Chip Scale Mass Spectrometry

. . .Yet another contender for Harsh Environments? Or can it help redefine "Harsh Environments"?

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Consultants

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Collaborators

T&E Team

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Ryan Bell, Friso van Amerom, John Nicosia, Judd Sheets, James Baughman, Wei yang and more!

Detect-Ion LLC ("Detection")

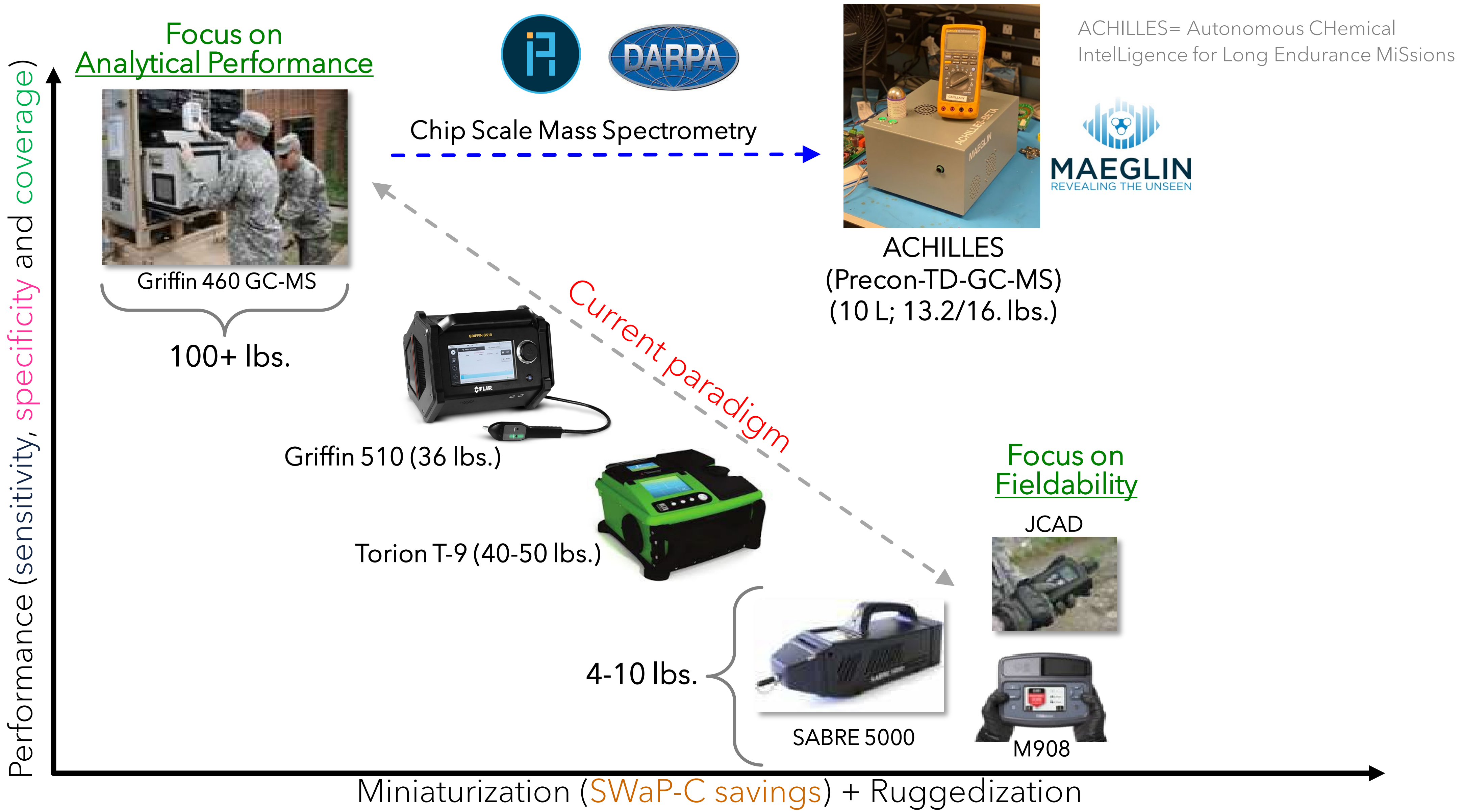
Mission: Next Generation Sensor Development For Enhanced CBRNE Sensing

Vision: Bring Traditional Mass Spectrometry Performance to the Masses

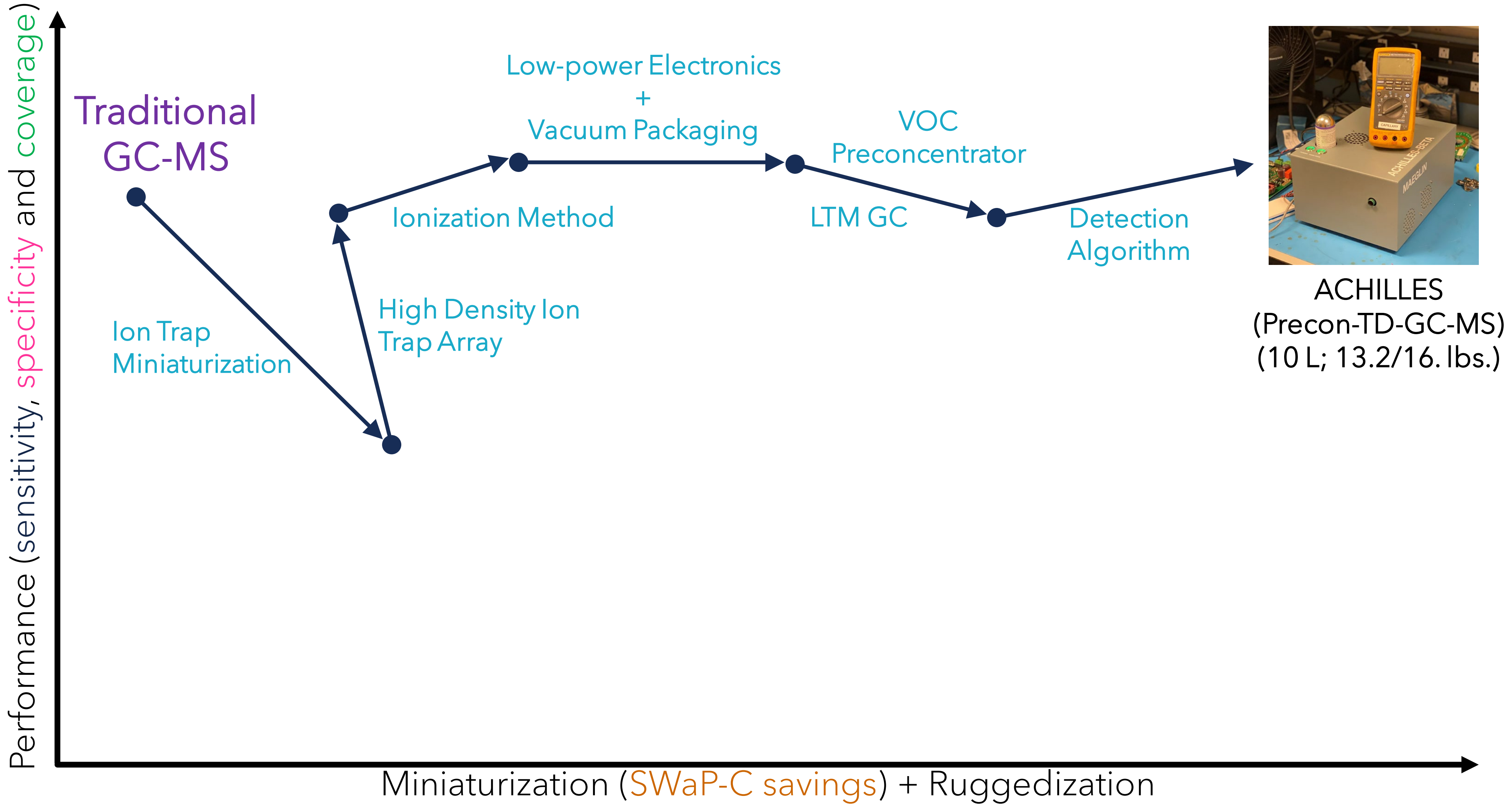
- Small business technology startup (October 2021)
- Technical team hails from SRI International
  - Performers on IARPA MAEGLIN and DARPA SIGMA+ CWMD programs
- Inducted into the Tampa Bay Technology Incubator (TBTI) and housed on USF Tampa campus
  - Dedicated laboratory space
    - Onsite rapid prototyping
  - Access to shared high-value lab resources through the TBTI program
  - Florida Hi-Tech Corridor Matching Funds

