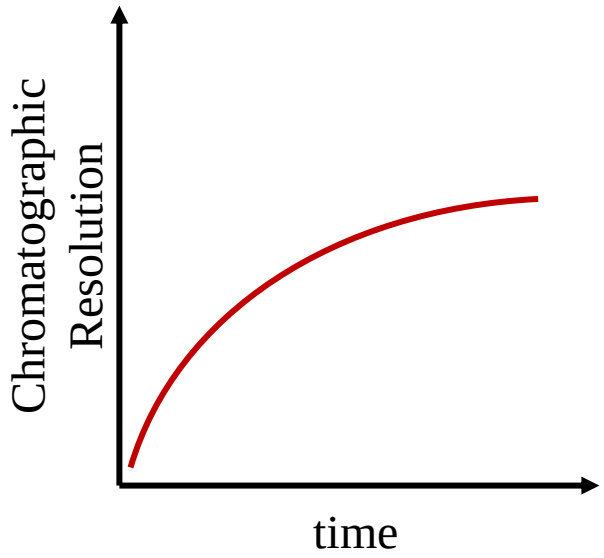
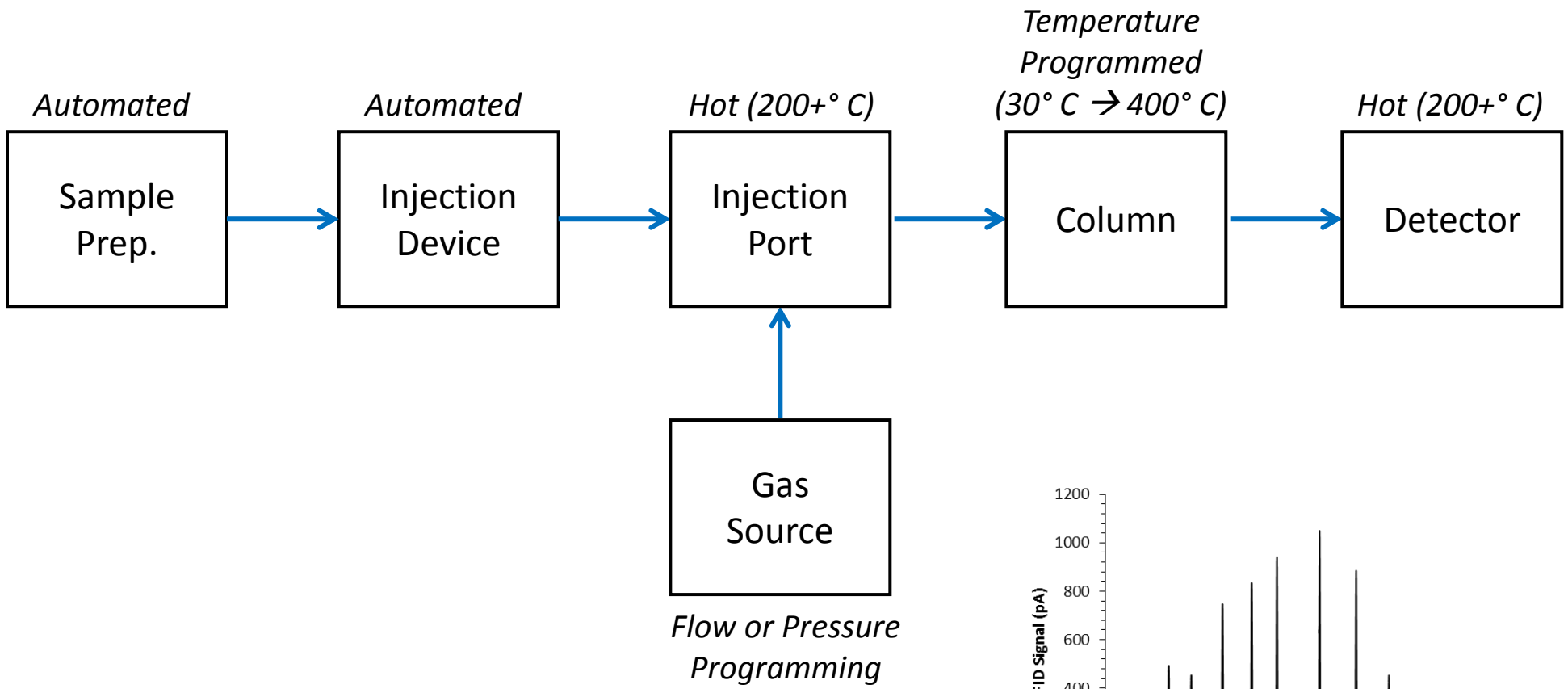
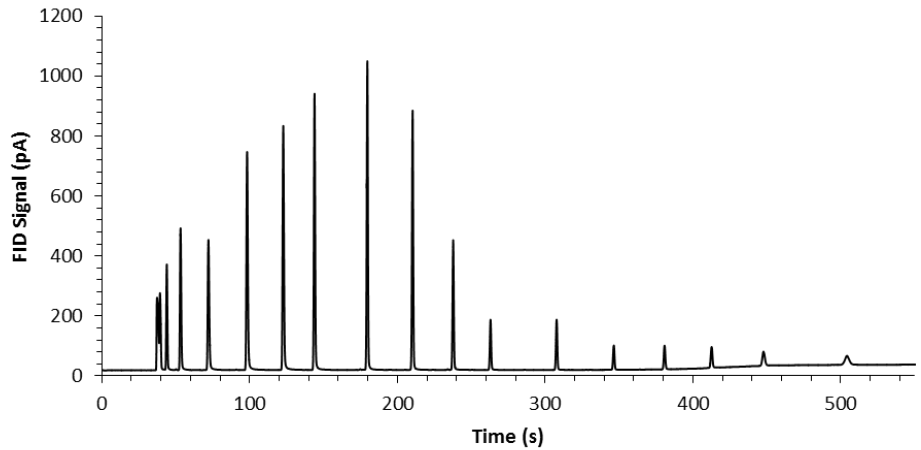


Gas Chromatography (GC); Differential Migration

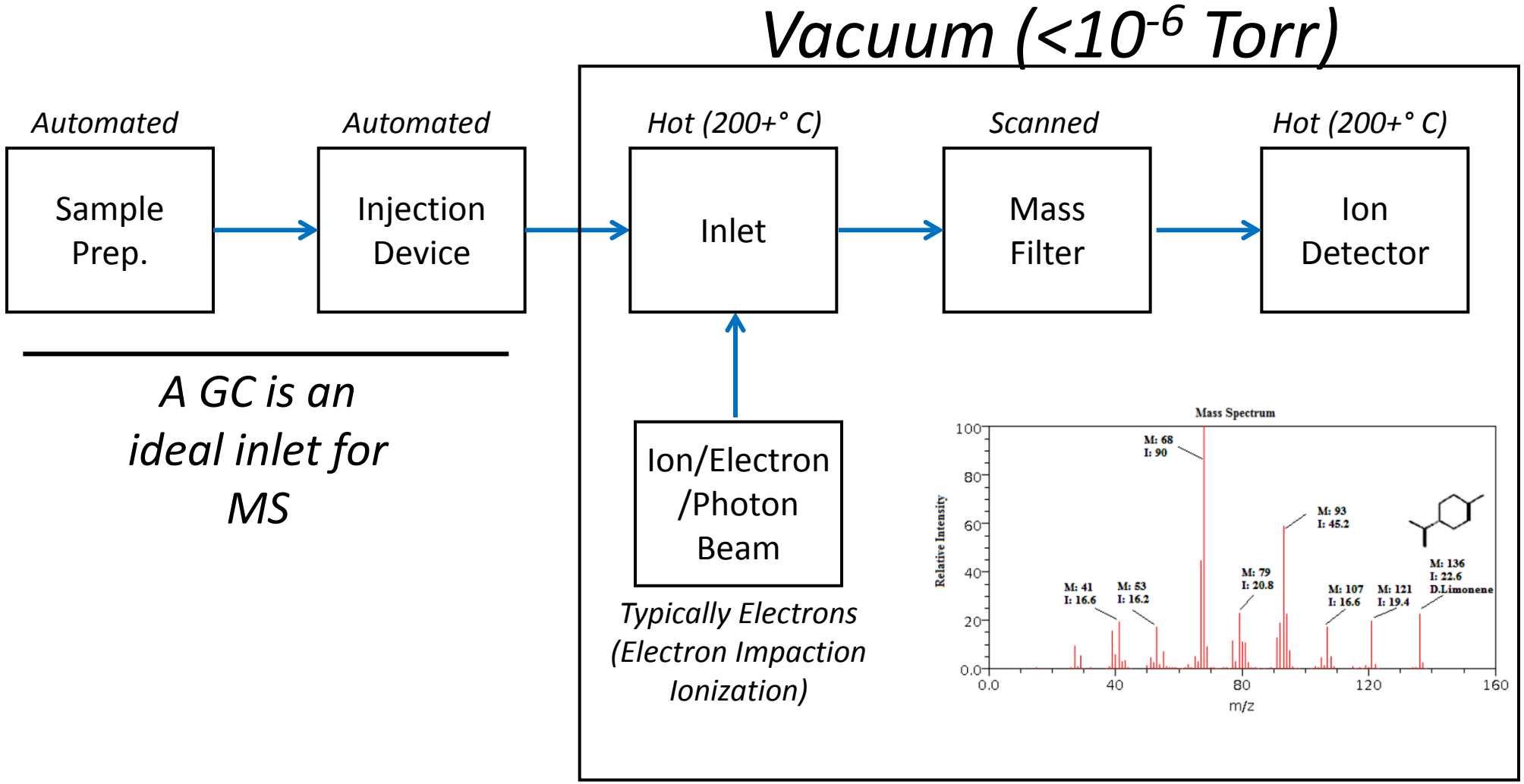
Components of a GC





Mass Spectrometry (For Gases and Vapors)

