Microfabricated GC for Sub-ppb_v Determinations of TCE in Vapor Intrusion Applications

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FRTR General Meeting

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Project Team

- Jim Reisinger, MS – PI
- Dave Burris, PhD, PG – Co-PI
- Rob Hinchee, PhD
  Integrated Science & Technology, Inc.

- Ted Zellers, PhD – U of MI Project Manager
  University of Michigan
  Center for Wireless Integrated MicroSystems

- Kyle Gorder, PE & Jarrod Case, PE
  Hill AFB, UT

- Paul Johnson, PhD
  Arizona State University

Technical Objectives

- Overall: **Build & demonstrate new VI analyzer tools using existing & emerging technologies.**

"Big picture" is ultimately have analyzers that are compound-specific for many VOCs – this project focuses on TCE, the most serious current DoD VI concern.

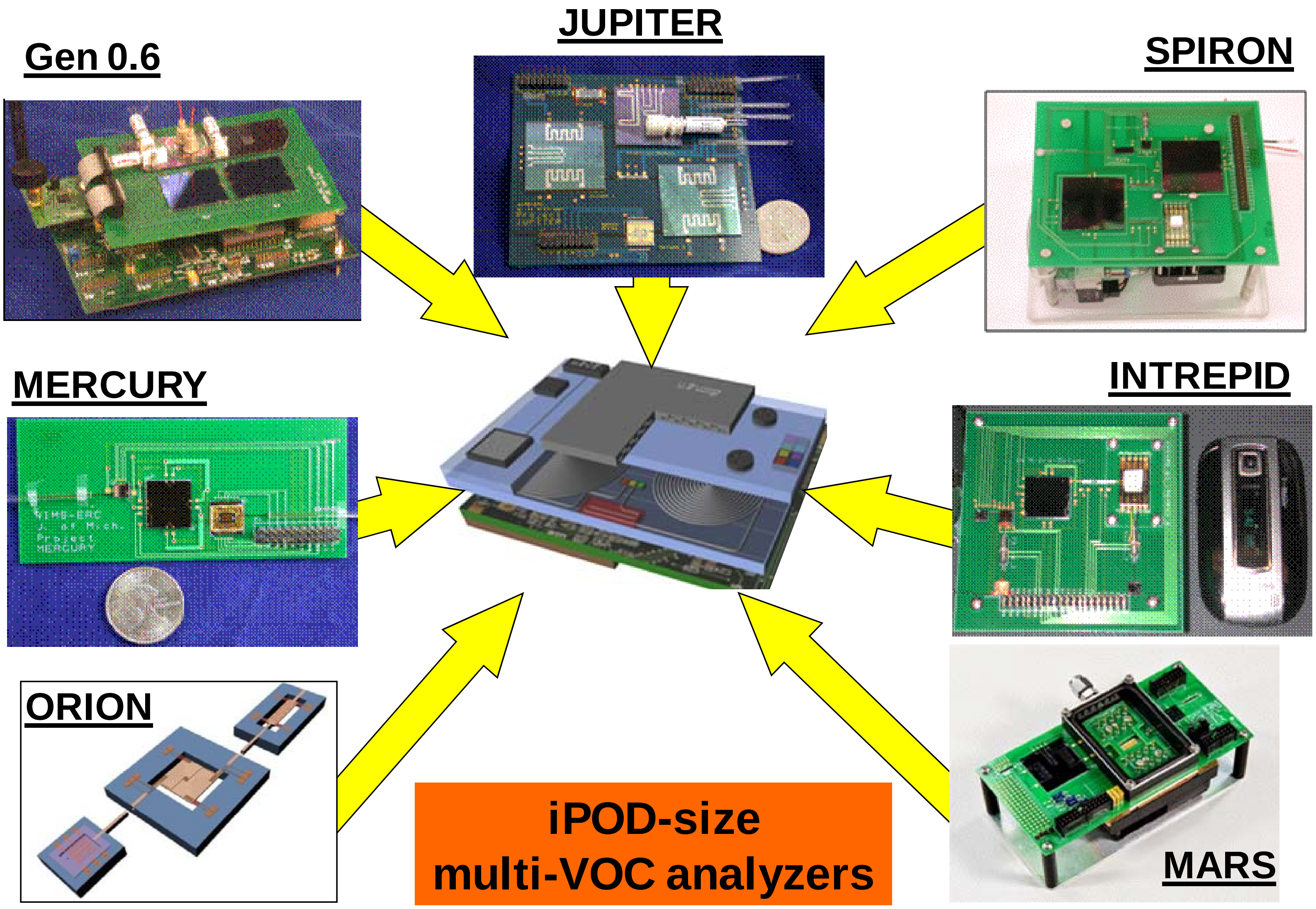
This will promote future evolution of analyzers.

- **Portable "sniffer" μGC unit** for hand-held short term compound-specific "forensic" identification.
- **Fixed "smoke alarm" μGC unit** for long-term compound-specific exposures with remote communications.