Proud partners with TBTI TAMPA BAY TECHNOLOGY INCUBATOR USF UNIVERSITY OF SOUTH FLORIDA

Motivation: Disrupting the Monotonic SWaP vs. Performance Trade off

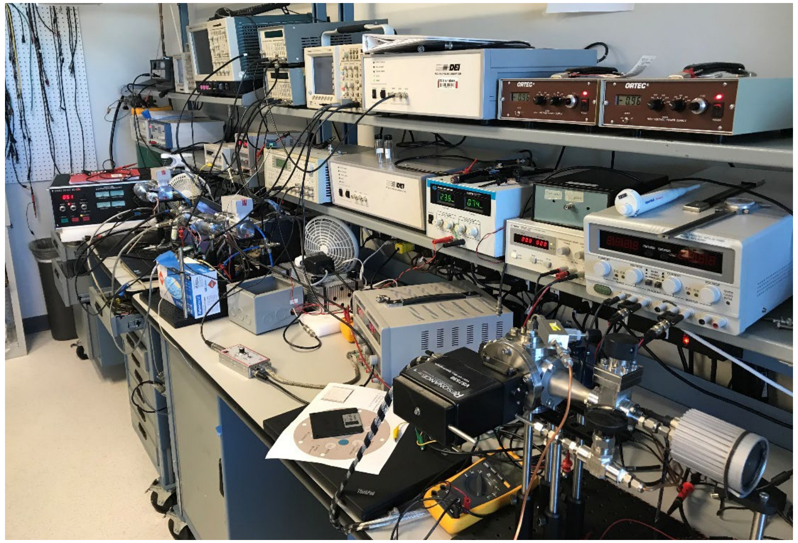


Research Themes that enabled ACHILLES



Roadmap

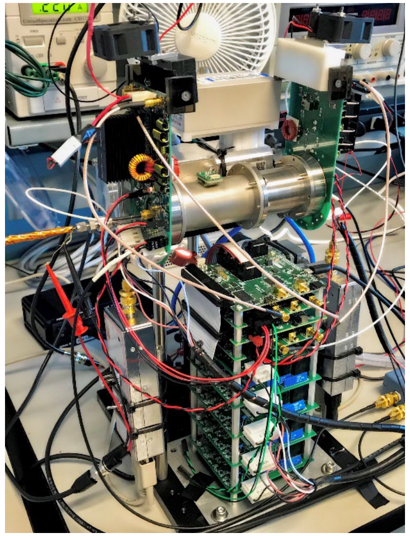
Half a lab!



Validation Testbed (2017)

MAEGLIN P-1

Lots of ancillaries

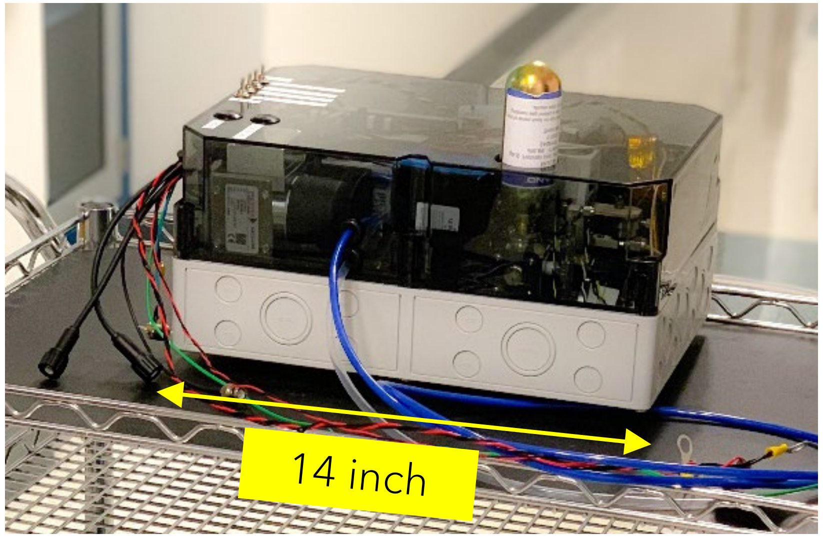


Lab Model (2018)

SIGMA+ (Yr-1)

DARPA

17.4 L



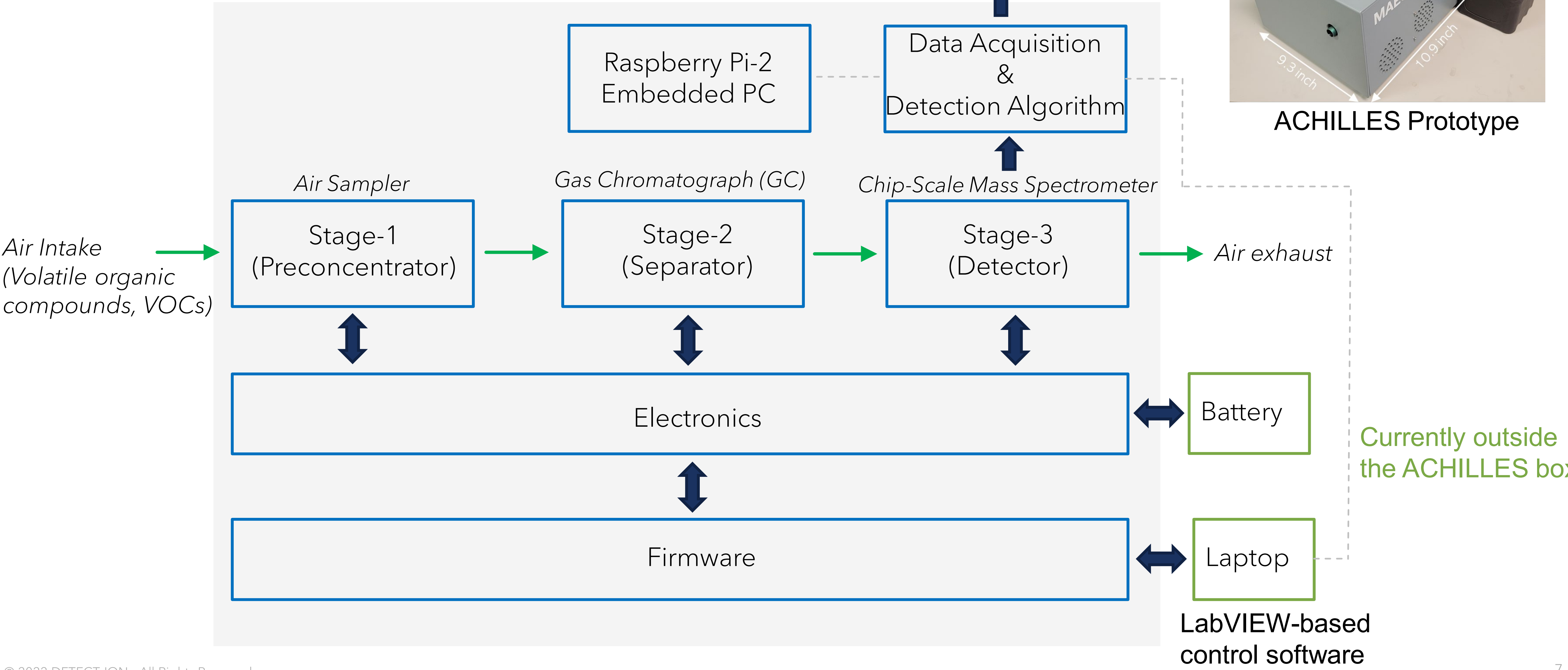
Transportable Prototype (2019)

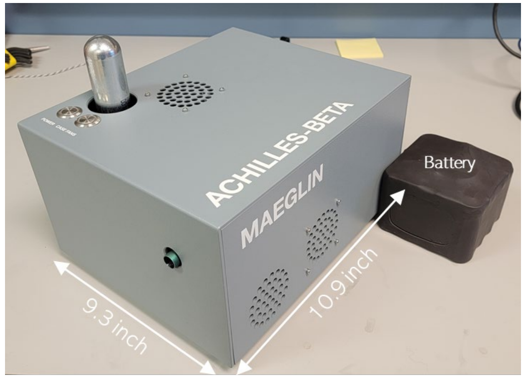
MAEGLIN P-2

~10 L

ACHILLES (2021)