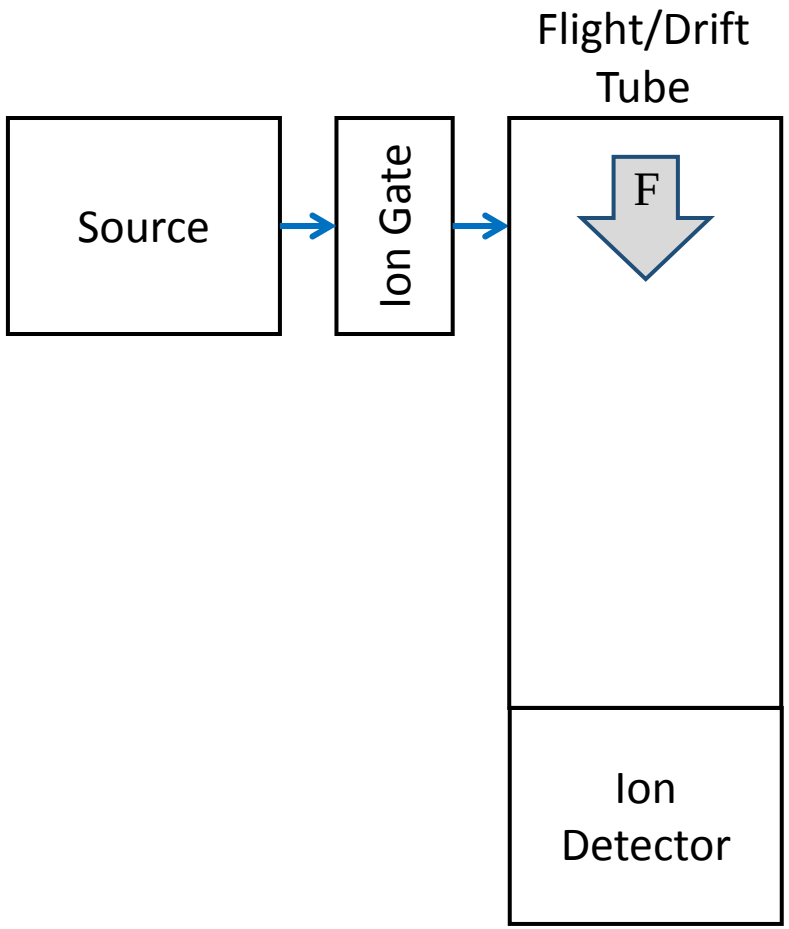
Identification of molecules by mass analysis of ion fragments



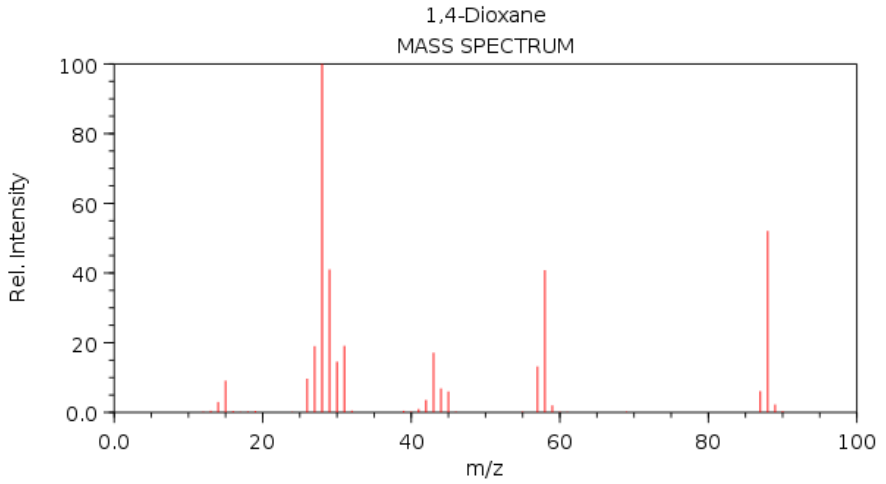
Mass Spectrometry (For Gases and Vapors)

Mass Filters, electromagnetic separation of ions in vacuum ($F=ma$ … $m = a/F$)

Time of Flight (TOF)

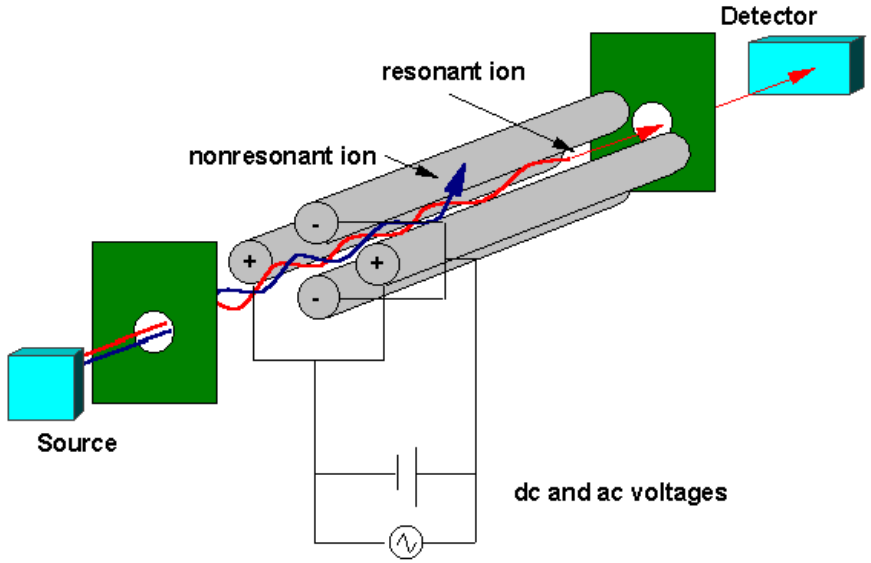


$\Delta t \rightarrow m/z$



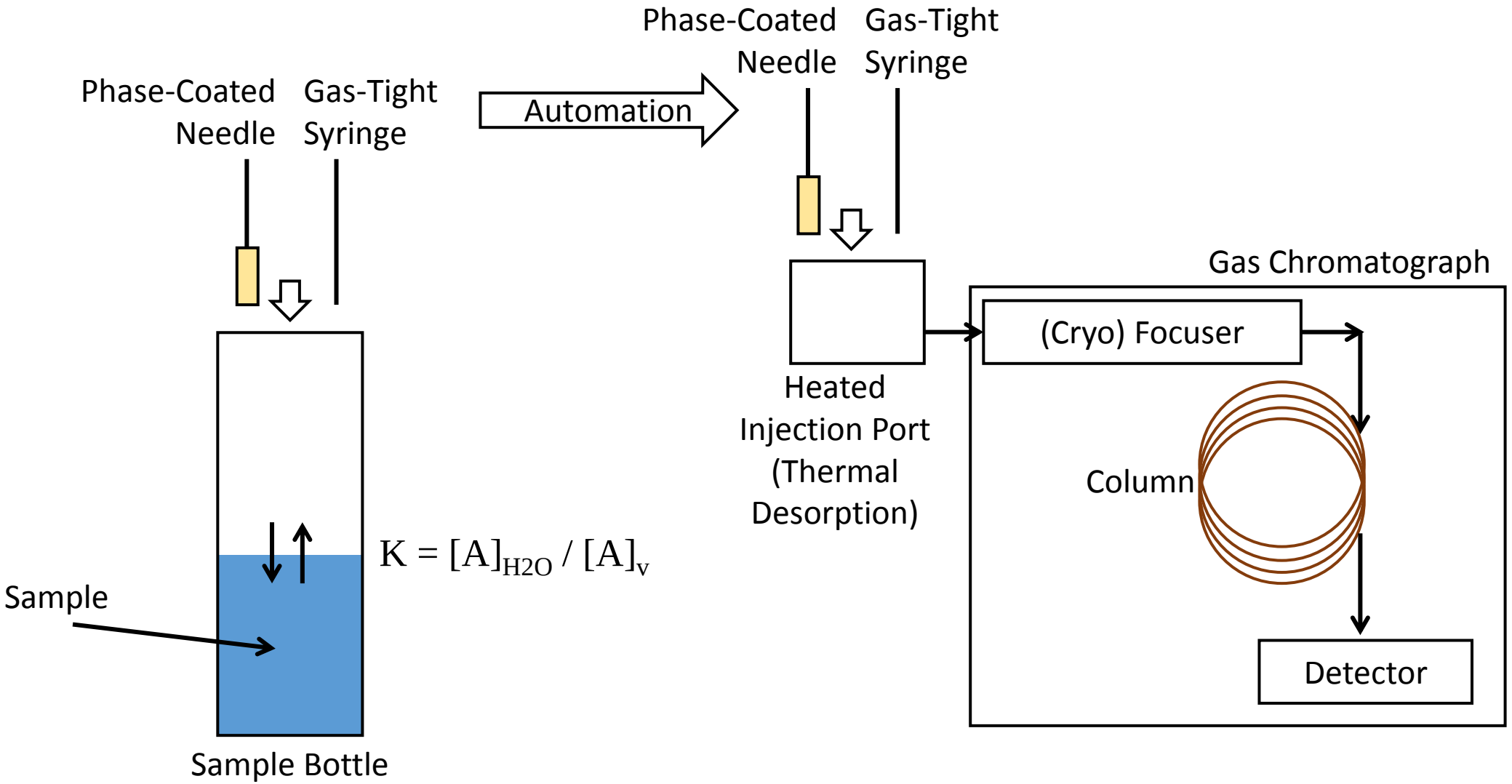
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Quadrupole (Quad, Q)