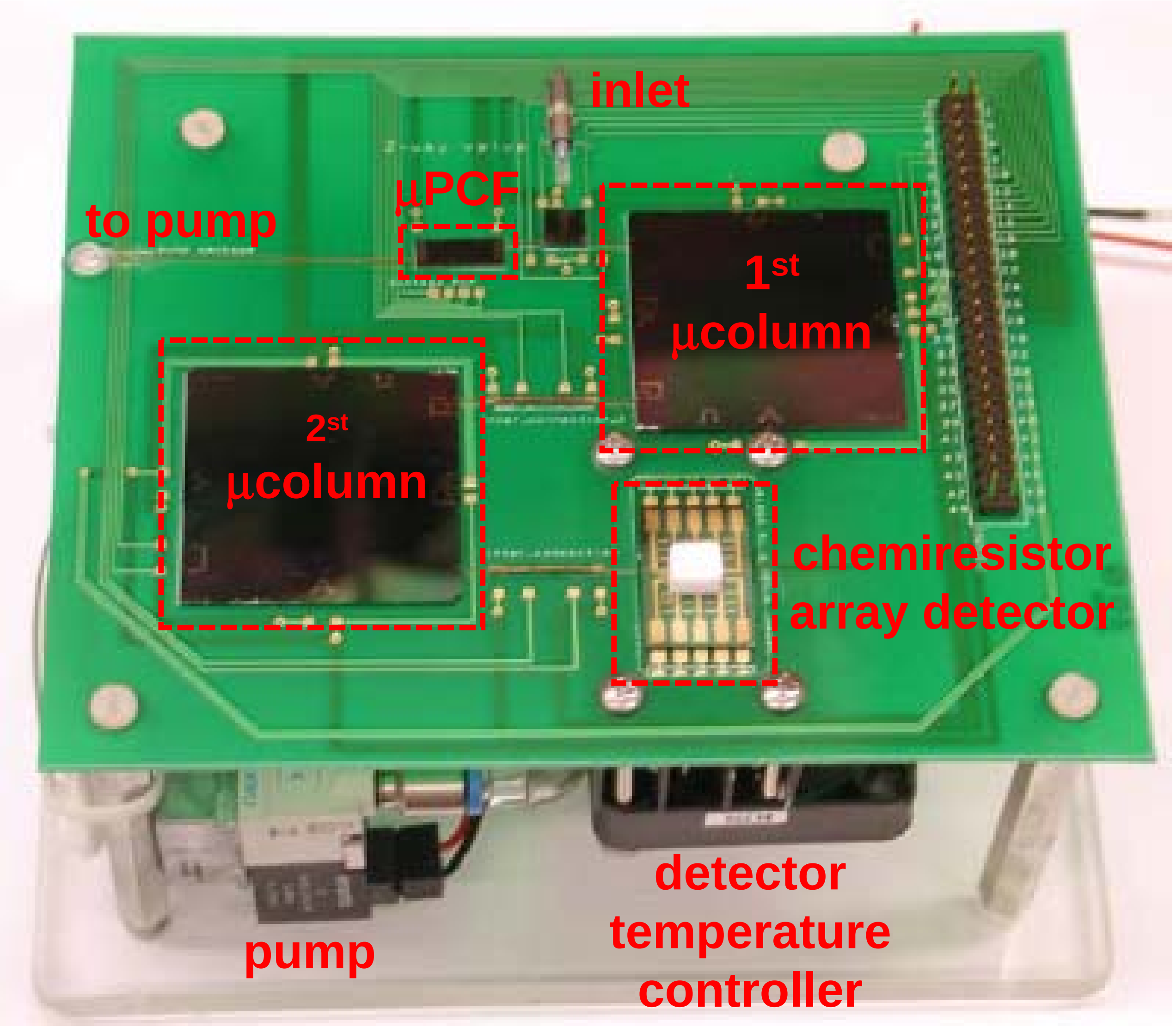
Specific μGC Project Goals

- Fast Sample Turn-around Times (approaching 15 minutes)
- Detect TCE in Presence of Common Indoor Air VOCs (i.e., compound-specific determinations)
- Low Detection Limit for TCE (0.06 ppb_v for portable μGC and 0.03 ppb_v for fixed μGC)
- Portable μGC – Forensic Assessment: VI or Indoor Source?
- Fixed μGC – Long-Term (weeks, months) Exposure Monitoring with Wireless Remote Communications

Advances in Component & System Designs Toward a Wireless μGC



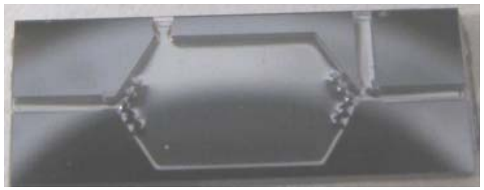
SPIRON – Prototype µGC



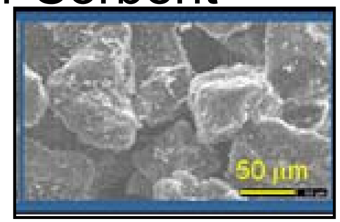
A Versatile µ-Analytical System

Key Component: µPreconcentrator/Focuser (µPCF)

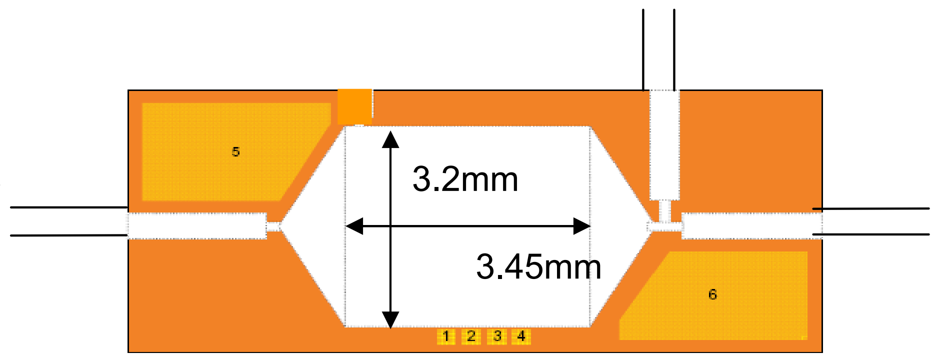
1-Stage Granular Sorbent



Si/glass



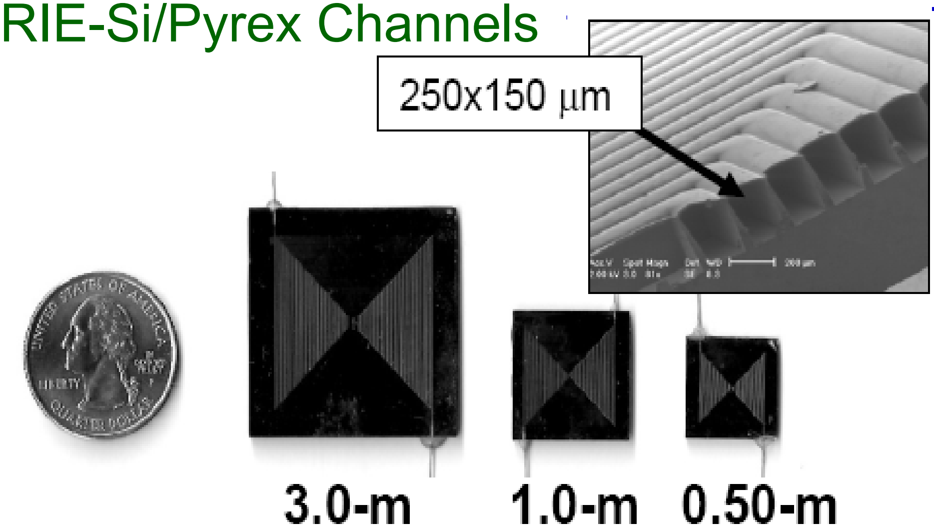
Carbopack X

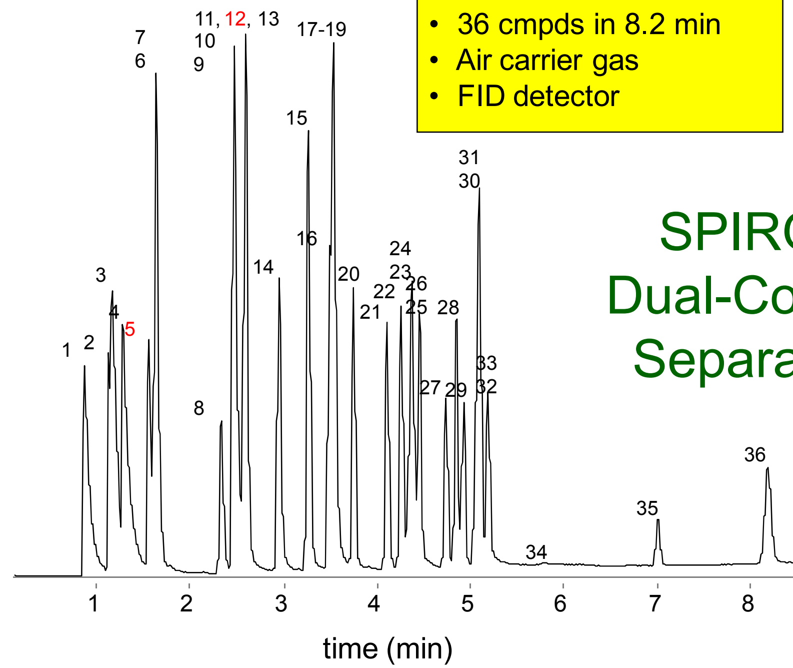


- µGC requires a µPCF to minimize "injection" volume (room temp to 200^{o}C in 0.2 sec)
- µPCF fluidics limits volumetric flow rate
- High-volume samples obtained with **<u>high-flow sampler</u>**/µPCF combo