ACHILLES Block Diagram





ACHILLES Prototype

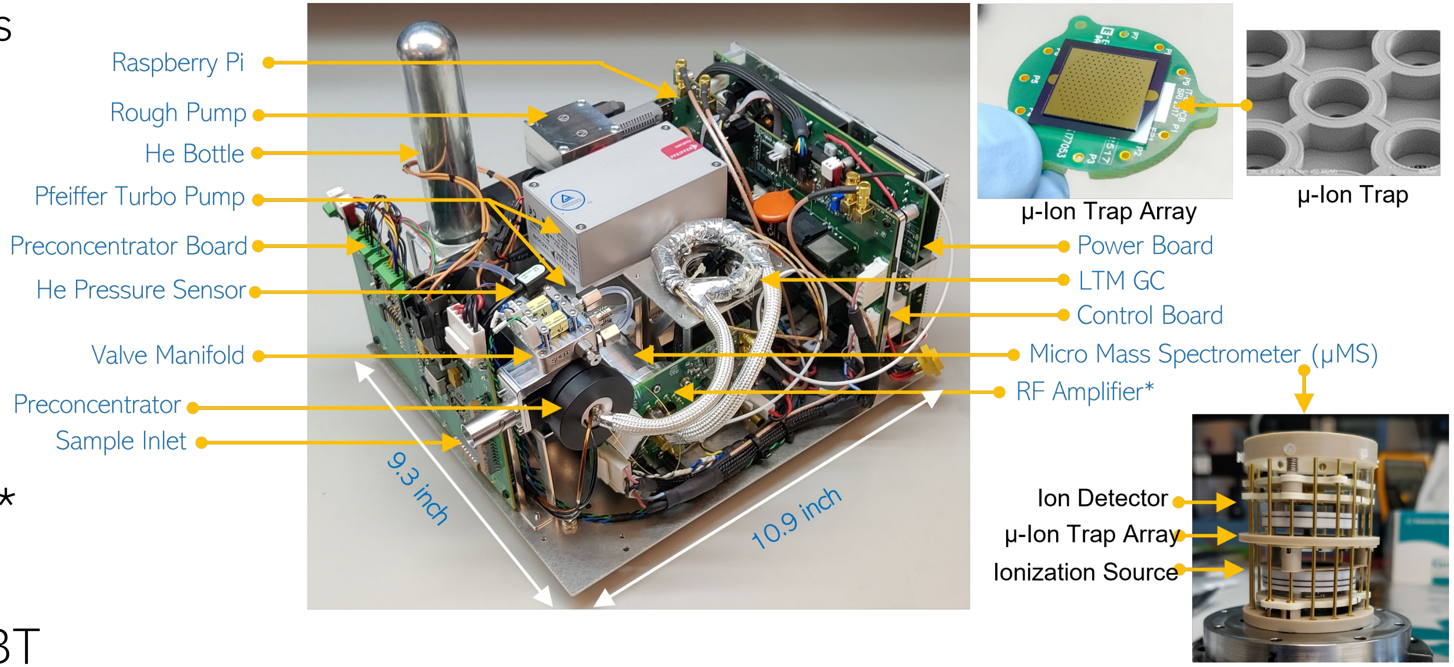
ACHILLES (TRL-5/6)

Technology Highlights

- World's lowest Swap-C [TD-GC-MS] platform
- High sensitivity validated for >200 VOCs
- Chemical portfolio: semi-volatile and volatile organic compounds (VOCs) including, but not limited to, common solvents, precursors, TICs, TIMs, CWA surrogates, and explosives related compounds (ERCs).
- Detection algorithm leverages separation (RT) and near 1-amu resolution(m/z) mass spectral signature
- Similarity with NIST mass spectral libraries

Independent Government Validation

- 100% (+ true known) in NRL test campaign*
- Successfully flight-testing for USAF/AFRL
- Grand Central Station (NYC) under DHS CBT program

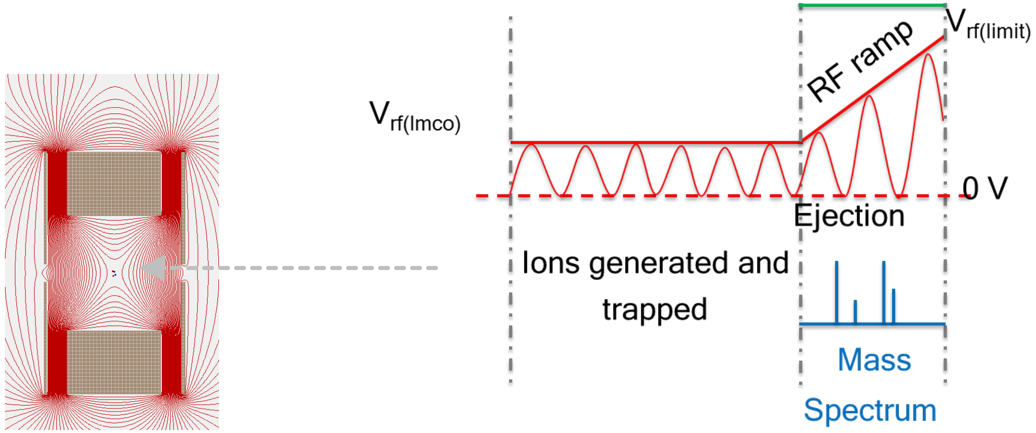


*DeWitt K. "Advancements in compact gas collection and analysis from IARPA's MAEGLIN program." CBRNE Sensing XXI. Vol. 11416. International Society for Optics and Photonics, 2020.

Ion Trap: Background

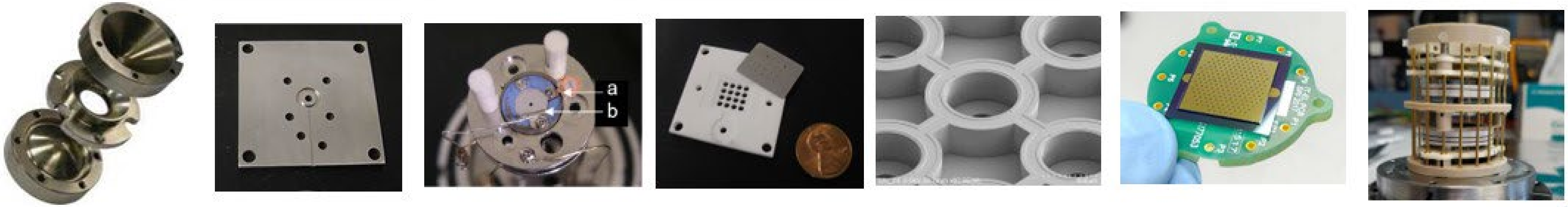
Mass-selective instability mode operation of RF ion traps

$$V_{rf} = \frac{m q_z r_0^2 \Omega^2}{4 A_2 e}$$



Design simplification → New design/fabrication → Sensitivity compensation → Resolution optimization → Sensitivity scaling ($n \propto r^{(1.5)}$) → Vacuum integration

Conventional Hyperbolic Ion Traps → Cylindrical Ion Traps → Non-conductive substrate → Array approach → Chip-Scale Ion Trap → High Density Array (200 traps) → Fully Integrated chip-scale MS

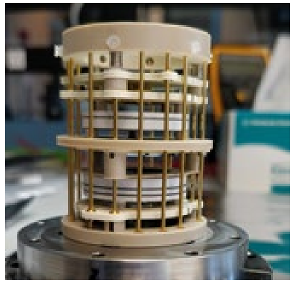


r_0= 10,000 μm | r_0= 2,000 μm | r_0= 1375 μm | 16-pixel array | r_0= 315 μm → 200-traps | Chip-Scale MS

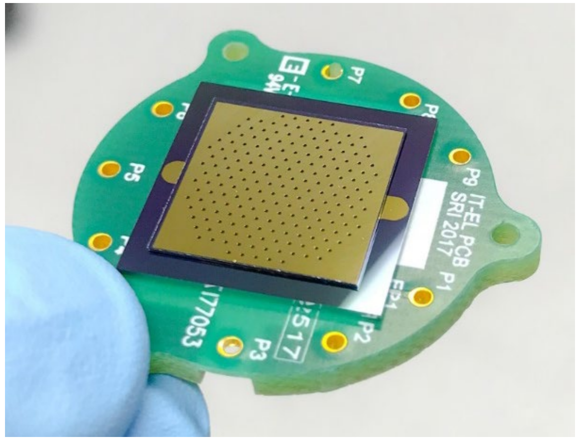
Miniaturization of ion traps in micromachined high-density arrays has led to low-SWaP MS design