Headspace Sampling

Syringe or Phase-Extraction of VOCs in headspace, equilibrated with liquid



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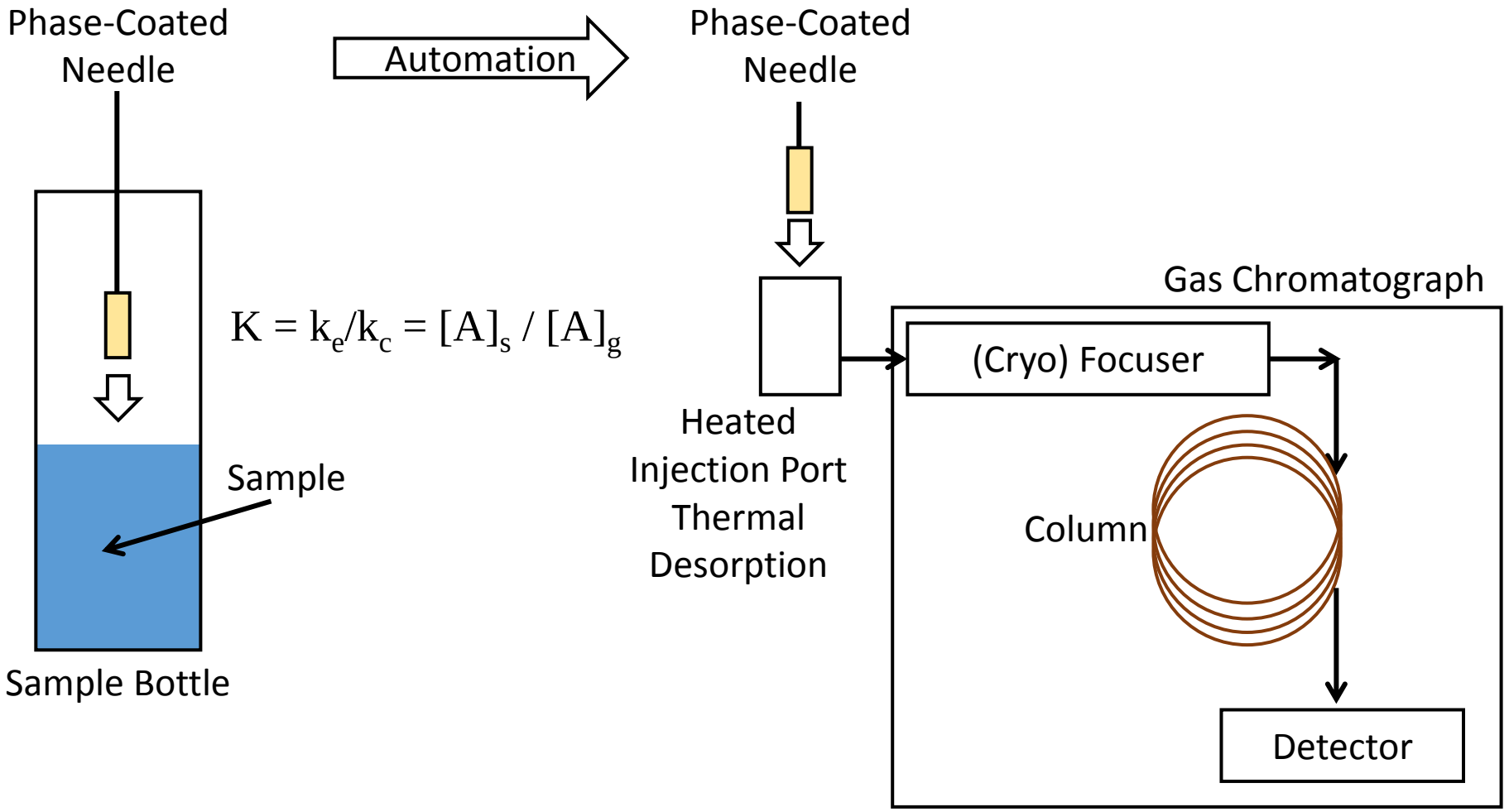
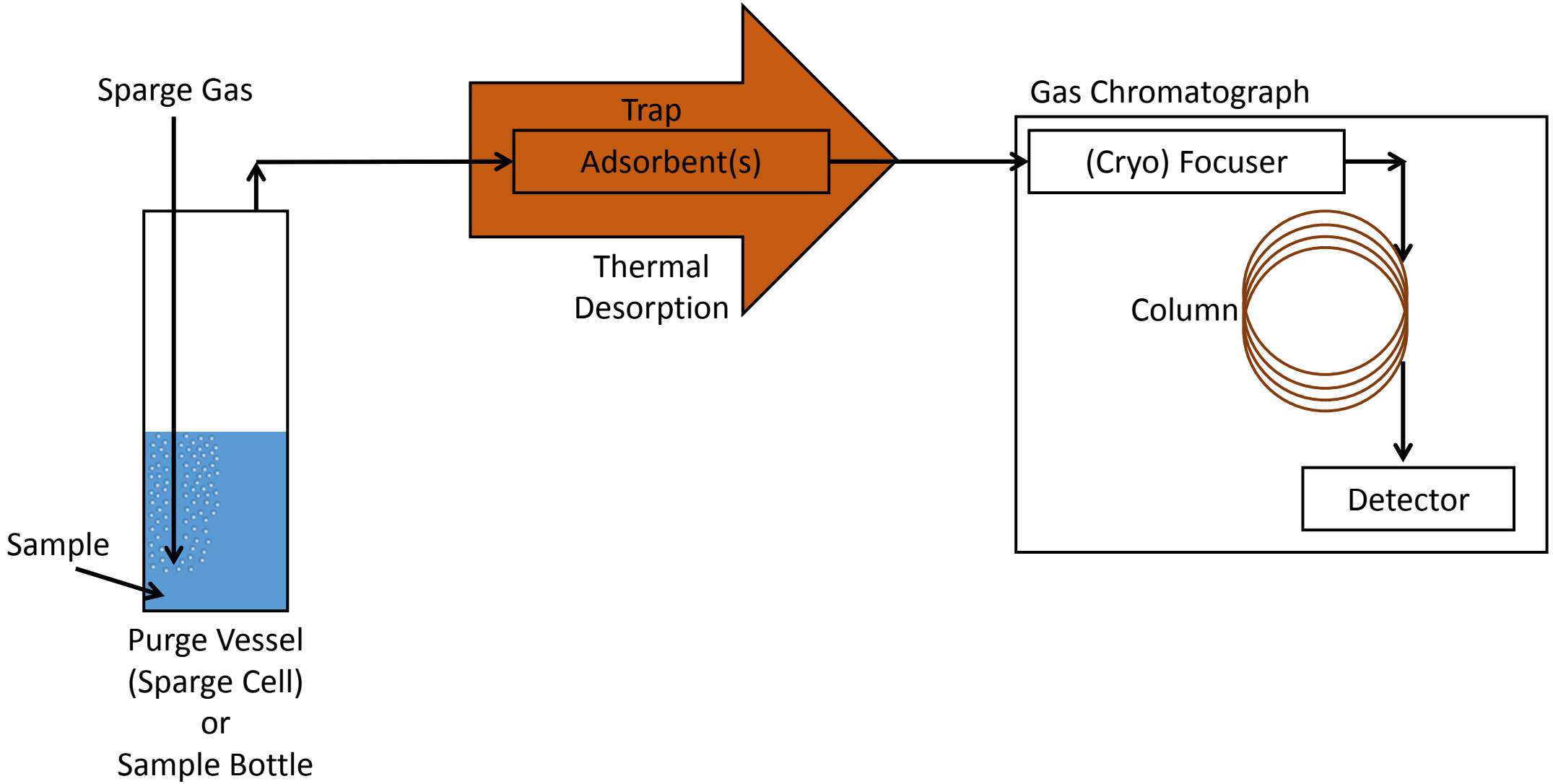
Solid Phase (Micro) Extraction

Extraction of VOCs from water into a solid (stationary) phase; thermally desorbed into GC



Purge and Trap Sample Introduction

Purging (Sparging) of VOCs from water onto a trap; thermally desorbed into GC

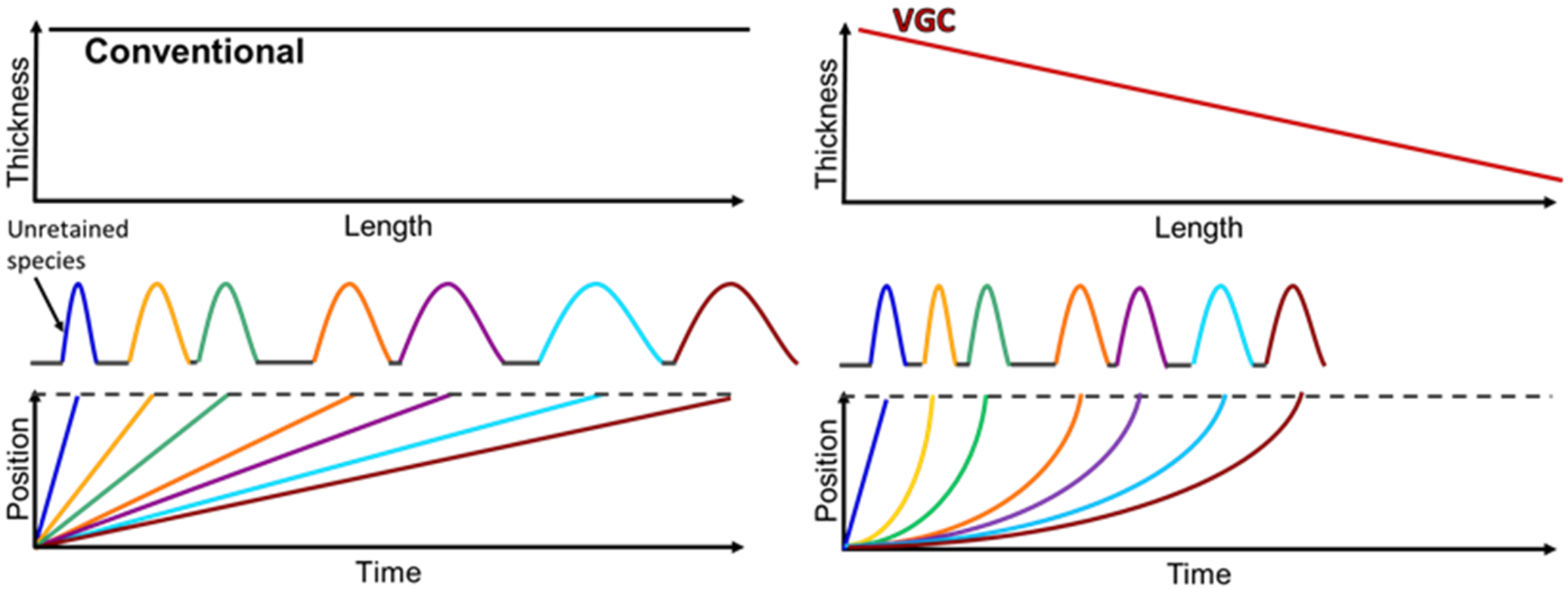


New Developments in Sample Introduction

- Sigma/Supelco's patents on SPME are running out
  - Look for new SPME vendors
- New extraction mechanisms
  - Twister (by Gerstel, Stir Bar Solid Extraction)
- EST Analytical (Cincinnati) took lead in Purge and Trap market
  - Former leader was Tekmar (also Cincinnati)
- Use of sample vial as purge cell becoming more popular
  - Better automation, reduces analyte loss and contamination
- Fracking measurements
  - Look for water sample prep methods to be coupled to petroleum analyses as more concerns arise regarding contamination of ground water
  - Huge volatility range (adsorbent challenges), biogenic decomposition

Highlights of Recent GC Advances

Differential Acceleration by Variable Geometry Columns

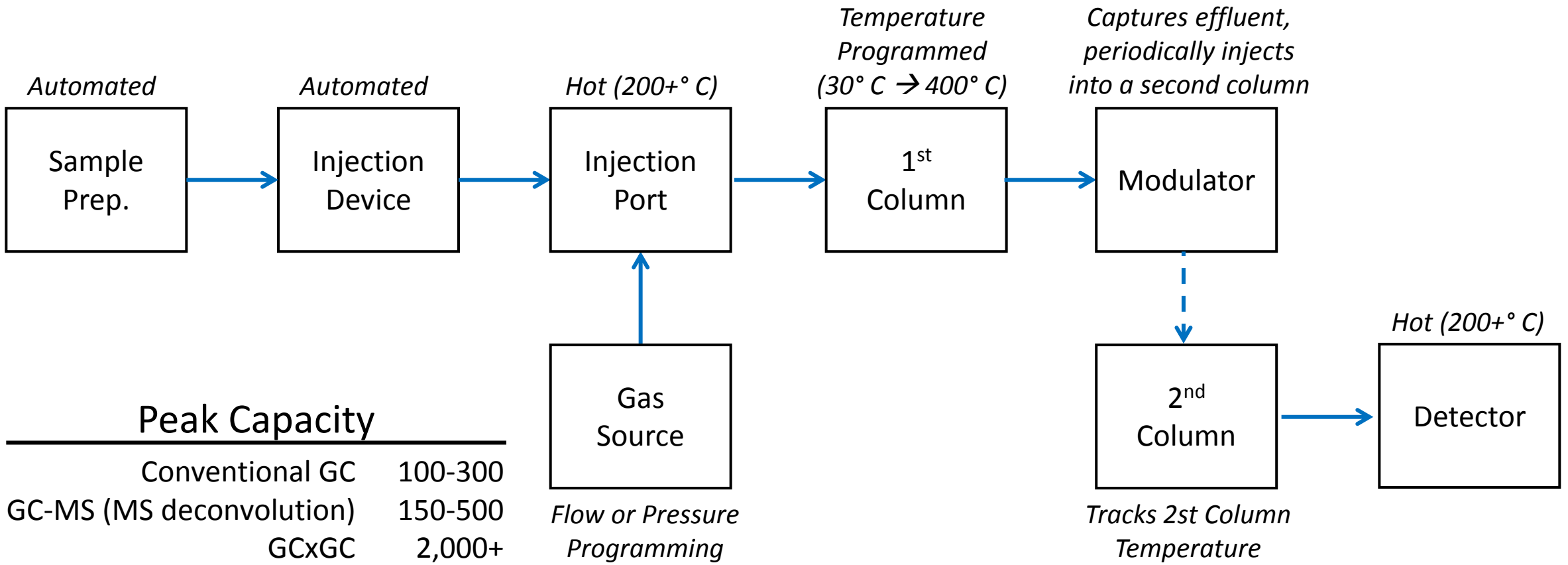


- 40% faster for similar “size” columns
- Larger sample capacity (thick inlet film)
- Less susceptible to column overload and matric induced retention shifts

Invented by me! Available from VGC!

