# Novel Approaches for the Investigation of Submarine Air Quality

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# Overview

**1. Problem Statement:**

- Chemically diverse sample has special needs
- Current sampling methods are costly and inefficient

**2. Advancement Opportunities**

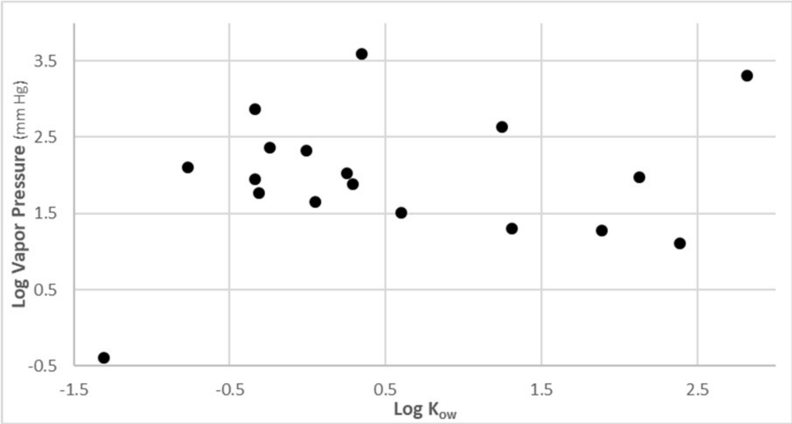
- Evaluation of two new passive sampling devices
- SIFT-MS with automated, online thermal extraction

**3. Pilot Field Study**

- Dosimeters stationed onboard submarine at multiple fixed locations
- Samplers worn by crew member for comparison

# Diverse Analyte Classes Are A Challenge for Analysis

| Chemical | BP | Vapor Pressure (mm) | $LogK_{OW}$ |
|---|---|---|---|
| Monoethanolamine | 170˚C | 0.4 | -1.31 |
| Methanol | 64.6˚C | 127.2 | -0.77 |
| Acetonitrile | 81.6˚C | 88.8 | -0.34 |
| Acetaldehyde | 20.8˚C | 740 | -0.34 |
| Ethanol | 78.4˚C | 59.3 | -0.31 |
| Acetone | 56˚C | 231 | -0.24 |
| Acrolein | 53˚C | 210 | -0.01 |
| Isopropanol | 82.5˚C | 45.4 | 0.05 |
| Acrylonitrile | 77.3˚C | 107.8 | 0.25 |
| 2-butanone | 80˚C | 77.5 | 0.29 |
| Formaldehyde | -19˚C | 3890 | 0.35 |
| Crotonaldehyde | 100˚C | 32 | 0.6 |
| Dichloromethane | 39.6˚C | 435 | 1.25 |
| MIBK | 118˚C | 19.9 | 1.31 |
| 1,1,2-trichloroethane | 110˚C | 19 | 1.89 |
| Benzene | 80˚C | 95.1 | 2.13 |
| 1,1,1,2-tetrachloroethane | 130.5˚C | 13 | 2.39 |
| 1,2-dichlorotetrafluoroethane | 3.5˚C | 2014 | 2.82 |




- Alcohols
  - Methanol (low MW)
- Aldehydes (labile compounds)
  - Formaldehyde

- Alkanolamines
  Ethanolamine (Polar)
- Halocarbons
- Hydrocarbons

# Characteristics of Current Approaches

- SAHAP (Submarine Atmosphere Health Assessment Program) Badge (Assay Technologies, Inc.)
  - Developed under SBIR
  - Multiple components incorporated
  - Multiple analyses required
  - Time-weighted average of calibrated components

Photo courtesy of Wisconsin Occupational Health Lab

- Active Sorbent Sampling
  - Pumping required – power supply needed
  - More restricted duration vs. passive samplers
  - Can measure concentrations
  - Requires multiple sorbent types for coverage
  - Polar and reactive analytes problematic