Key Component: μColumn

DRIE-Si/Pyrex Channels

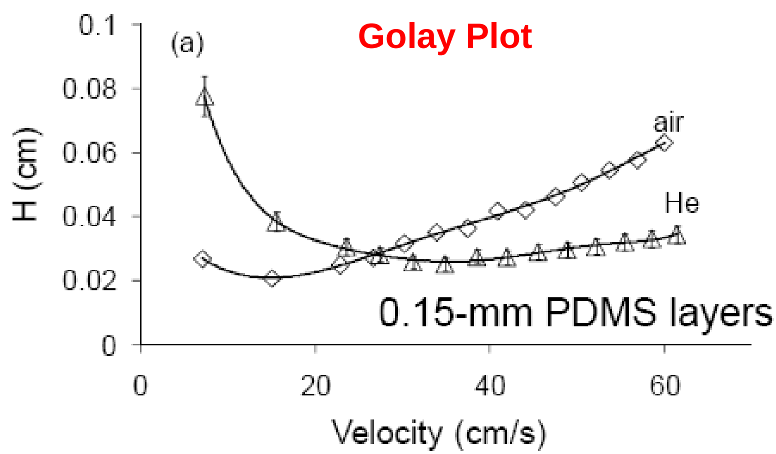




- 36 cmpds in 8.2 min
- Air carrier gas
- FID detector

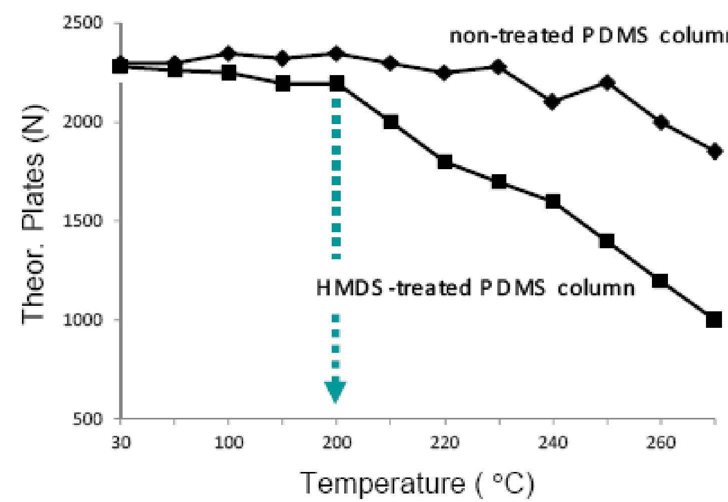
SPIRON Dual-Column Separation

Reproducible, Efficient Coatings



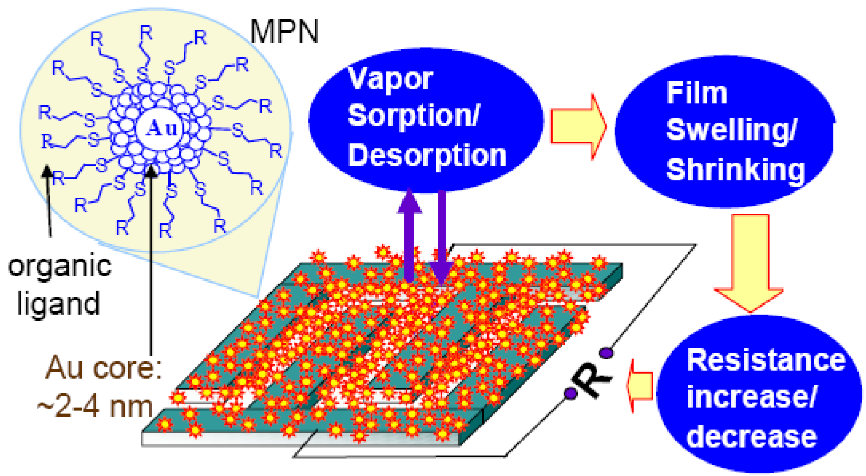
5 columns, statically coated, provide 4200 ± 200 theor. plates per meter

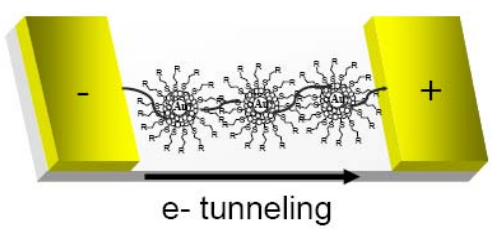
Stable in Air up to ~200 °C

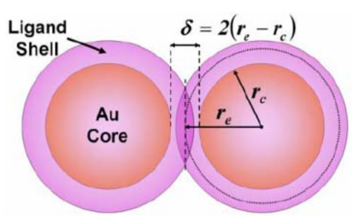


Key Component: µDetector

Gold Nanoparticle Chemiresistor Array

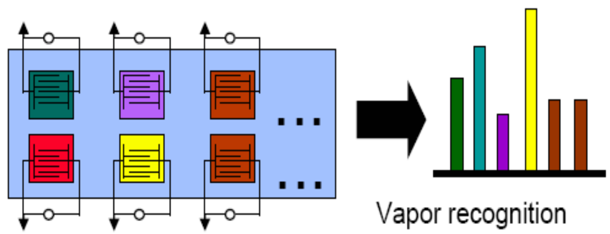


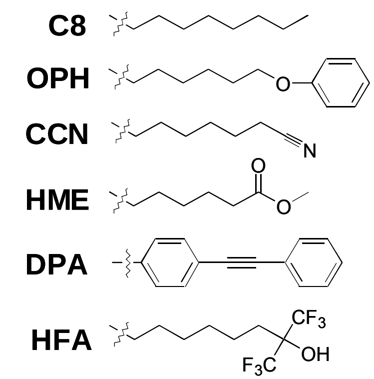




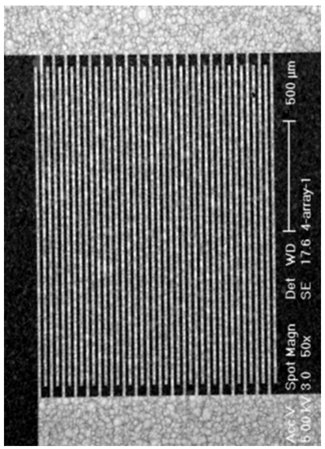
- Resistance based on analyte partitioning
- Partitioning based upon conc. not mass
- Allows scaling down in size
- Rapid, reversible, partially-selective
- Micro-interdigital Au/Cr electrodes

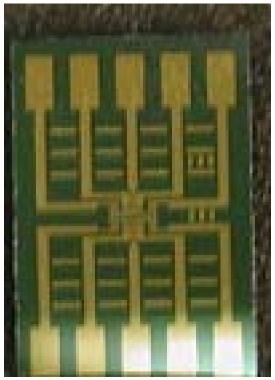
Chemresistor Array – More "Information"