Highlights of Recent GC Advances

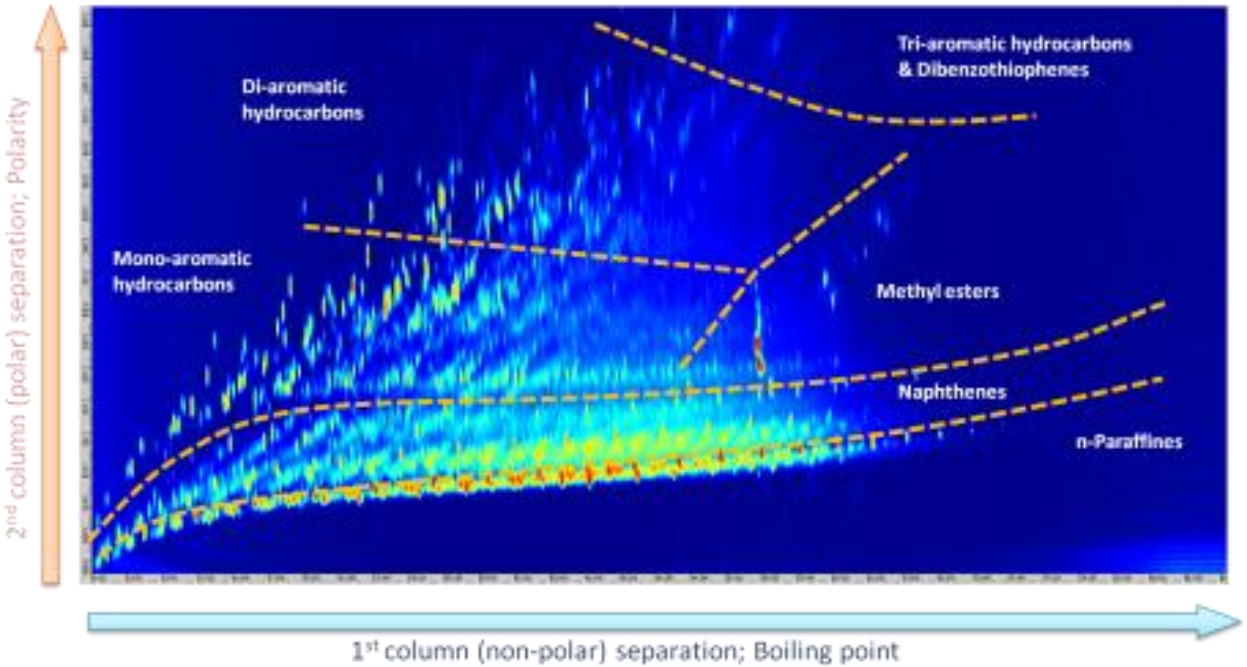
Comprehensive Multi-Dimensional GC (GCxGC)

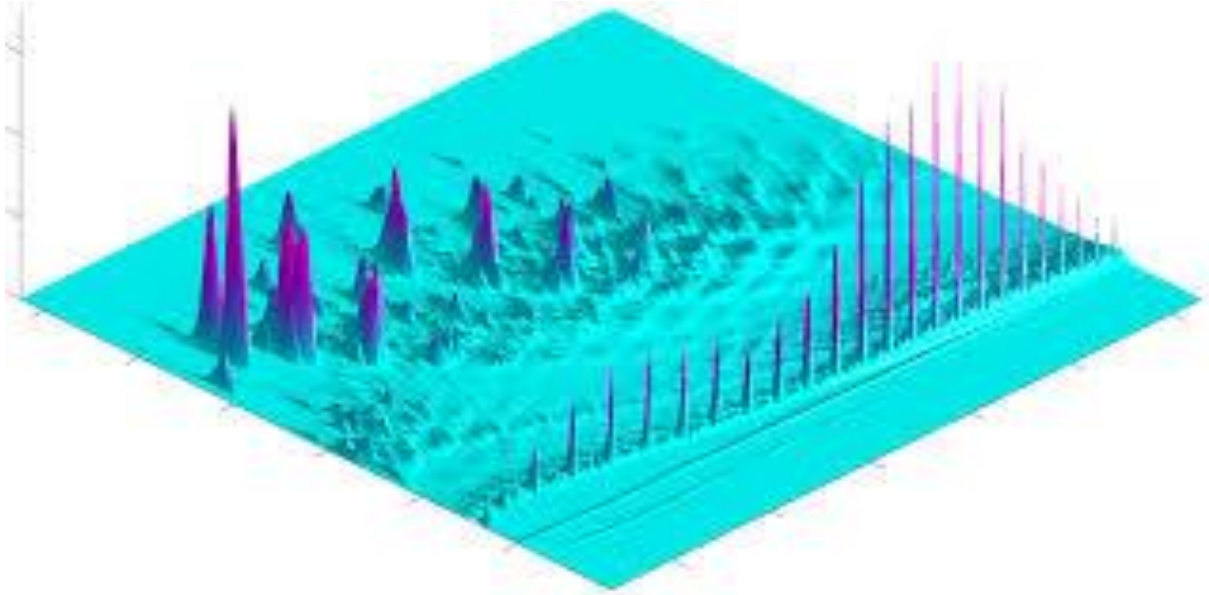


Peak Capacity	
Conventional GC	100-300
GC-MS (MS deconvolution)	150-500
GCxGC	2,000+

Highlights of Recent GC Advances

Comprehensive Multi-Dimensional GC (GCxGC)





Rail Autosamplers

New Applications for GC in Water Testing

Chloramines in water treatment, indoor air

CDC Wants to Pressure EPA, OSHA to Regulate

"chlorine" (complicated equilibrium) + ammonia (from amines or urea) → $ClNH_2$, Cl_2NH, Cl_3N

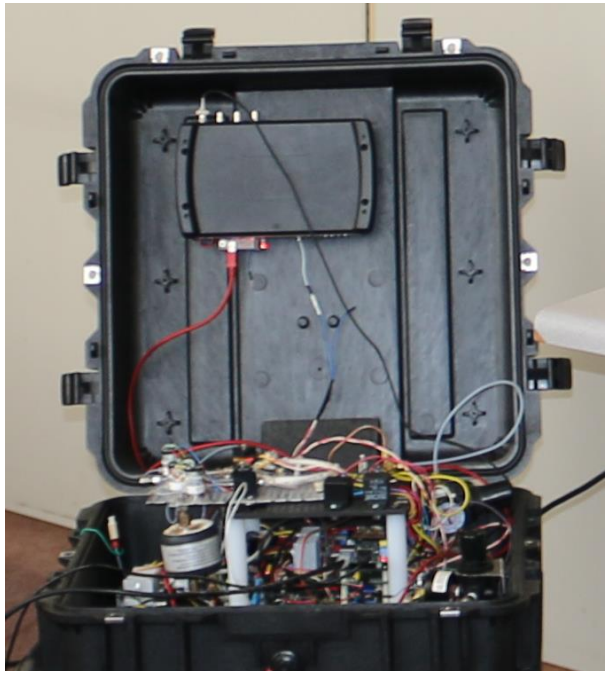
- *No accurate tools have been commercialized for chloramines*
- *Typically estimated by difference*
  - *Total chlorine sensor – individual chlorine species = total chloramine*
    - *Can't speciate*
    - *Need equilibrium data*
    - *Chlorine sensors have varying sensitivity to each chloramine species*
- *VGC is working on a GC method for simultaneous determination of all three chloramines*
  - *Can retrofit laboratory GC*
  - *Can custom-build dedicated chloramine GC (with any sample introduction)*
  - *Can adapt automated online system to chloramines*

Summary of Recent Activity in GC

- DA-Columns (from VGC) first drop-in speed improvement in 30-40 years
  - Most valuable to high-throughput applications with fast sample prep
    - Refineries, environmental labs
- GCxGC growing in popularity (slowly)
  - Struggling to find the “killer application”
  - Most common criticism is, “what do you do with all the data?”
  - Need for fast MS (>$150k) makes it very expensive for environmental labs
- New applications (like chloramines) developing
  - Driving new standard method development
  - Driving new sample prep/injection methods
- Rail “autosamplers” enabling automation
  - Permits more complicated sample prep, auto calibration