# SAHAP BADGE


Multiple Chemistries

- Alcohols
- Aldehydes
- Alkanolamines
- Flourohydrocarbons
- Halocarbons
- …others

## Pros

- Gold-standard sampling device
- Broad spectrum (multiple chemistries)
- Commercial analysis pipeline

## Cons

- Higher per unit cost
- 2 units for all 19 targets!
- Cumbersome form factor – not suitable for crew monitoring

# Our Goals…

Validation of a Universal Passive Dosimeter

- Current goals: Verify collection of target constituents of concern
  - Collection of other VOCs for surveillance sampling
  - Establish universal extraction and analysis methods
  - Determine sampling rates for targets (to determine conc.)
- Long-term goal: Provide **individual** longitudinal exposure records

# Silicone Wristband Samplers

**Sampling Device (MyExposome)**


**Analysis**

- Analysis by thermal extraction -> TD-GC/MS

**Pros**

- Low cost and easy to obtain
- Non-intrusive wearable
- High-capacity sampler
- VOCs and SVOCs

**Cons**

- Extensive pre-cleaning required
- Currently require offline thermal extraction
- Confined space requirement for determining **concentration** of VOCs

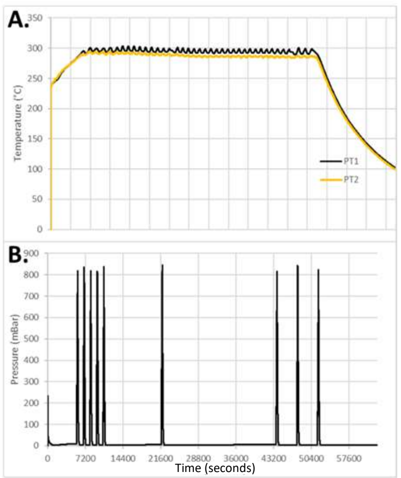
Fick's Law: $N_i = -D_i \nabla C_i$

$N_i = molar\ flux\ (mol \cdot m^{-2} \cdot sec^{-1})$

$D_i = diffusion\ coefficient\ (m^{-2} \cdot sec^{-1})$ — surface geometry

$C_i = concentration\ (\mathrm{mol} \cdot \mathrm{m}^{3})$

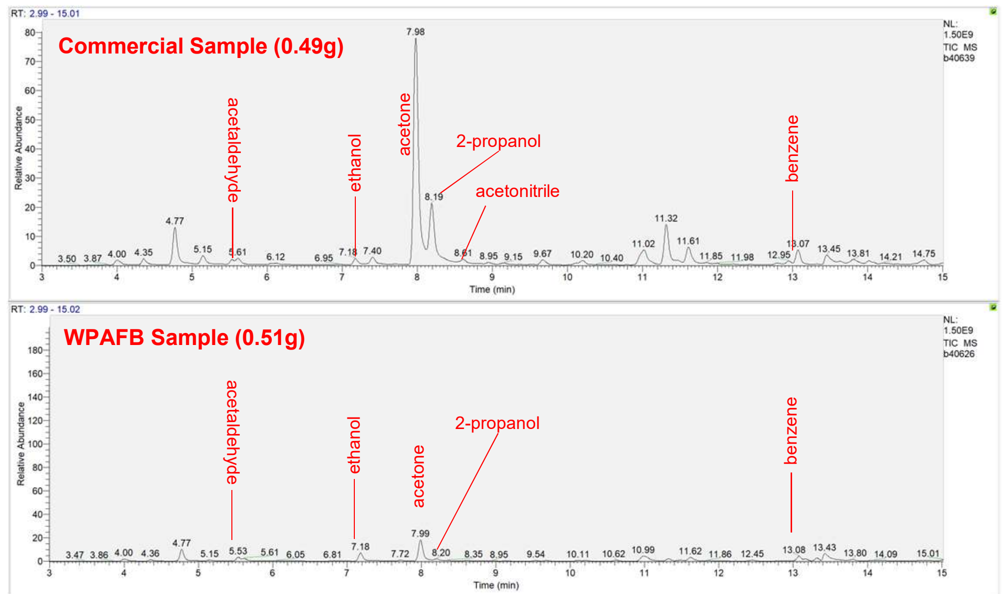
# SWB Preparation for Passive Sampling




## SWB Prep Cycle

- Vacuum oven treatment
- ~300°C/ 2mbar
- 72-96 hours total time
- **Multiple $N_2$ purge cycles**
- Store under inert gas in glass containers
- Transport/short-term storage in PTFE bags