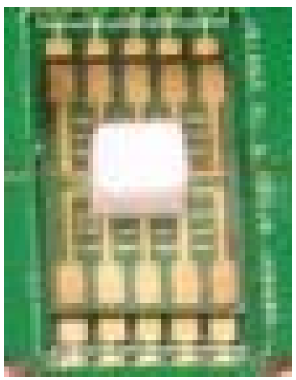




Response Patterns – Peak ID



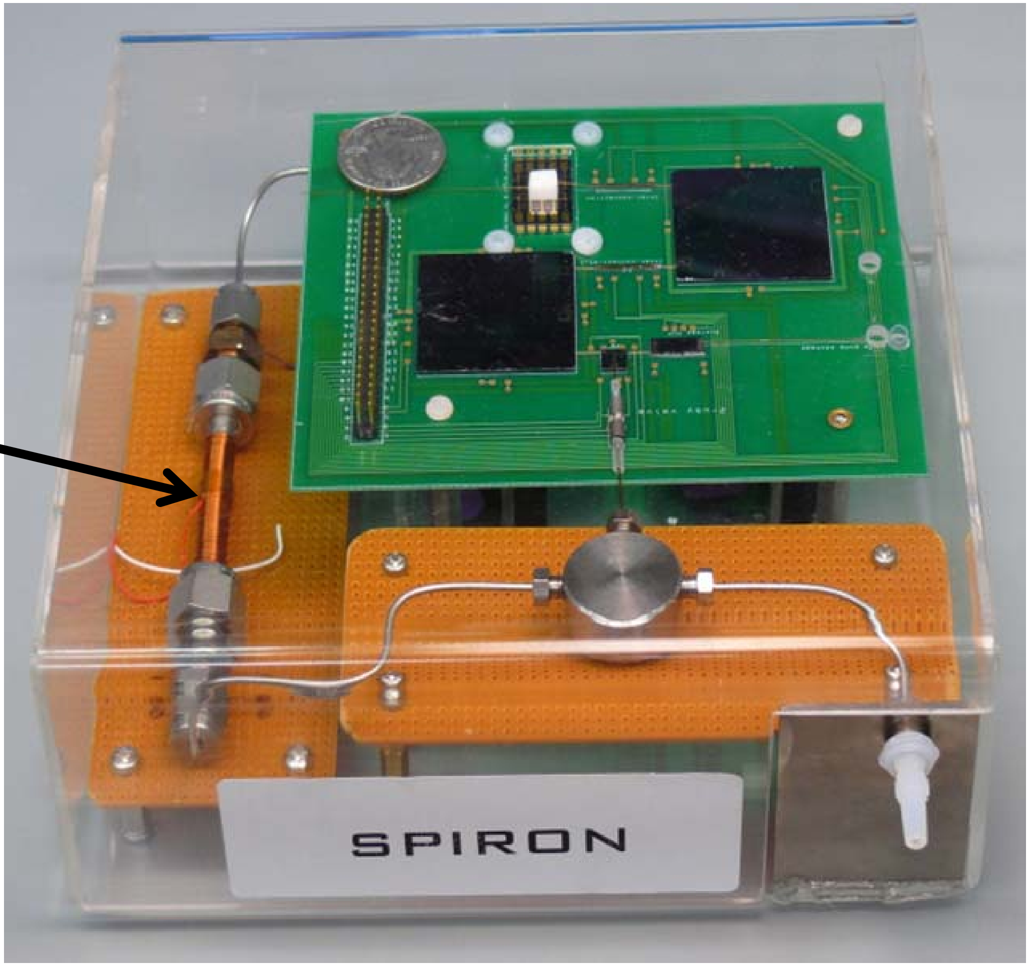




Flow Cell Volume: as small as ~ 1.5 µL

SPIRON – Prototype with High-Flow Sampler (Mock-Up)

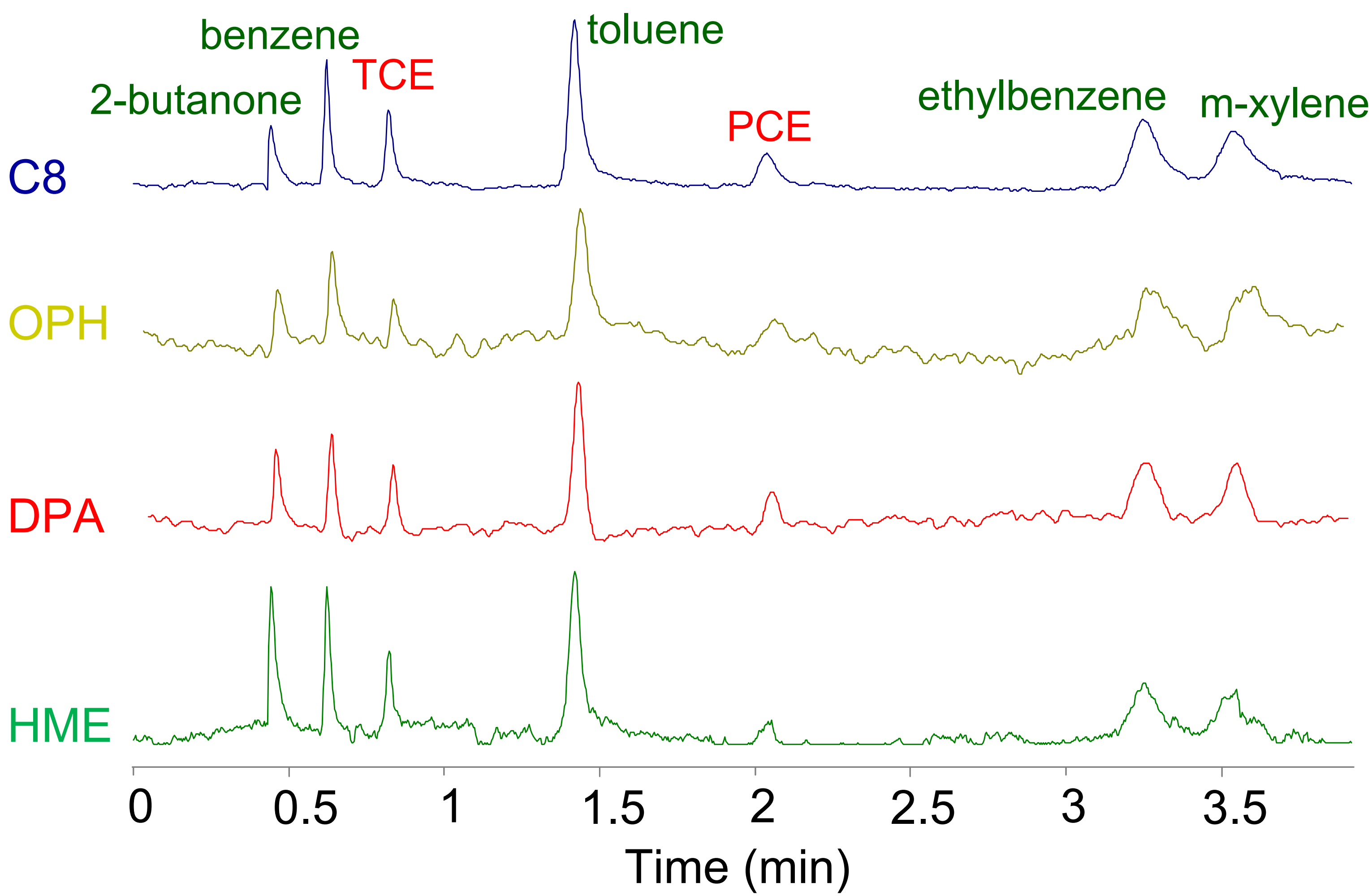
High-Flow Sampler



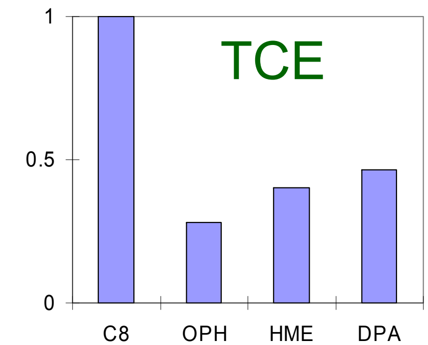
High-flow sampler is needed for VI applications.