On-line, Automated VOC monitor

purge and trap micro-gas chromatograph



CITY OF DAYTON
water
one source
Regional • Reliable • Renewable

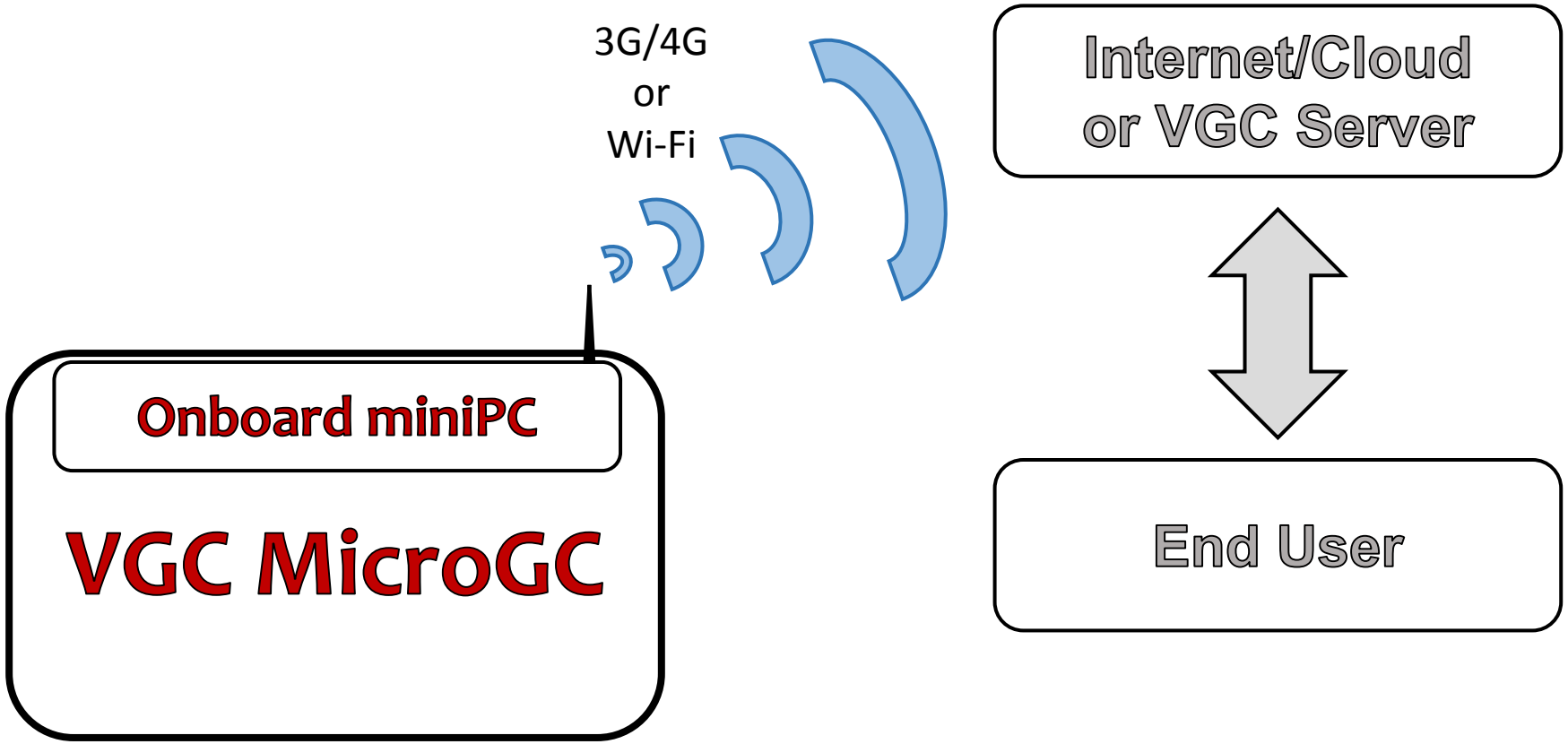
VGC Chromatography

www.vgcchromatography.com

Minimal technical specifications

- 1 ppb LOD for vinyl chloride [MCE], 1,2-dichloroethylene (cis) [cDCE], 1,2-dichloroethylene (trans) [tDCE], trichloroethylene [TCE]
  - Accomplished by purge and trap microGC system. Multiple column configurations possible, but not required.
  - Parts per billion as mass/mass units in the aqueous phase, approximately equal to micrograms per liter
  - *note: EPA and similar organizations use ppb in gas/vapor phase as the mole fraction (aka ppbv)
- Less than 30 minutes per analysis, at least one analysis per day with average SW Ohio sun (solar charging)
  - More analyses uses more power, reducing the cycle rate will extend battery life for low-light periods
- Automatic liquid sampling (onboard pump pulls ground water into system for analysis)
  - Purge and trap sampling of ground water, flush cycle used to ensure representative sample
- Autonomous system (runs without direct human control)
  - Configuration issues can be set by user through web portable, but the system automatically manages everything else
- Automatic data processing
  - MCE, cDCE, tDCE, TCE concentration determined from chromatogram, saved in system memory
- Automatic data reporting:
  - MCE, cDCE, tDCE, TCE concentration measurements available to user via internet webpage (RaspPi portal), can be exported by user to local text file and imported to spread sheet or similar software.
- Weather proof package, compatible with stick-up and flush-mount wells (flush mount can survive a lawn-mower driving over it)
  - Uses geothermal heating/cooling, will be sealed against weather/water, may included dehumidification system
  - Solar panel will require sunlight, small antenna will be at/near top of system
  - Tube will be installed permitting sampling of the well, some applications may require insulation or heating of sampling line in winter

Electrical Architecture, Accessibility



Web Interface

Chromatography

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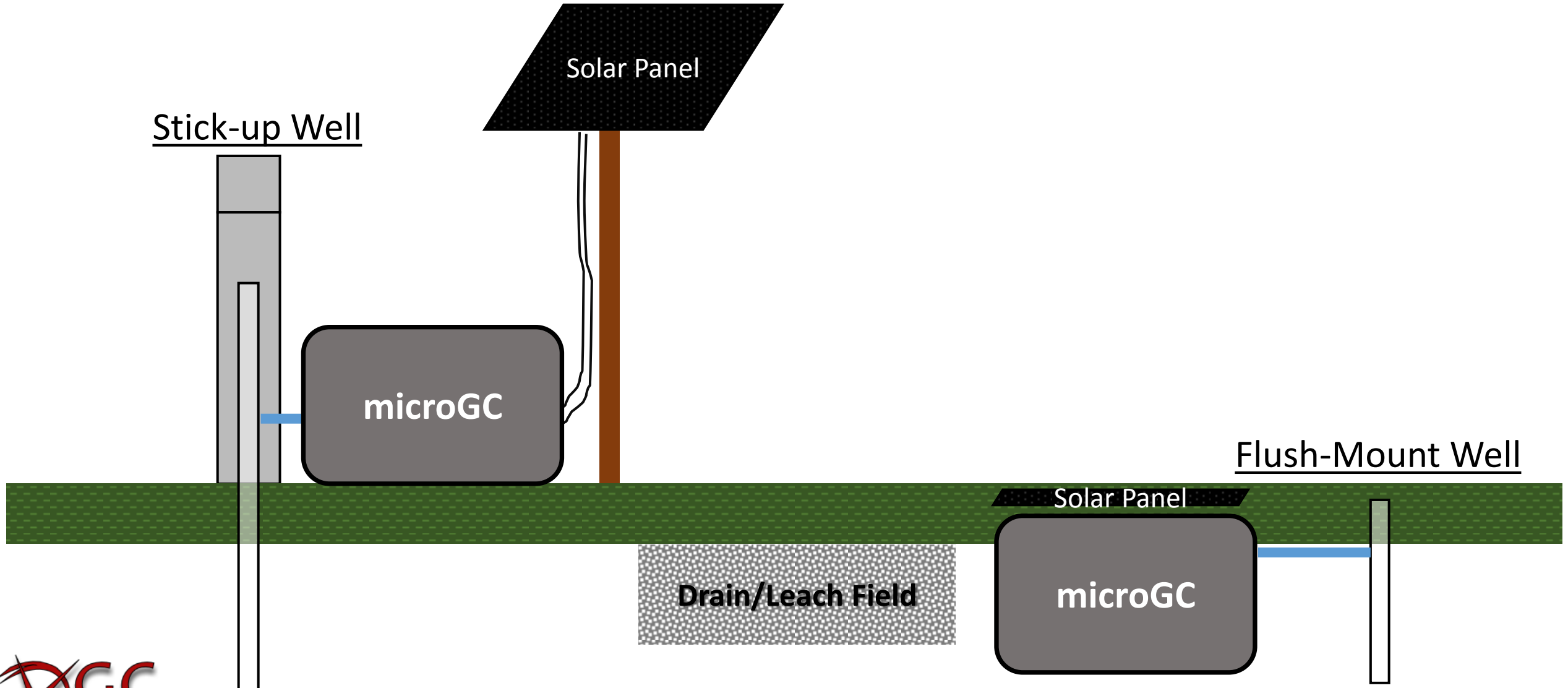
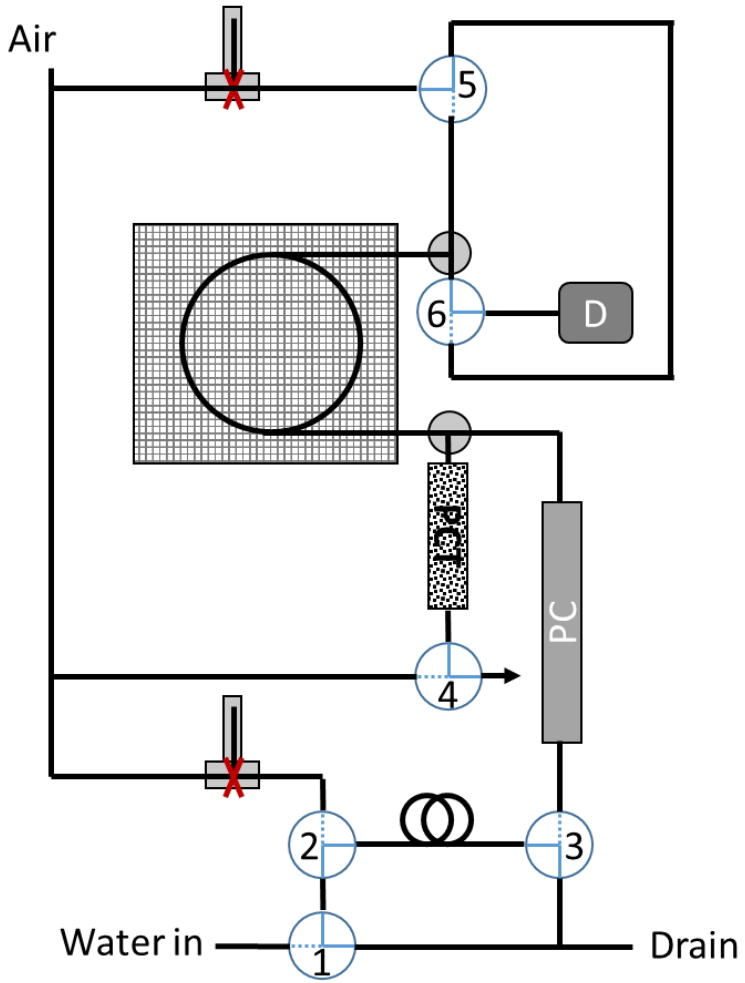
Field Installations