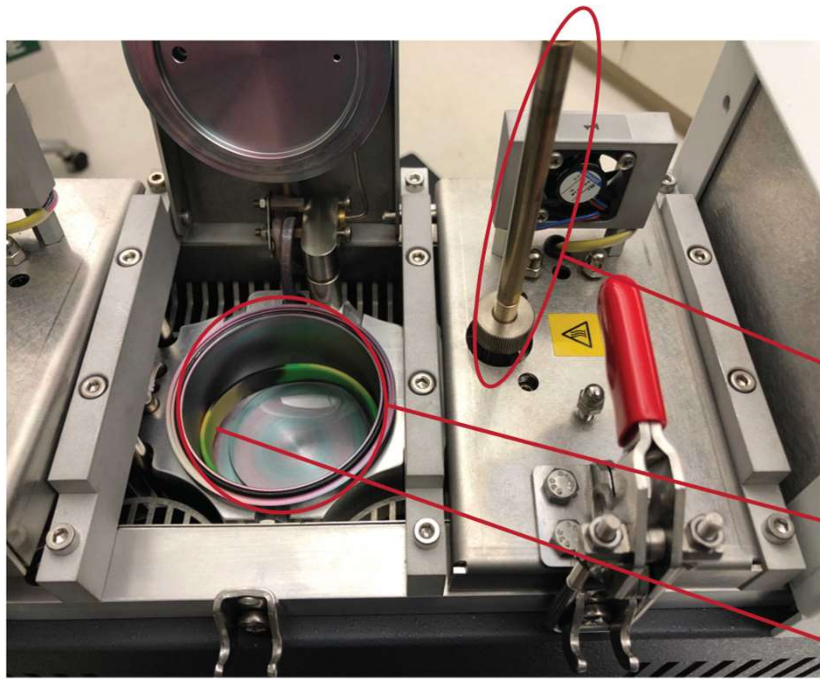
- SWB are unusable direct from vendor due to high background and contamination of instrument
- Vacuum oven treatment results in ~300mg loss in mass (7-8%)
- High cost of commercially available pre-cleaned SWB led to development of in-house prep method




Current methodology yields SWB with lower background contamination vs commercial vendor.

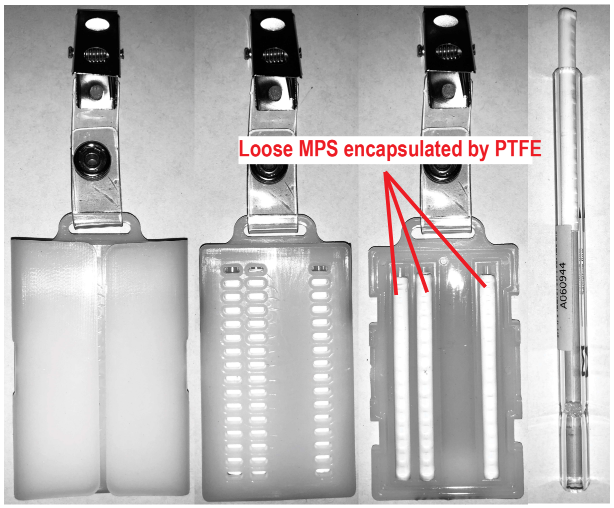
# Offline Thermal Extraction of SWB:

- Reduces throughput
- Requires additional equipment
- Increases potential for error