We achieved near 1-amu resolution

Good mass spectral resolution is key to accurate chemical ID in real-world clutter environment



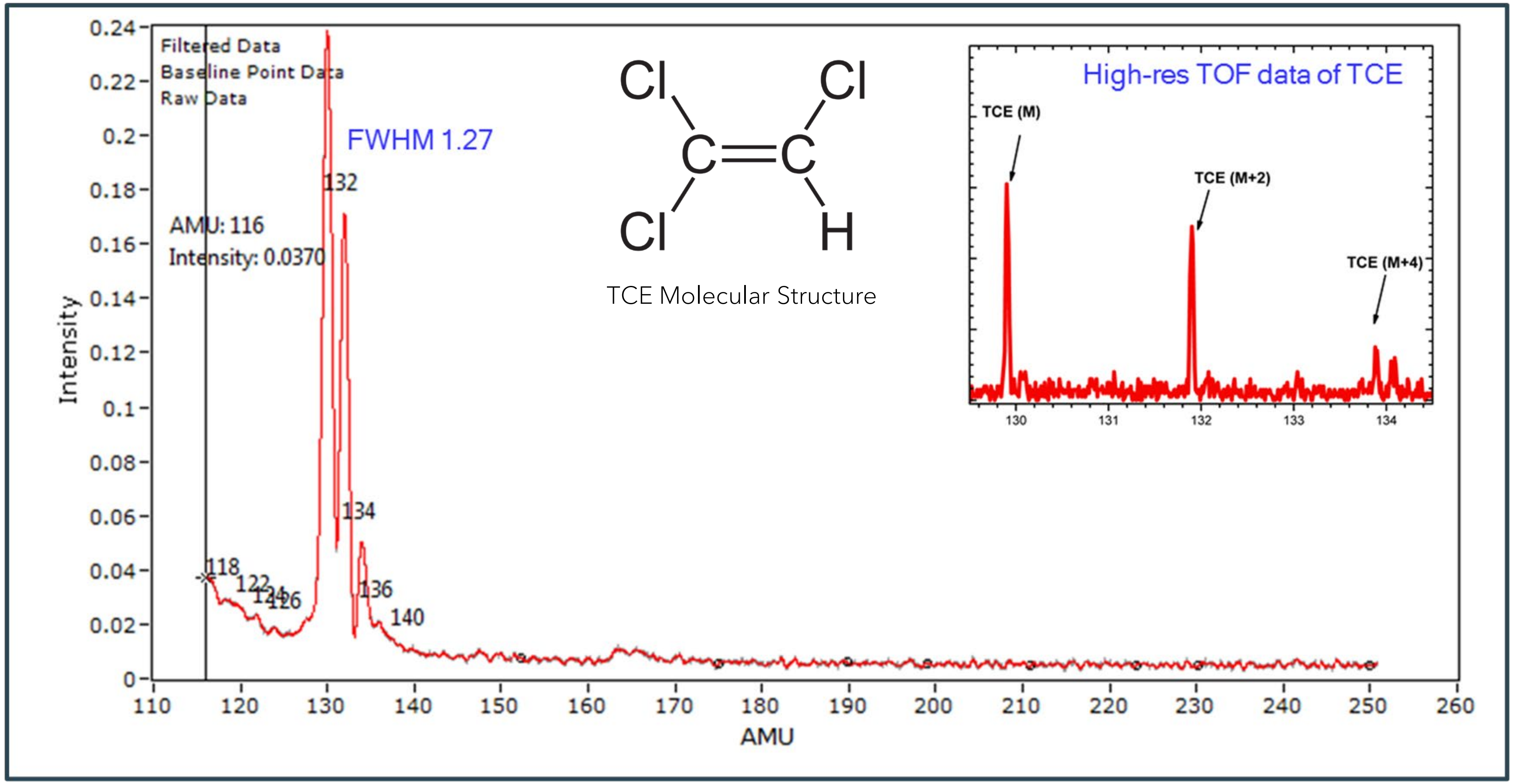
~200 traps operated in unison; while maintaining 1-amu mass resolution for the collective signal from the array



200-pixel chip-scale ion trap array

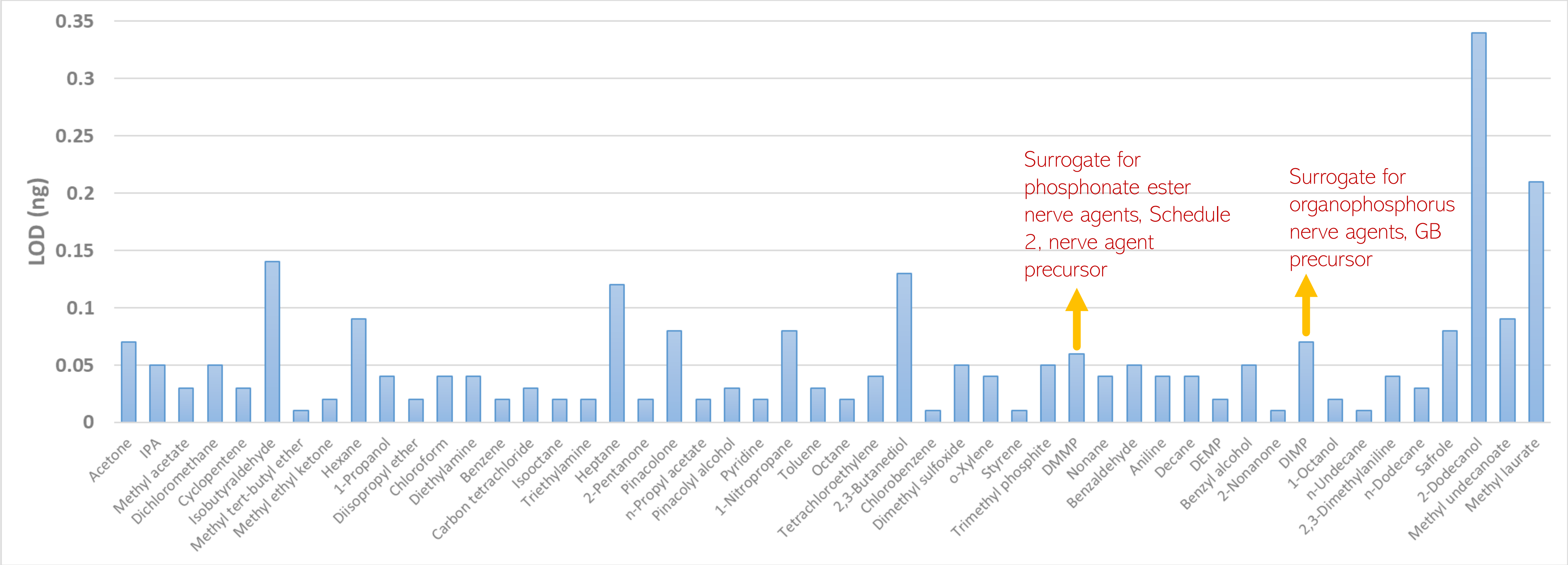
High-density chip-scale ion trap array with distributed localized ion trapping across 200 traps overcomes the peak broadening due to space-charge and ion-neutral collision effects that results in poor resolution of high-pressure miniature ion traps.

Partial mass spectrum of Trichloroethylene



Chip Scale MS: Limits of Detection (LOD) (nanogram)

- Chip-Scale MS has been demonstrated for ~200 chemicals with diverse chemical classes
- These LODs are 10-15x better than currently fielded systems (typically 1-10 ng)



ACHILLES (ppb may be more interesting than ng)

	Sampling time (s)			
	120 s	60 s	30 s	LODs
Toluene	3.23	6.45	12.90	µg/m³
	0.86	1.71	3.42	ppbv
DMMP	17.25	34.5	69	µg/m³
	3.39	6.79	13.58	ppbv
DEMP	81.45	162.9	325.8	µg/m³
	13.07	26.15	52.29	ppbv

- LODs of chemicals listed above are a good representation of the LOD range for the volatile organic compounds (such as toluene) and semi-volatile organic compounds (such as DMMP and DEMP).
- ACHILLES can be operated with a wide range of sampling time to fit with the detection requirements.
- Concentrations higher than the range mentioned above will be detectable with a slight compromise in the mass spectral resolution. Additionally, the sampling time can be optimized for the target range of concentration, as needed.