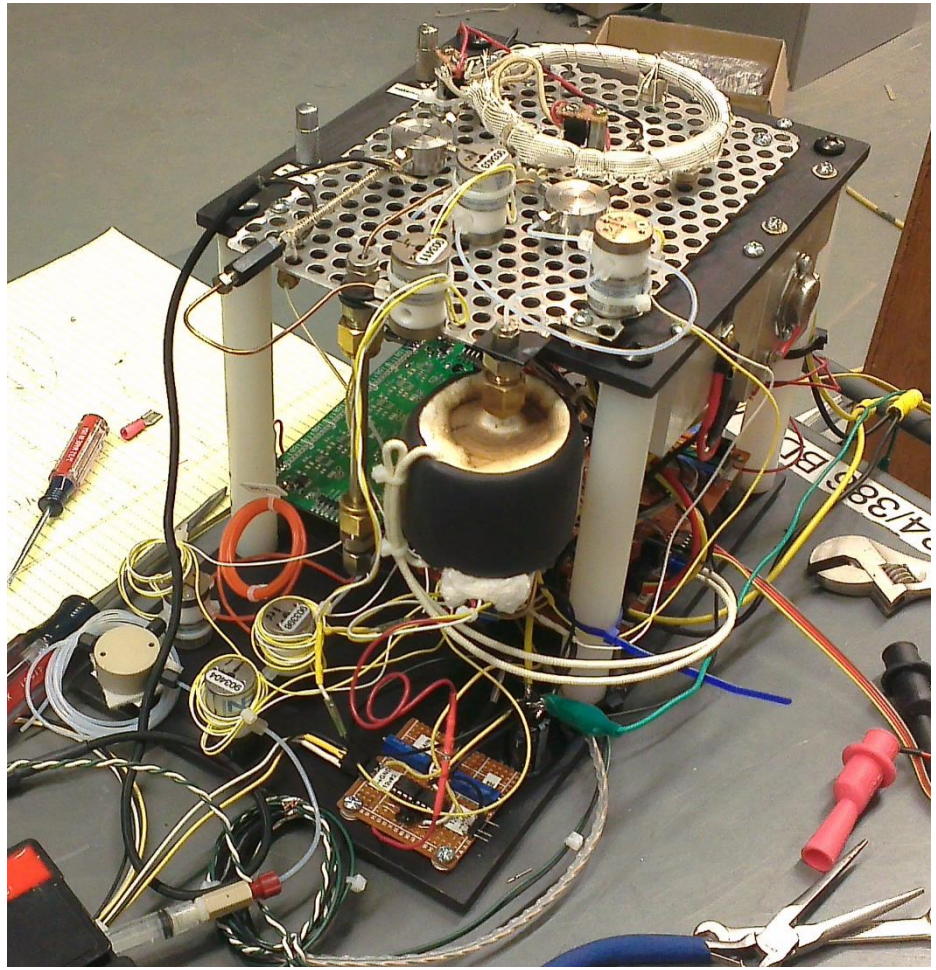


Risk Assessment – Is this feasible?

- Outdoor Operation
  - Weather proofing — Achieved
  - Temperature control — Achieved
  - Size — Reasonable, improving daily
  - Solar panel — Achieved
  - Power requirements — Reasonable, improving daily
- microGC Performance
  - 1 ppb (m/m in water) LOD — Achieved 100x better!
  - Battery power — Achieved, 1 analysis per day

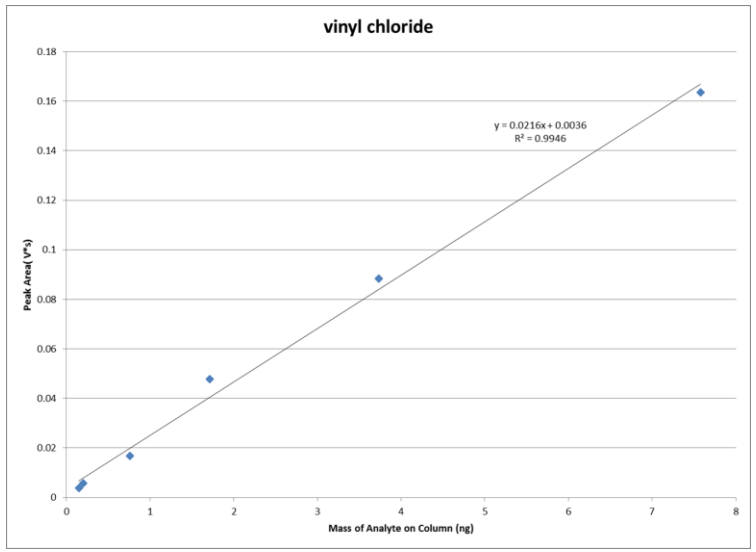
MicroGC

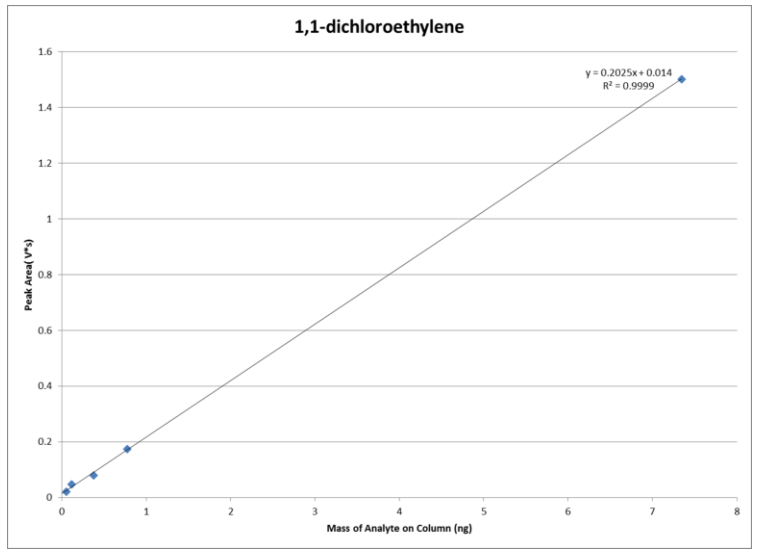


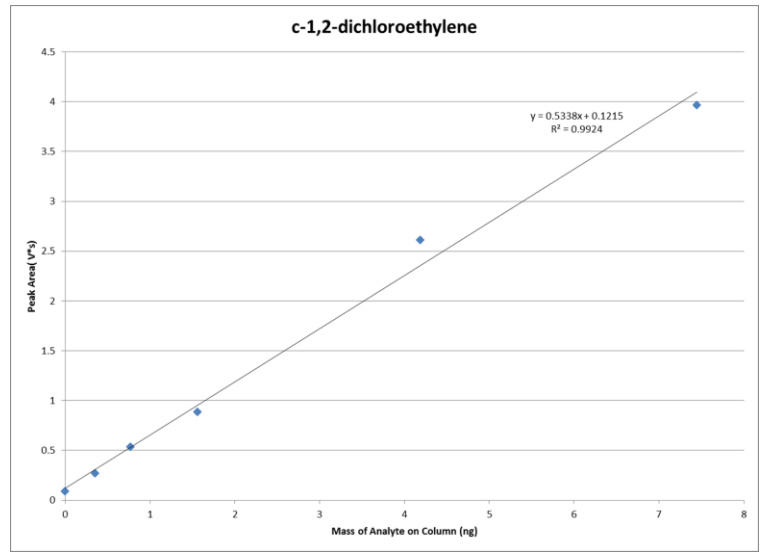


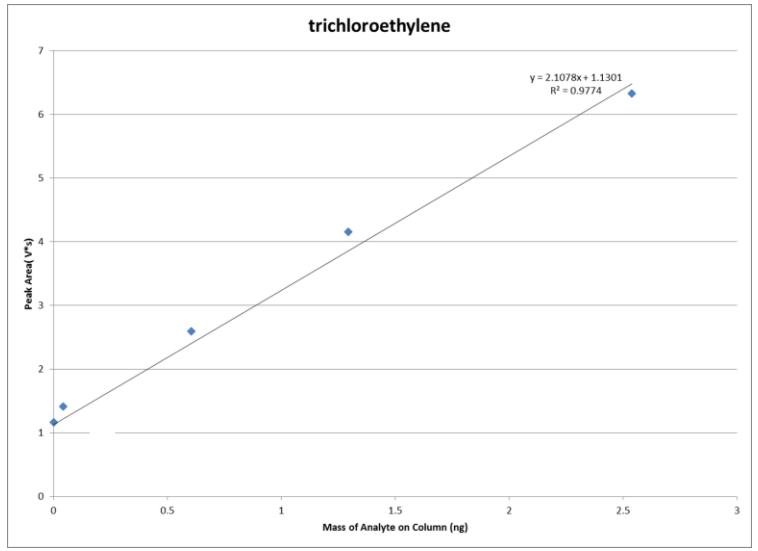
Quantitative Performance

0.01 ppb LOD for TCE with 1 mL water sample!