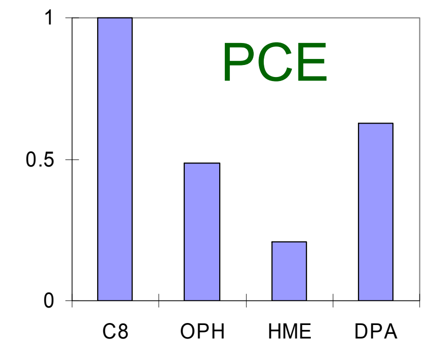
Preliminary SPIRON μGC Results

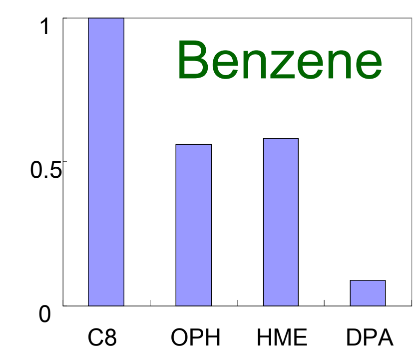
Determination of TCE & PCE among 6 common interferences found at Hill AFB



Unique Response Patterns

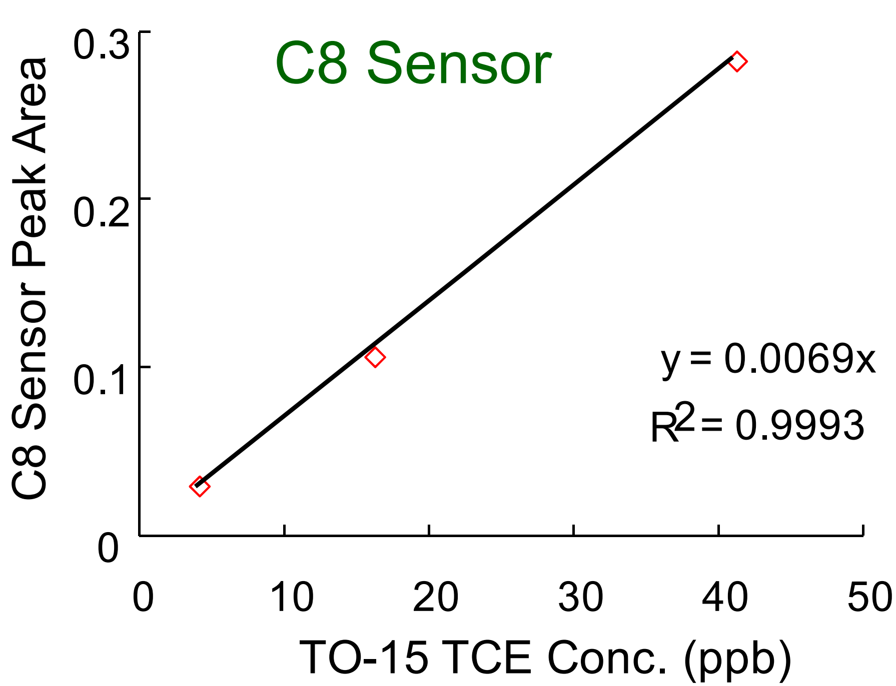


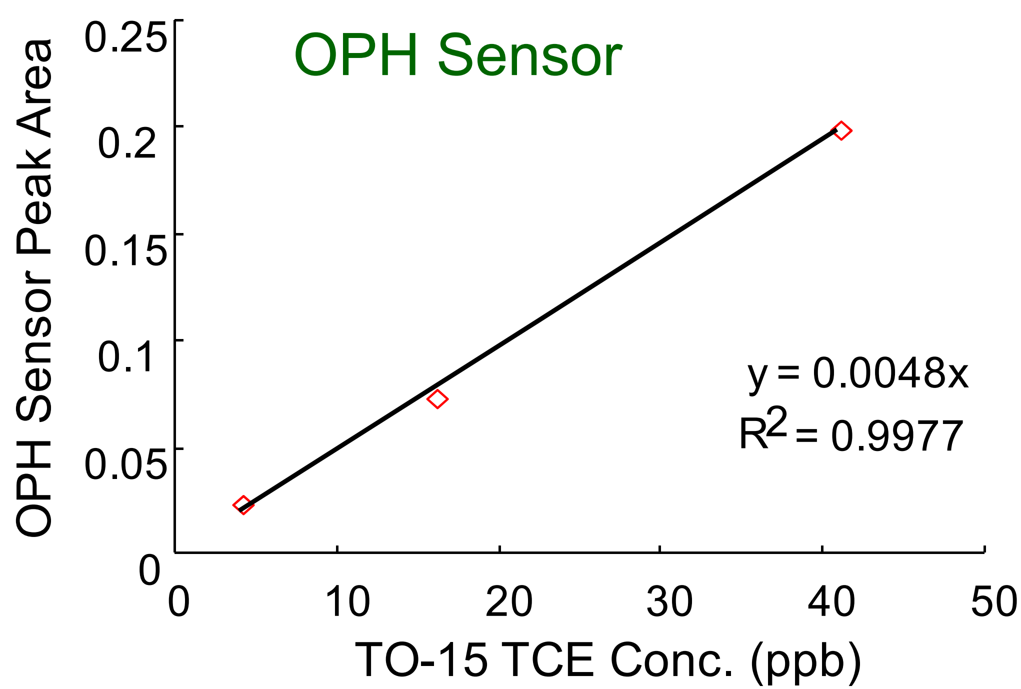




Preliminary SPIRON μGC Results

TCE Calibration Curves