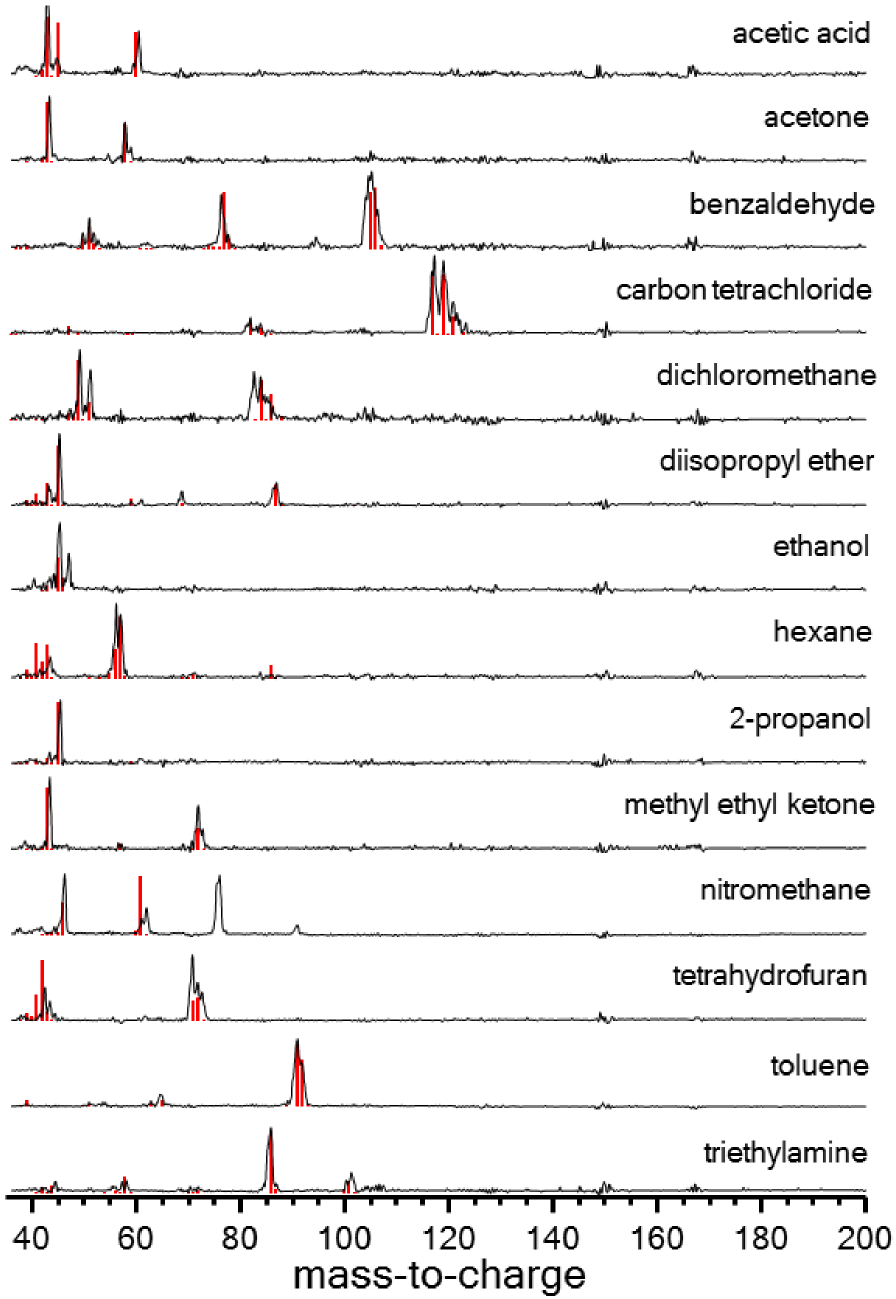
Our GC split throws away >96% collected molecules; Only 3-4% reach the MS for detection

Sneak peak: We have figured out how not to do that!

Library Development

Red: NIST mass spectra

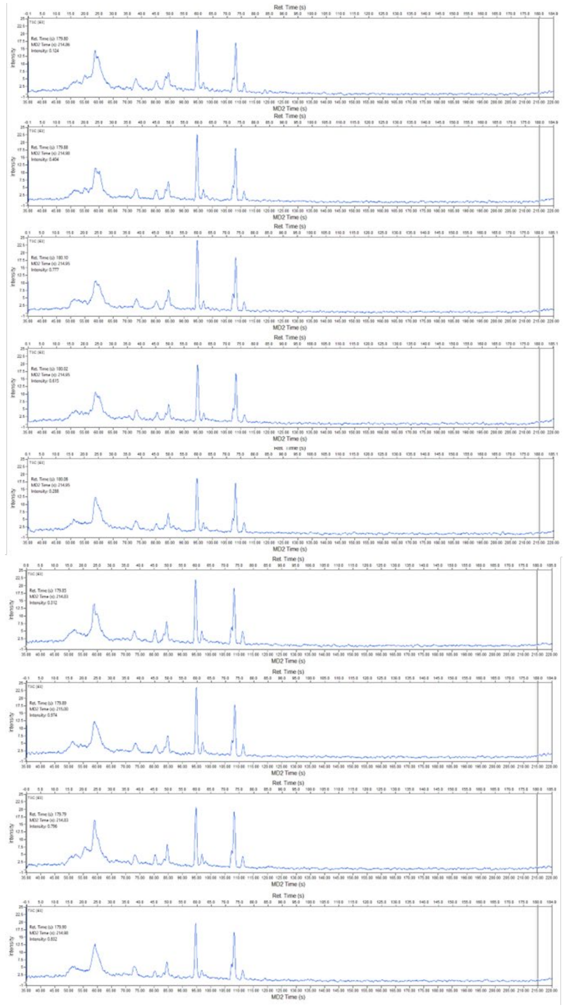
Black: μMS mass spectra



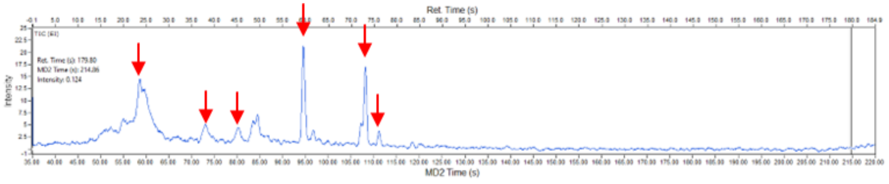
- μMS produces mass spectra similar to NIST libraries
  - Rapid library development for >100s of chemicals
  - "Gotchya's" due to minor deviations
  - In MAEGLIN we developed custom library/chemical
- ML model could enable an ["infinite library"]() platform