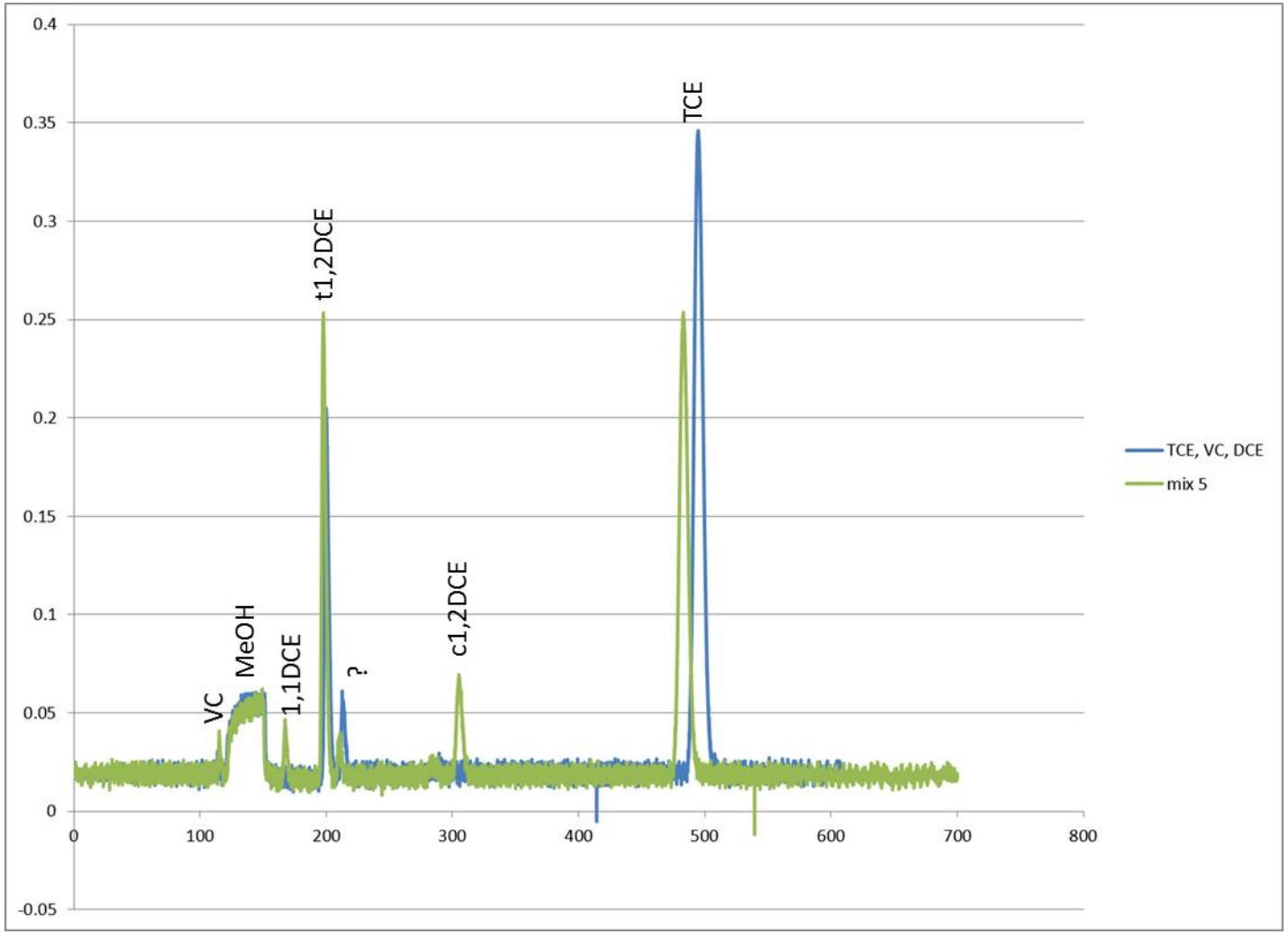




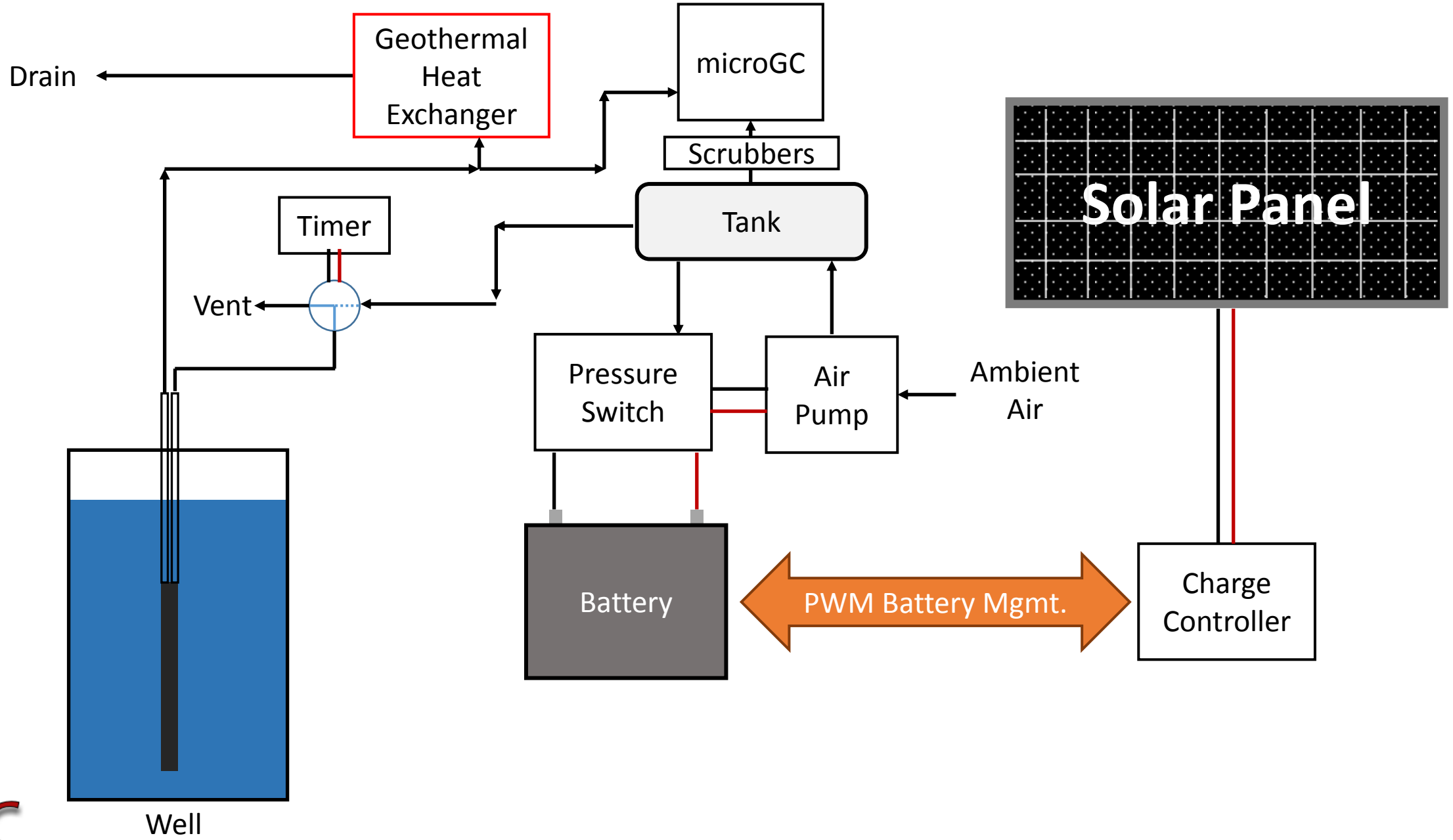
VGC Chromatography

www.vgcchromatography.com

Chromatographic Resolving Capability

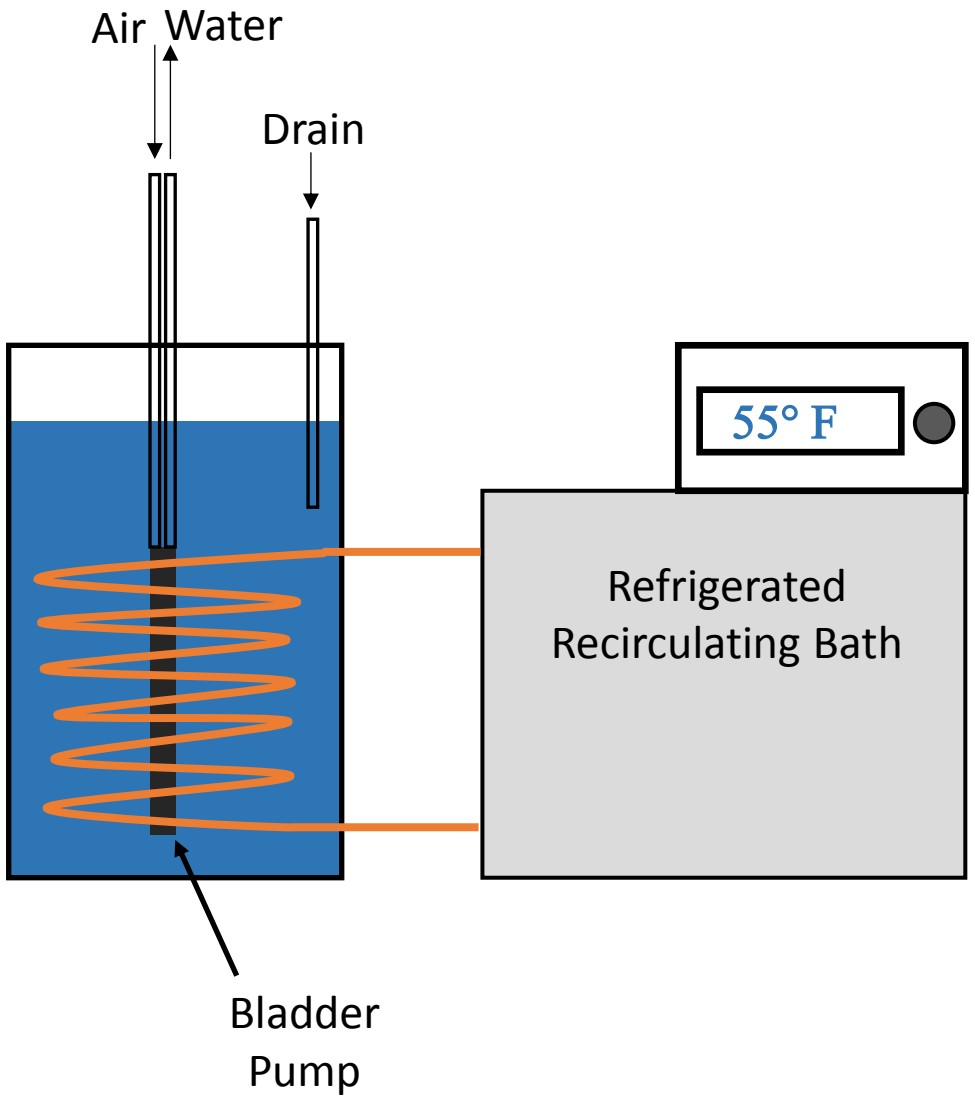


Solar, Geothermal, Pneumatic Systems



VGC Chromatography
www.vgcchromatography.com

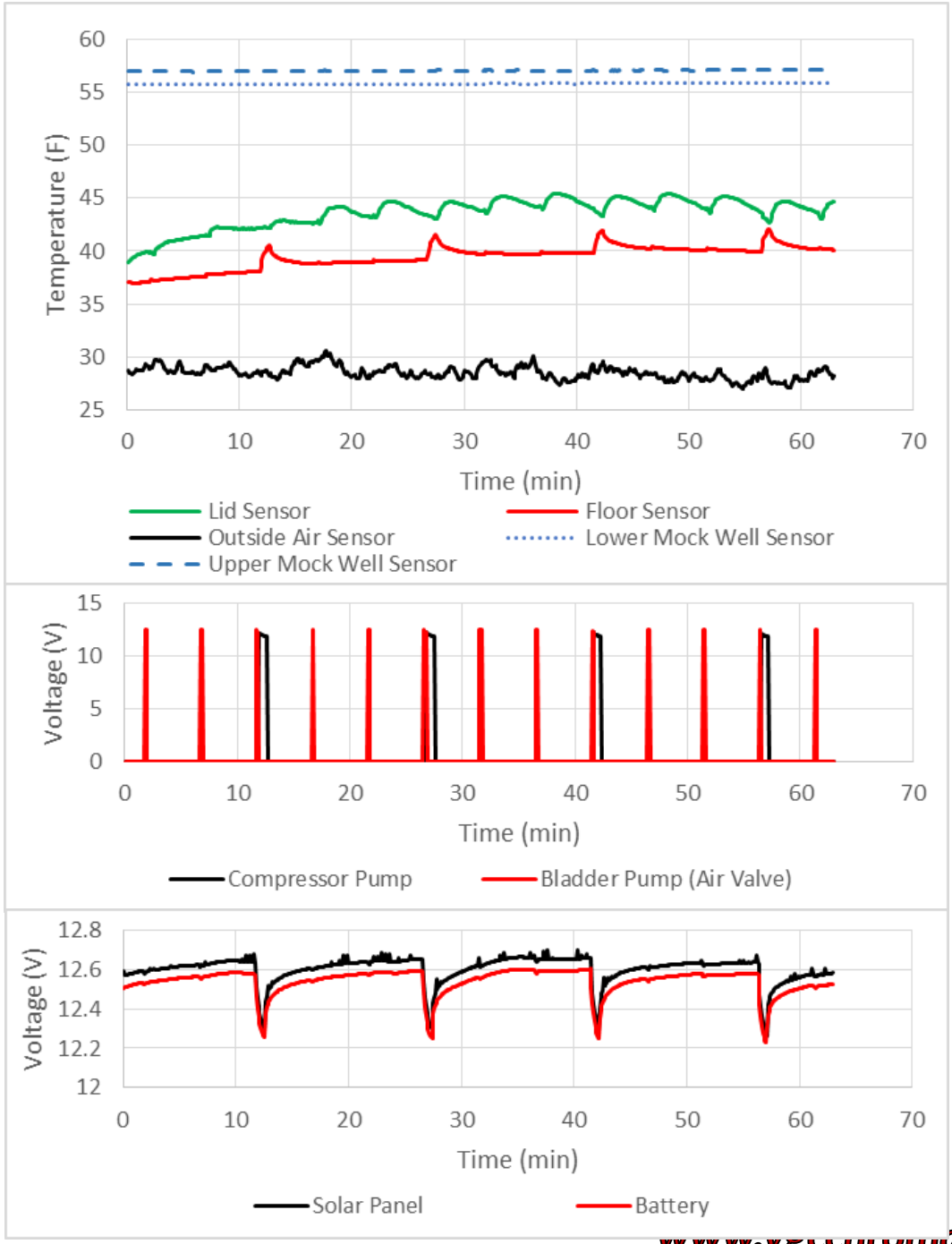
How to test? Mock Well



Roof Testing

Geothermal Performance

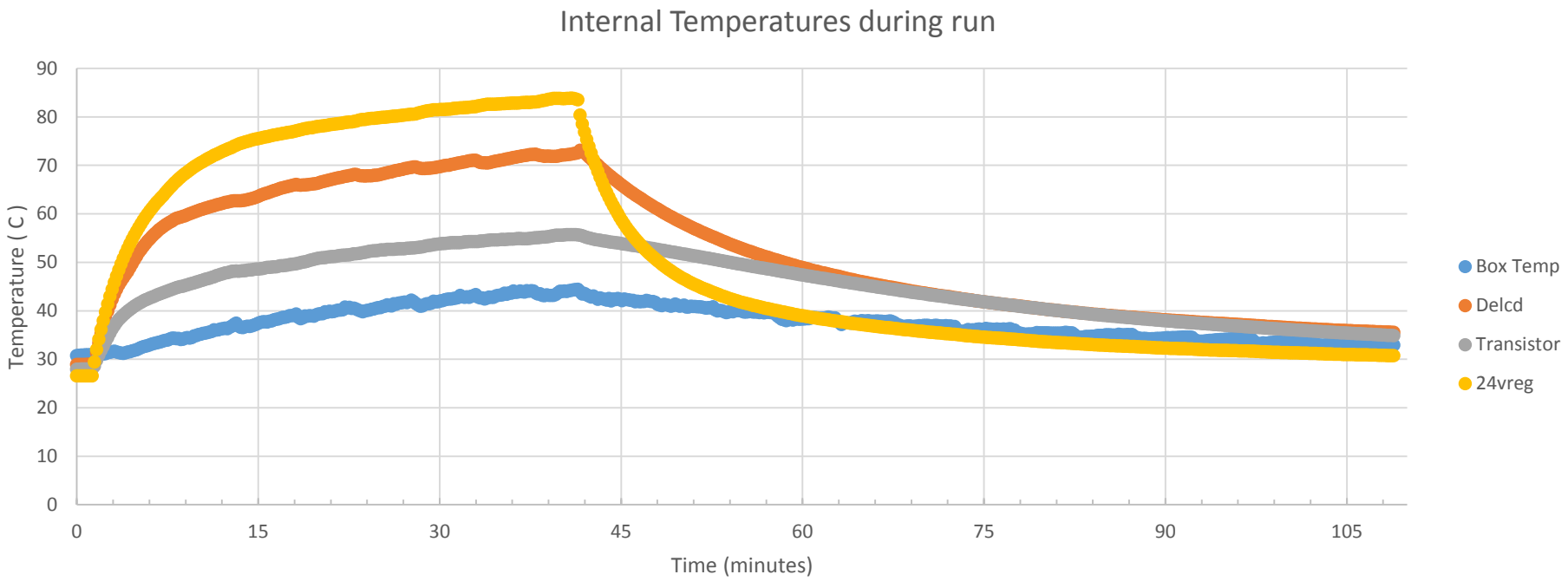
- 5 months roof testing
  - 138 Days
  - 13,248 pump cycles
  - 39,744 valve/bladder pump cycles
  - 19 kW-hrs of solar power
- Consistently maintained >35° F
  - Ambient dropped below -15° F
- Freeze/failure testing
  - No permanent damage
  - Self-starts when thawed



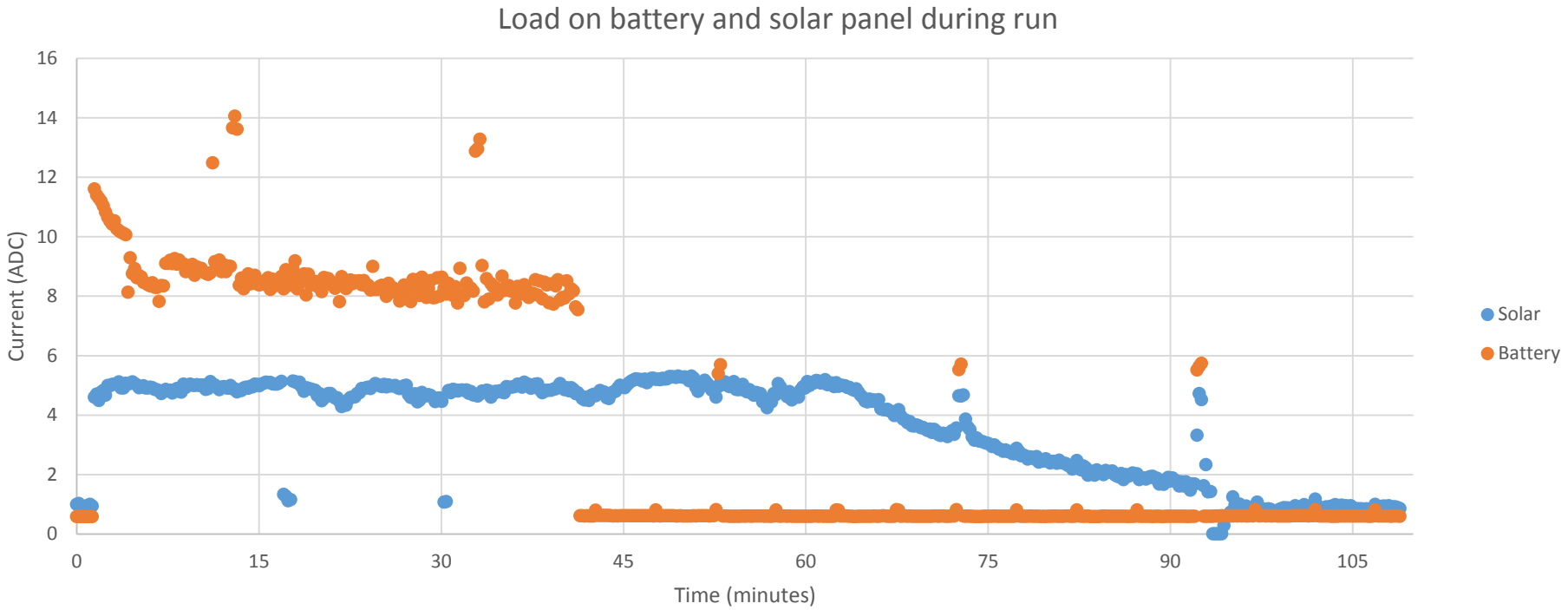
www.vgcchromatography.com

Power, GC Issues

- Electronics are heated when used
- GC generates heat