Sensor calibrations are linear

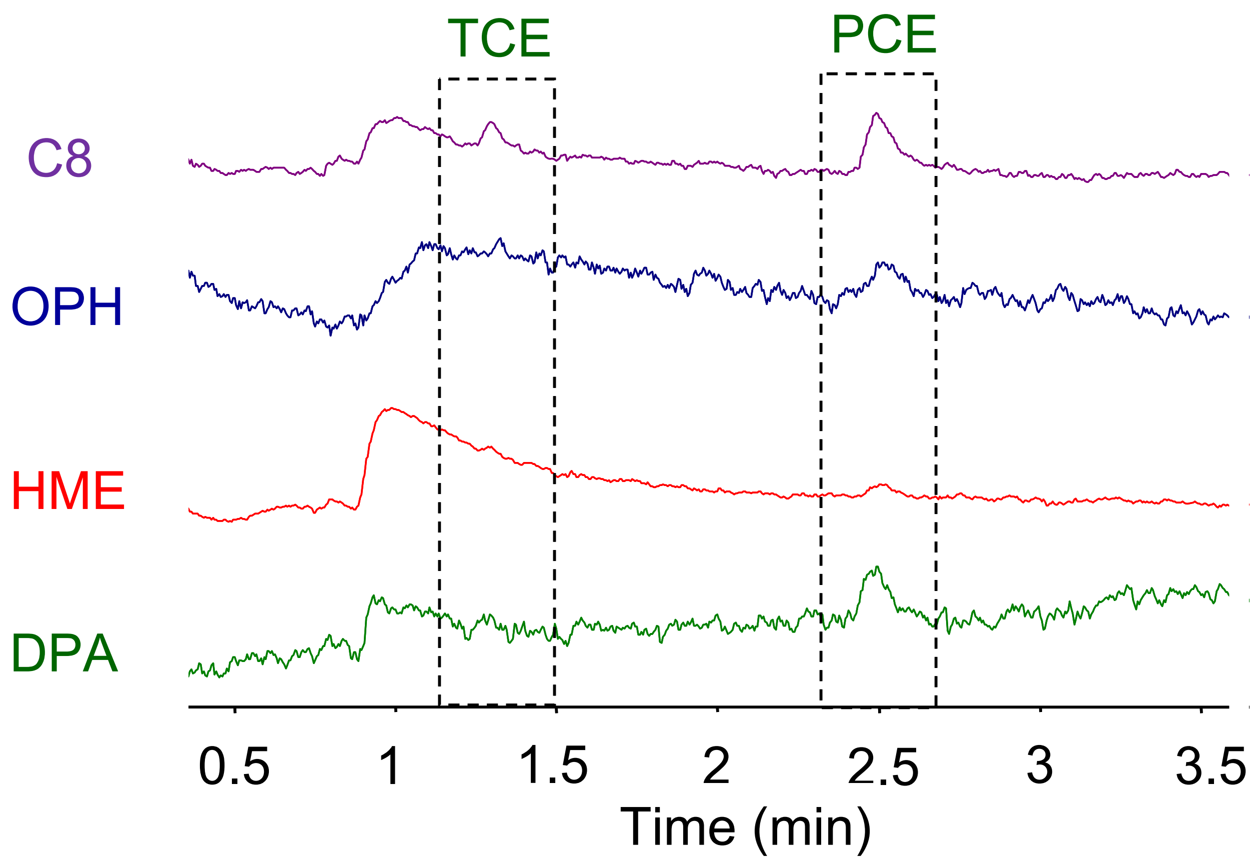
Preliminary SPIRON μGC Results

TCE Limits of Detection (LOD, ppb)

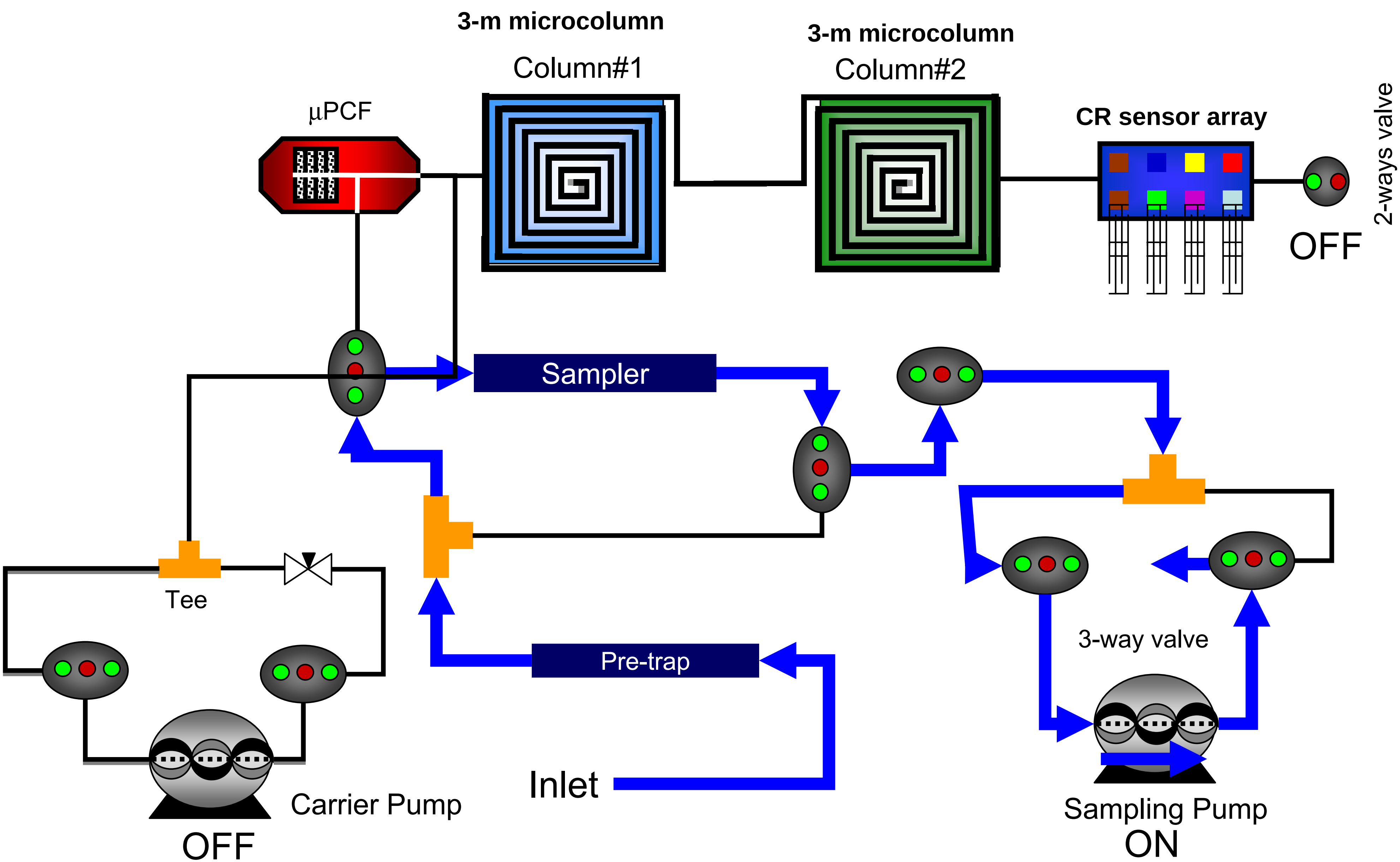
	C8	OPH	DPA	HME
Sensitivity (V/ppb$_v$)	0.1095	0.0465	0.0643	0.0493
SD of noise (V)	0.0212	0.1539	0.0821	0.0643
LOD (ppb$_v$ in 1L)	0.58	9.9	3.8	3.9
LOD (ppb in 6L)	0.10	1.7	0.64	0.65