ACHILLES: System stability → Quantification and Identification

Back-to-back experiment (n=9) from a stable test environment



Average RSD (intensity) across all six chemical components ~ 10%

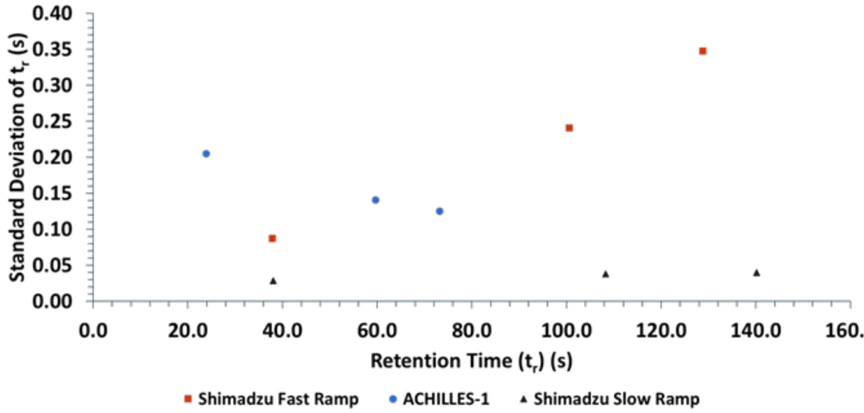


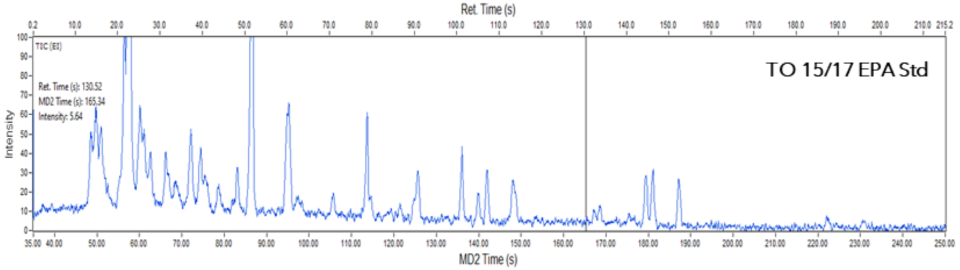
RT (s)	23.61	37.85	45.11	59.35	72.88	76.08
Run-1	14.40	4.93	4.37	21.00	16.90	3.75
Run-2	11.50	4.67	4.18	22.80	18.00	3.79
Run-3	10.60	4.77	4.06	24.00	18.40	3.71
Run-4	10.70	4.89	3.91	19.70	16.90	3.10
Run-5	12.40	4.46	3.65	18.50	16.90	3.95
Run-6	13.90	5.09	5.35	22.00	19.10	4.85
Run-7	12.30	5.09	4.52	23.60	17.80	4.78
Run-8	16.40	4.84	4.90	20.80	19.20	4.42
Run-9	12.70	5.38	3.87	19.60	16.50	4.01
STD	1.87	0.27	0.54	1.90	1.01	0.56
Avg	12.77	4.90	4.31	21.33	17.74	4.04
RSD	14.67	5.45	12.56	8.92	5.69	13.83

Average RSD (Intensity) across all six chemical components ~10%

Important for absolute and relative quantification of VOCs

Good RT stability (Std dev < 0.25 s)





Important for identification

Identification Algorithm

Approach/Status:

- 2D GC-MS data
- Pre-developed library cards
  - Curated identification based on "maximally disjointed" AMU peak positions
  - Some adducts (evolving)

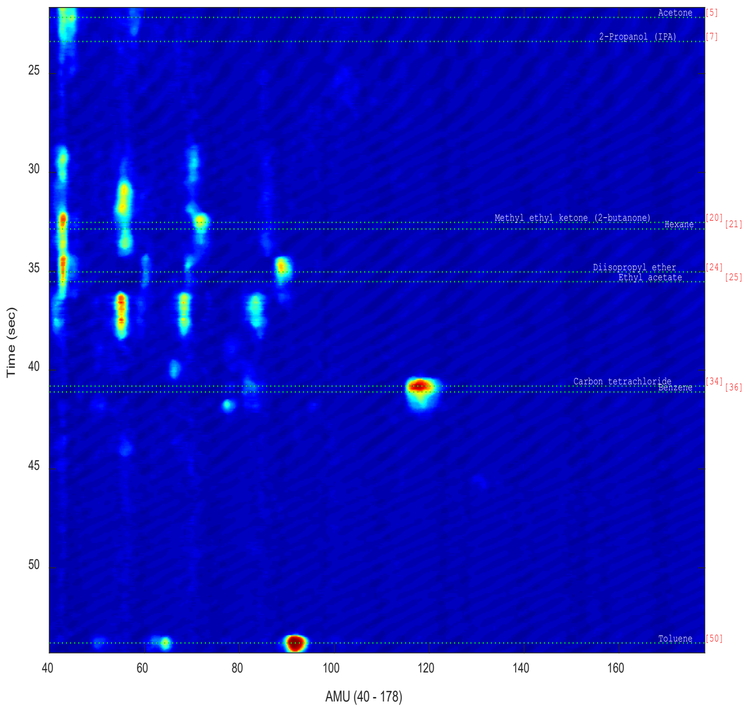
Process

- Background subtraction
- Noise reduction (Savitzky-Golay, FFT etc.)
- Peak finding, centroiding
- RT and AMU window threshold optimization

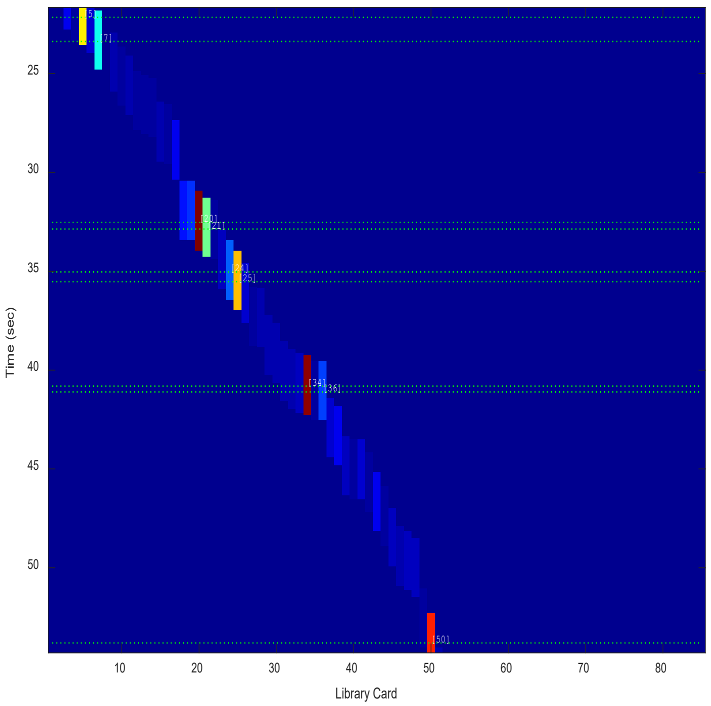
Key achievements so far:

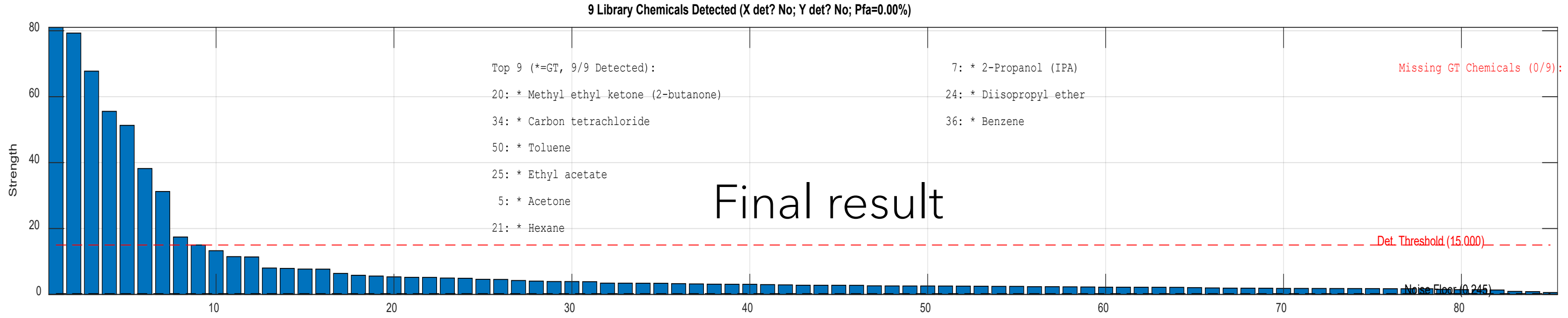
- Repeatable detection of co-eluting chemicals
- <1-min analysis time (~133 cards)
- Low P_{fa} (1 - 2%)

Full 2D Map of processed GC-MS data



Library cards examined w.r.t. RT

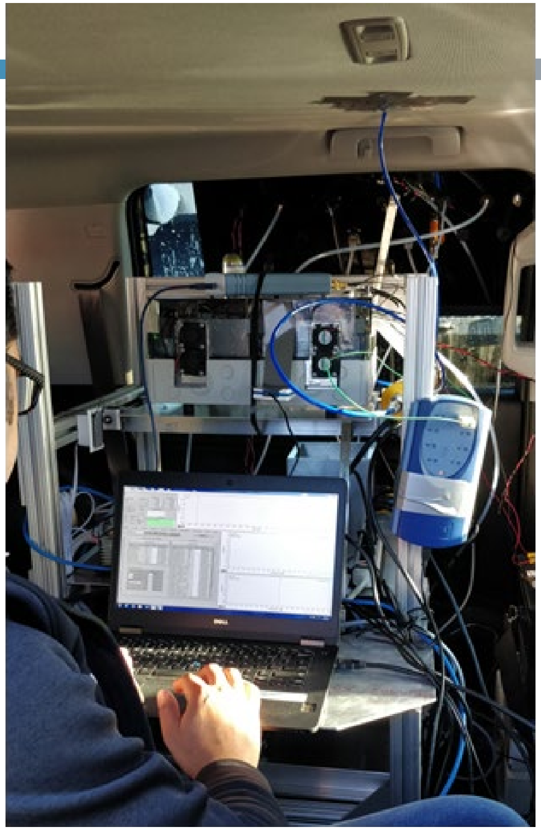




Deployment/Use-Case

Outdoor Sampling (NRL)