- Geothermal cools
- 45-60 minutes of GC operation does not overheat critical components
- **30-60 minutes downtime required between runs for cooling**

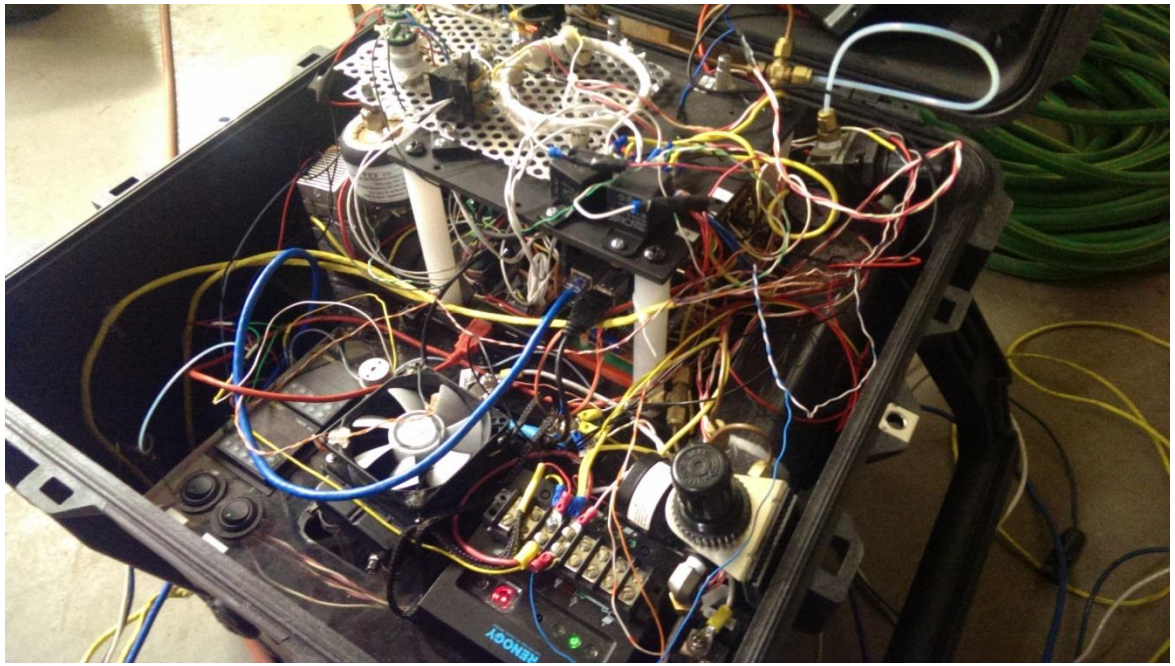


- Max current draw is 14 amp
  - Average is ~9 amp
- Solar current on cold/cloudy day is 5 amp
- 1 hour GC operation requires at least 1 hour of partial sun to recharge battery
- **Multiple GC analyses per day are possible!**



GC Chromatography

Pictures



Summary

- Automated VOC monitoring is here!
- New ground water management strategies
  - Plume tracking
  - Data-driven operation decisions
    - Air stripper operation
    - Interception well operation
- Surface water strategies
  - Continuous screening of water quality
- Water treatment, waste testing
- Taste certification (“food and flavors” is a popular use for GC)
  - Online VOC testing