*Method developed by O'Connell and Anderson et al. of Oregon State U

# Mesoporous Silica Tokens (Xplosafe LLC)




**Sampling Device**

- 50mg OSU-6 sorbent inside PTFE sleeve
- Current form factor: Nylon clip-on badge

**Analysis**

- Direct TD-GC/MS analysis (MPS tokens)

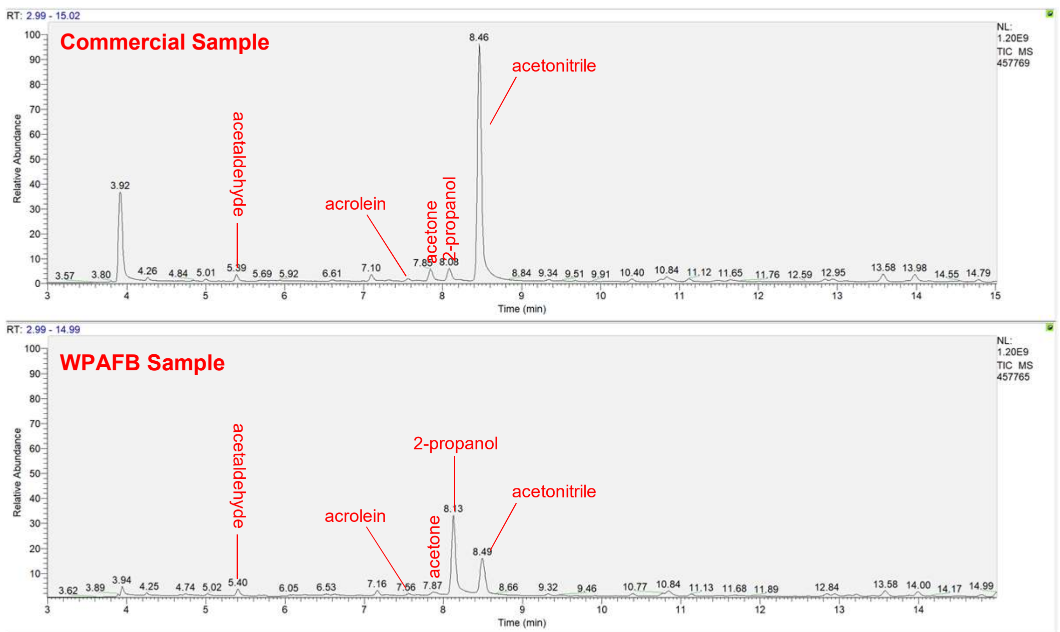
**Pros**

- No thermal extraction step
- Enclosure enables rate determination
- Potentially 100% reusable
- Integral subtraction control

**Cons**

- Higher per unit cost (vs SWB)
- Impact of humidity unknown
- Some pre-cleaning required*

# MPS Sampler Preparation by Supercritical $CO_2$




## MPS Prep Cycle

- Supercritical fluid extraction
- Liquid $CO_2$ extraction under 300 bar pressure
- 3 hr treatment in vacuum oven at 200°C
- SFE prep reduces interfering contaminants from manufacture

*Note: Commercial product is still in R&D. Batch to batch variability can be attributed to improvements and changes to cleaning processes by commercial vendor.

# Pilot Study – 22 Days Aboard Fast-Attack Submarine

**Ethanol**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 96200 | 19117 | 606 |
| F2 | 128000 | 42669 | 1435 |
| F3 | 112000 | 38342 | 1125 |
| A1 | 70000 | 35976 | 0 |
| A2 | 120000 | 38770 | 486 |
| A3 | 104000 | 30962 | 0 |

**Acetone**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 16300 | 17561 | 1537 |
| F2 | 17000 | 20322 | 1266 |
| F3 | 15900 | 20425 | 1764 |
| A1 | 20400 | 31903 | 2082 |
| A2 | 25300 | 31609 | 2406 |
| A3 | 23800 | 33555 | 2270 |

**2-propanol**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 42400 | | 2451 |
| F2 | 37800 | | 3322 |
| F3 | 39400 | | 1702 |
| A1 | 55000 | | 3709 |
| A2 | 61800 | | 4490 |
| A3 | 55000 | | 4030 |