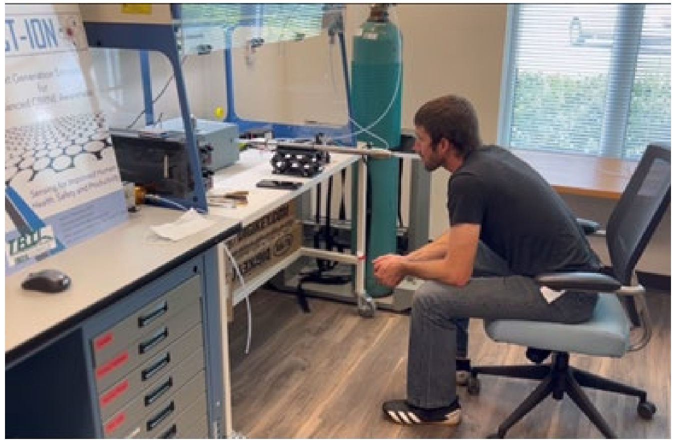
Tropical Bay (NRL)



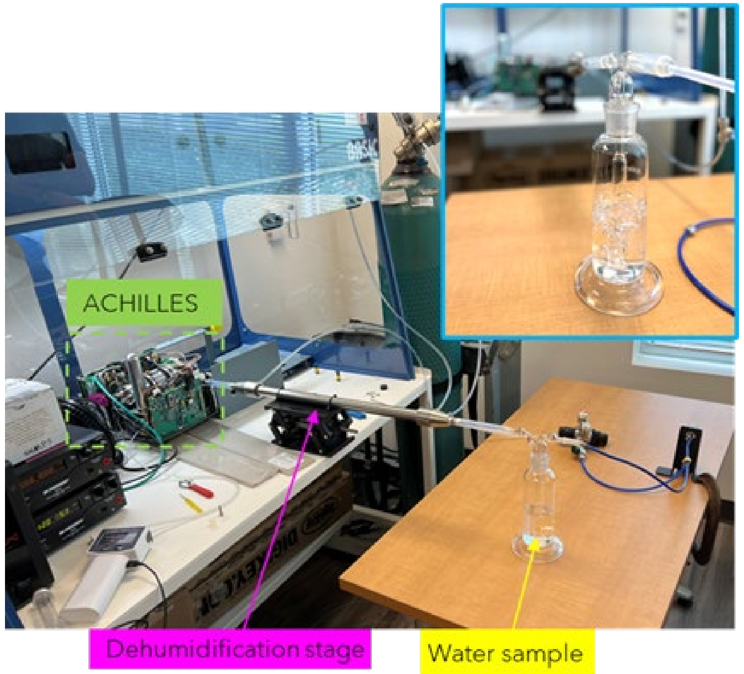
Mobile Deployment (Boston)

Grand Central Station (NYC)

USAF/AFRL Flight Testing



Breath Diagnostics

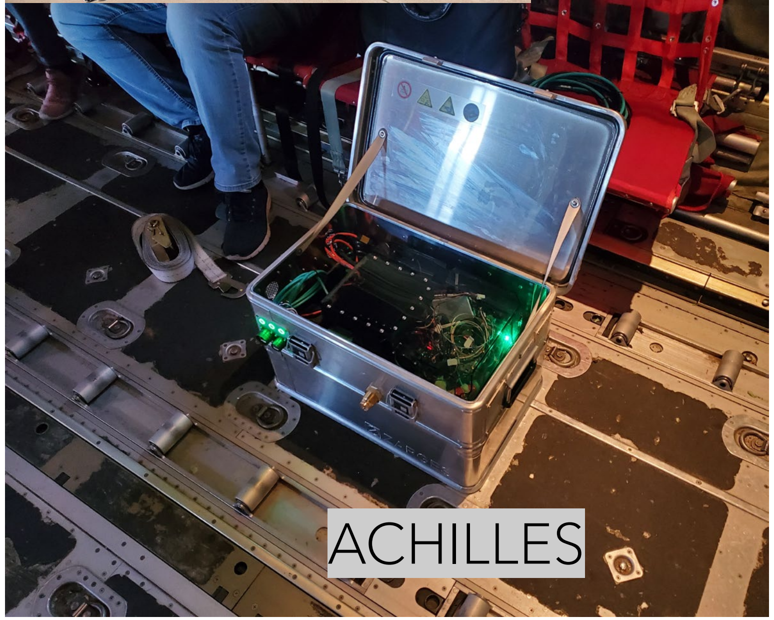


ACHILLES as Water Sensor

USAF CBRN Flight Testing (1/3)

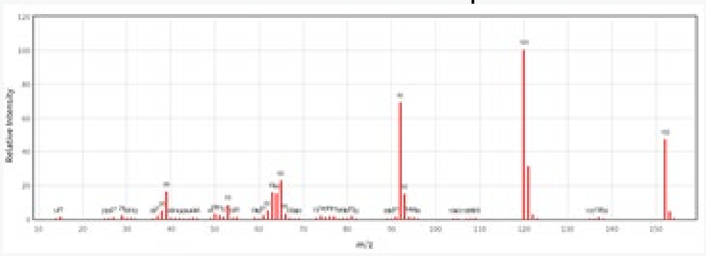
Office of the Director of National Intelligence
IARPA
BE THE FUTURE

- Objective: Real time measurement of Methyl Salicylate (MeS) with different flight maneuvers to understand the concentration change in a low altitude flight mode
- ACHILLES was operated during the flight (including take-off and landing) and was co-located with COTS chemical sensors
- During test, the forward cockpit hatch and both paratrooper doors were opened to purge the plane of the test compound

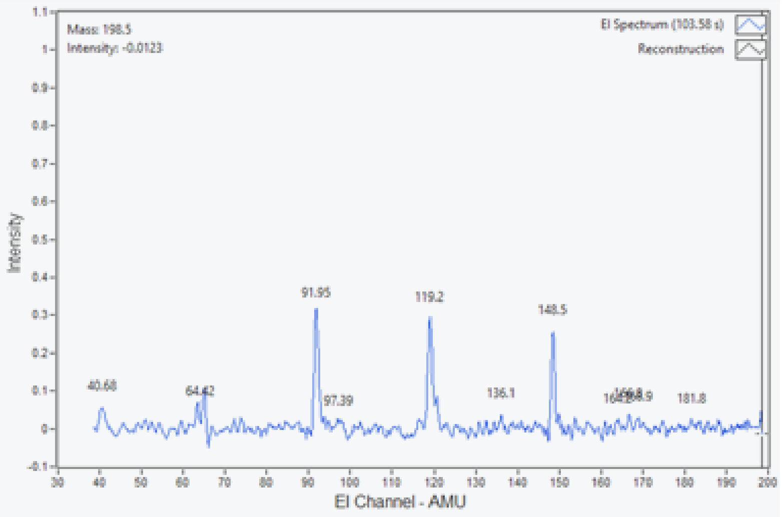


USAF CBRN Flight Testing (2/3)