4-ppb TCE & PCE measurement

- 2 L sample
- ambient RH
- raw data

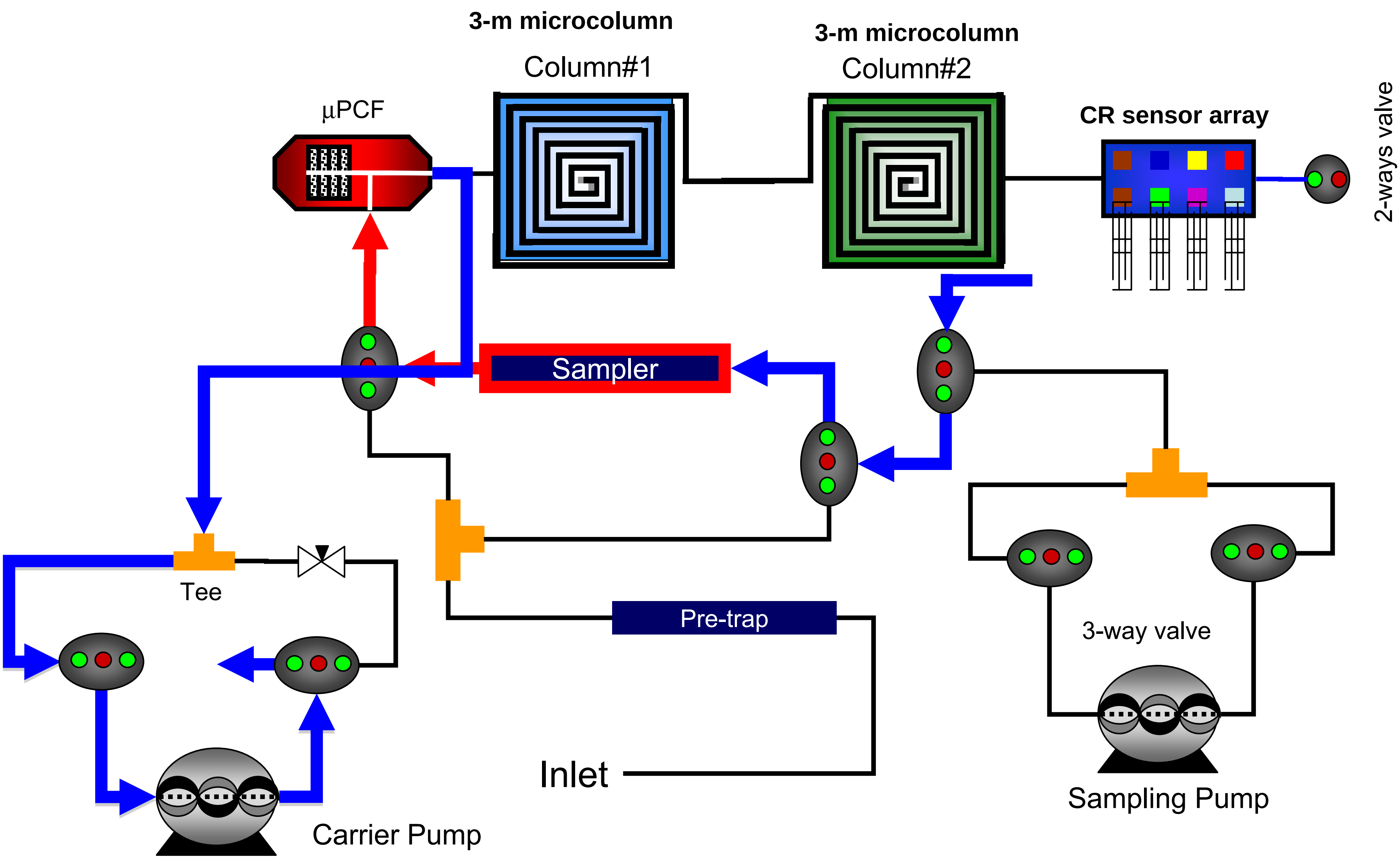


Sampling



3-m microcolumn
Column#1
3-m microcolumn
Column#2
µPCF
CR sensor array
2-ways valve
OFF
Sampler
Tee
Pre-trap
3-way valve
Carrier Pump
OFF
Inlet
Sampling Pump
ON

Focusing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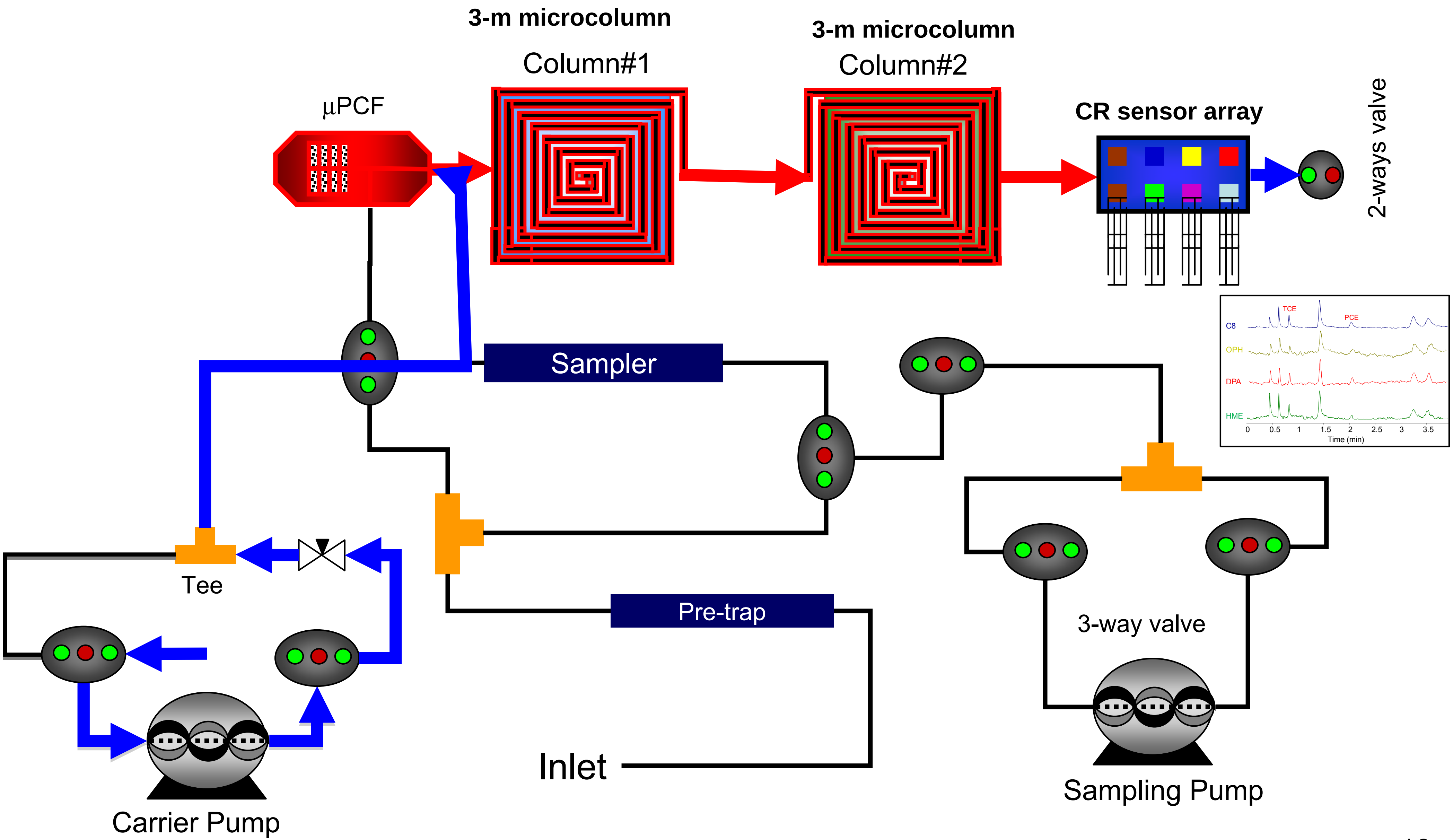
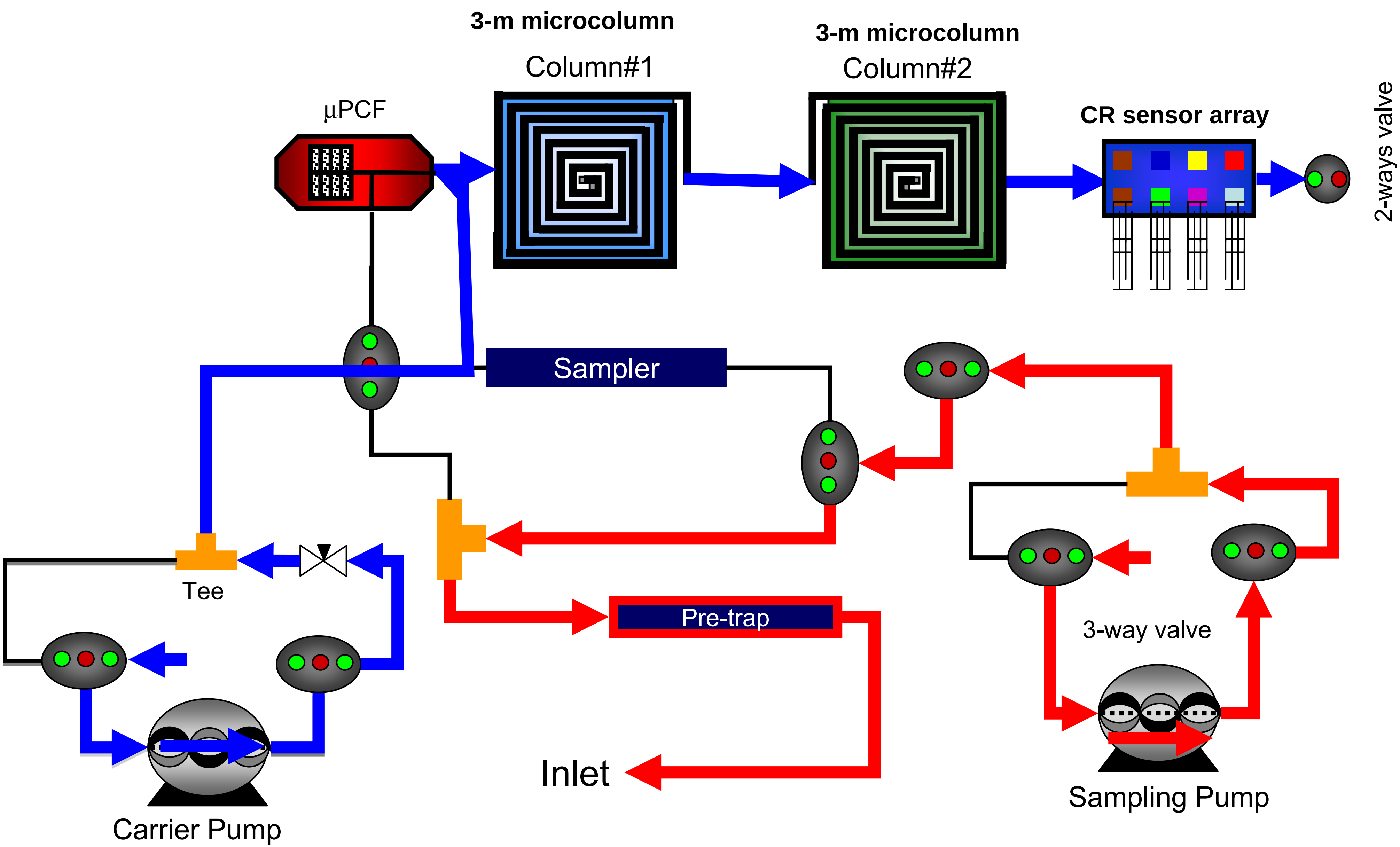
Sampler
Tee
Pre-trap
3-way valve
Inlet
Carrier Pump
Sampling Pump