NIST MeS Mass Spectrum

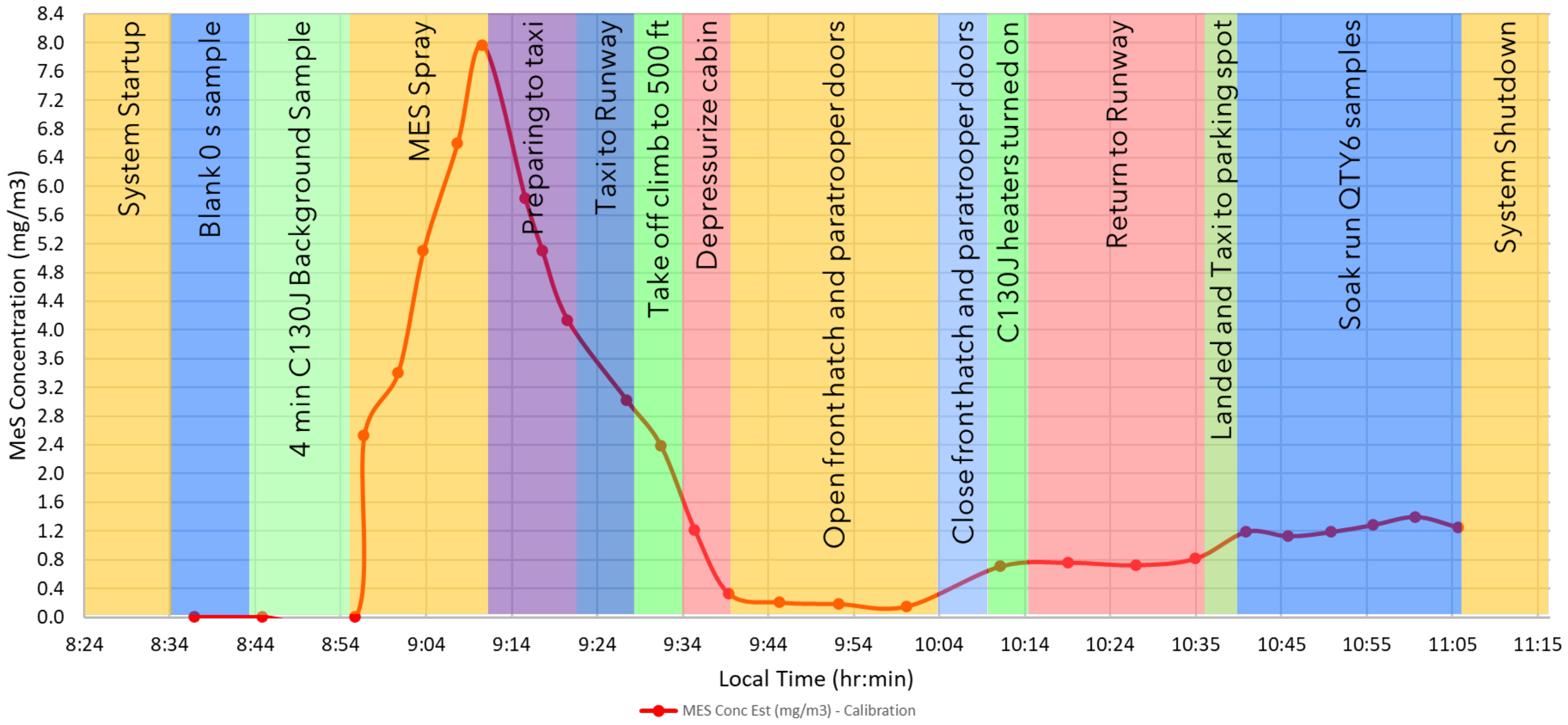


ACHILLES MeS Mass Spectrum



Methyl Salicylate (MeS) is a common chemical agent surrogate

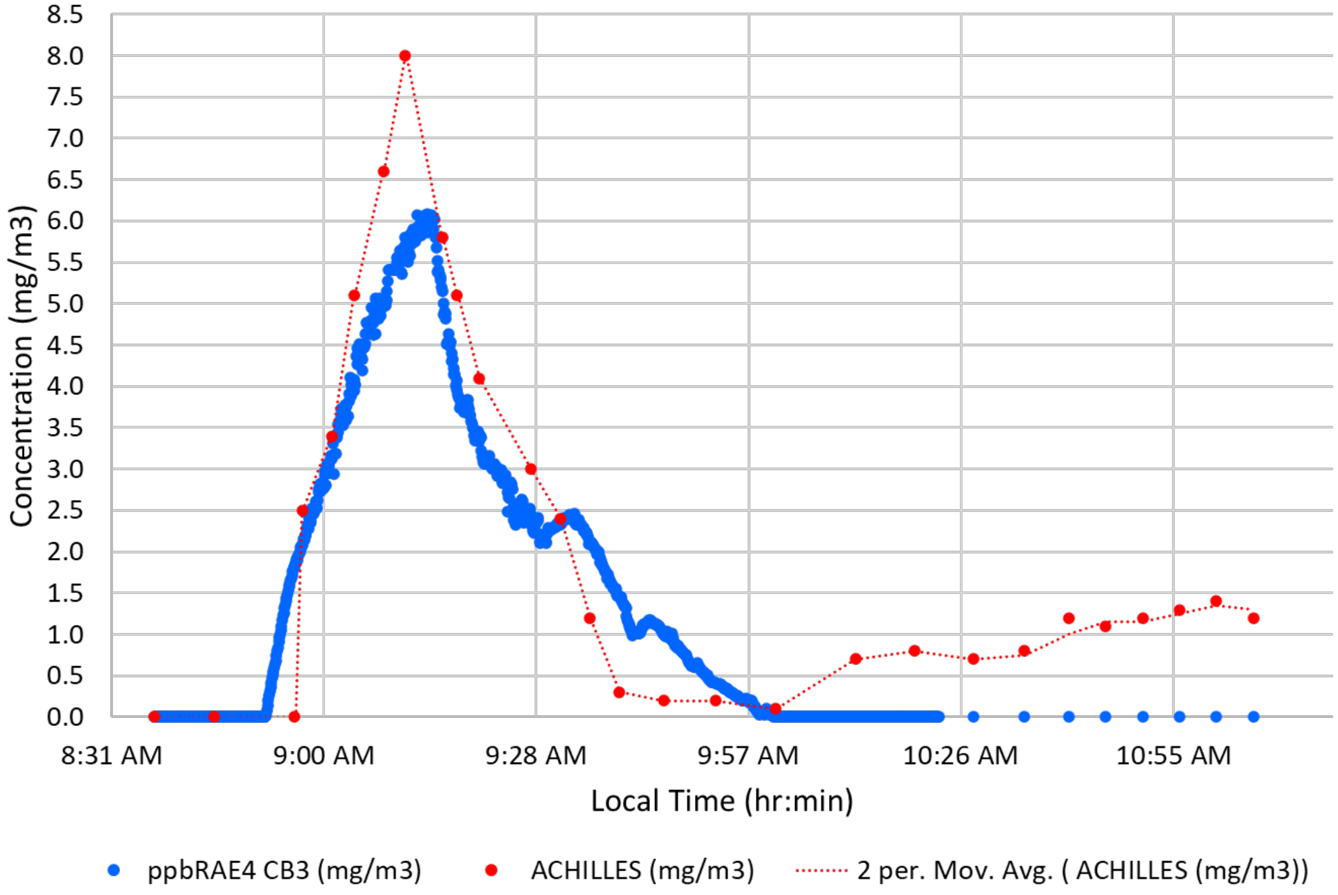
MeS Concentration Estimates vs. Local Time



USAF CBRN Flight Testing (3/3)

Major achievements/takeaways

- ACHILLES measured MeS concentration trends which corroborated with the flight maneuvers and matched with the trend measured by the co-located COTS PID (PPBRAE4 detector)
- During the tail end of the exercise ("soak"), ACHILLES was able to detected the onset of rise in concentration (MeS outgassing from aircraft surfaces due to tarmac temperature), which were missed by the COTS
- As mentioned by the activity lead, AFRL had flow COTS mass spectrometers in the past, but those platforms suffered from failure modes during the flight



Harsh Environments (Requirements)

"Harsh"

- Throughput /Latency
- Autonomy (operation, detection, clear-down etc.)
- Library expansion
- Consumables (Serviceability)

- Low system latency requires intelligent inputs for optimal sensor operation (Avoid saturation but maintain sensitivity)
    - Can complementary ionization enable a shorter GC method?
- Sampling to final answer (deconvolution, identification, quantification etc.)
    - Can we make the cleaning cycle intelligent based on signal detected?
- Ability to expand the libraries and move to a "training free" paradigm
    - Can an AI/ML model bridge the gap b/w ACHILLES and NIST libraries?
- Long endurance strategic emplacements limits serviceability
    - We are investigating N_2 and eventually "ambient air" as the consumable

Summary

- ✓ Chip Scale Mass Spectrometry shows a good promise to improve the state-of-the-art of fieldable trace chemical sensing
- ✓ There is room for further miniaturization and ruggedization
  - ACHILLES is the result of first prototype integration
  - Vacuum pump solution is an under-explored research theme
- ✓ Beyond hardware optimizations, software and application-specific AI/ML algorithm will be key areas of development necessary to reach a minimal viable product
- ✓ Detect-Ion is diversifying ACHILLES in areas of water security, health diagnostics, environmental monitoring

Thank you!