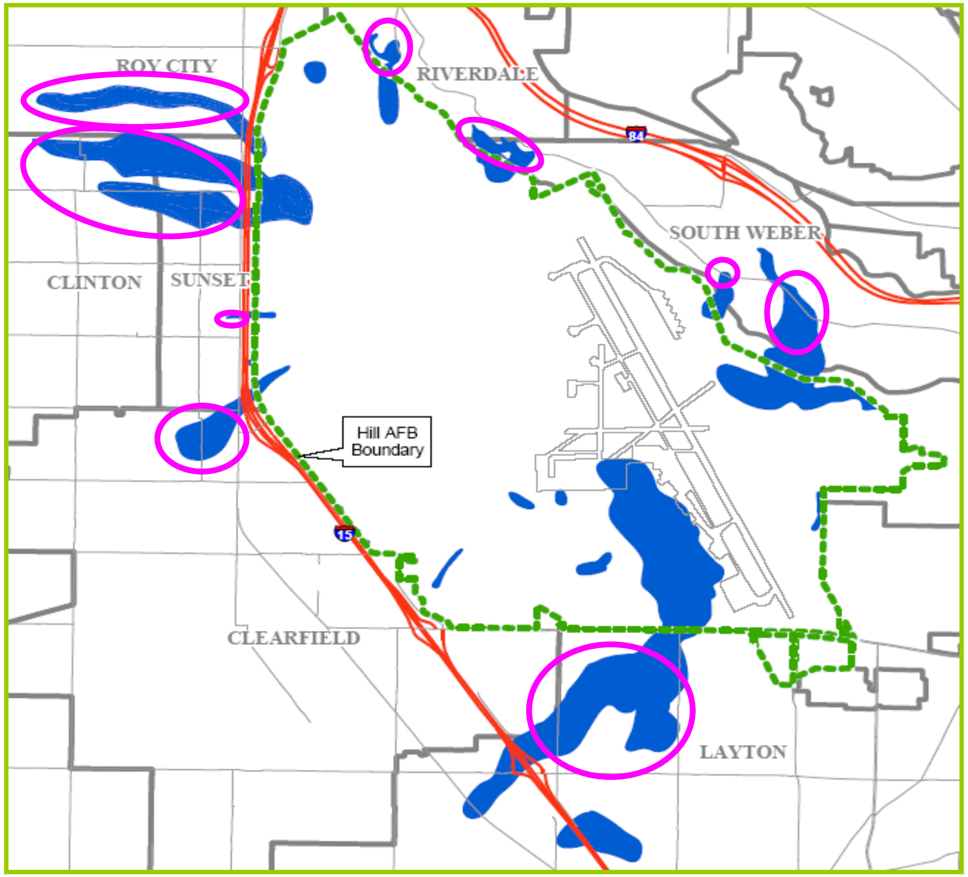
Separation & Analyzing



Cooling & Regeneration



Demonstration Site Description



Hill AFB, UT

(blue area symbol)	Areas of Shallow Groundwater Contamination
(magenta ellipse symbol)	General Area of Indoor Air Sampling Locations

Residential homes near Hill AFB are impacted by VI of TCE & are part of on-going indoor air sampling program

TCE Mitigation Action Level = 2.3 ppb$_v$

- Will coordinate with Hill AFB personnel on residential homes used in demo.
- Will also use SERDP Hill AFB VI-impacted research house (Dr. Paul Johnson) for portable and fixed µGC demonstration.

Phase II: Develop Field μGC Prototypes

- Improve TCE LOD (fraction of Hill AFB MAL of 2.3 ppb)
  - optimize high-flow sampler/μPCF system
  - optimize chemiresistor detector for sensitivity
- Robust-ize μGC – dependable operation is required
  - improve μPCF design for long-term operation
  - improve long-term stability of chemiresistor detector
  - dependable long-term retention time stability
- Rugged-ize μGC – dependable field operation
  - package μGC platform for field portability
  - ease of sampling and standardization
  - AC operation

Phase II: Develop Field μGC Prototype

- Develop chemometrics for co-elution with TCE
  - can be used to deconvolute an interfering peak
- Lab test with Hill AFB field samples
  - actual field interferences
  - address problematic interferences
- Automate field μGC operation
- Establish wireless communications with μGC
- Fabricate four field μGC prototypes

Schedule

- First Field μGC Prototype – January 2010
- Testing and Optimization – Spring 2010
- 4 Field μGC Prototypes (2 portable, 2 fixed) – Spring 2010
- Portable and Fixed μGC Field Demonstrations at Hill AFB – Summer 2010

Conclusions

- Adequate field analysis tools for VI do not presently exist (with exception of mobile analytical laboratories)
- μGC Prototype development has demonstrated compound-specific determination of TCE at low detection limit – Optimization is in-progress
- Will be first field demonstration of μGC
- μGC will provide a tool for VI investigations where none currently exists
- μGC can be adapted to other environmental analysis applications