**Benzene**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 7250 | 990 | 38 |
| F2 | 5870 | | 7 |
| F3 | 6660 | | 12 |
| A1 | 14000 | 213 | 7 |
| A2 | 14000 | | 7 |
| A3 | 13100 | | 7 |

**2-butanone**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 7330 | | 1568 |
| F2 | 5590 | 128 | 2208 |
| F3 | 6430 | 109 | 787 |
| A1 | 7950 | 235 | 1469 |
| A2 | 7720 | 292 | 980 |
| A3 | 7880 | 225 | 1292 |

**Acrolein**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 0 | | |
| F2 | 667 | | 46 |
| F3 | 657 | | 76 |
| A1 | 523 | 469 | 8 |
| A2 | 589 | | 34 |
| A3 | 639 | | 57 |

**Methyl isobutyl ketone**

| | SAHAP | SWB | MPS |
|---|---|---|---|
| F1 | 0 | | 1013 |
| F2 | 0 | | 980 |
| F3 | 0 | 27 | 1094 |
| A1 | 782 | 58 | 1562 |
| A2 | 803 | 27 | 1575 |
| A3 | 782 | 69 | 1398 |

**Sample Key**
**F1 – Aux machine room**
**F2 – Crew's mess**
**F3 – Fan room (aft bh)**
**A1 – Engine room LL aft**
**A2 – Engine room LL fwd**
**A3 – Engine room maneuvering**

| SWB | F1 | F2 | F3 | A1 | A2 | A3 |
|---|---|---|---|---|---|---|
| Acetaldehyde | 1032 | 3020 | 3634 | 4409 | 4051 | 3782 |
| Acetonitrile | 538 | 143 | 0 | 0 | 0 | 0 |
| Methylene chloride | 73 | 42 | 32 | 115 | 77 | 87 |
| 2-propenenitrile | 90 | 44 | 33 | 40 | 0 | 0 |
| 2-butenal | 0 | 0 | 0 | 0 | 0 | 0 |
| Toluene | 168 | 285 | 274 | 192 | 247 | 235 |
| 1,1,2,2-tetrachloroethane | 114 | 0 | 206 | 280 | 163 | 0 |

| MPS | F1 | F2 | F3 | A1 | A2 | A3 |
|---|---|---|---|---|---|---|
| Acetaldehyde | 28032 | 531 | 1797 | 324 | 444 | 273 |
| Acetonitrile | 235 | 0 | 0 | 0 | 0 | 0 |
| Methylene chloride | 3 | 5 | 7 | 9 | 8 | 7 |
| 2-propenenitrile | 260 | 9 | 26 | 12 | 9 | 4 |
| 2-butenal | 0 | 121 | 0 | 0 | 0 | 0 |
| Toluene | 31 | 40 | 46 | 24 | 25 | 17 |
| 1,1,2,2-tetrachloroethane | 0 | 0 | 0 | 0 | 0 | 0 |

- **Nanograms on 1 SWB or 1 MPS token**
- 1 SWB = ~3.75g; 1 MPS = 0.3g
- Good agreement between different media (presence/absence; rel. abundance)
- High background of SWB reduces sensitivity

# Reproducibility of Quantitation by Sampler Type

## SWB

| | A1 | A2 | A3 | F1 | F2 | F3 | Average ng |
|---|---|---|---|---|---|---|---|
| R114 | 163% | 148% | | 105% | 178% | | 0 |
| acetaldehyde | 7% | 17% | 9% | 33% | 22% | 19% | 2228 |
| ethanol | 9% | 7% | 3% | 33% | 3% | 5% | 34306 |
| acrolein | 9% | 12% | 10% | 172% | 10% | 4% | 469 |
| acetone | 6% | 7% | 5% | 16% | 5% | 4% | 25896 |
| 2-propanol | 6% | 4% | 4% | 38% | 3% | 7% | 0 |
| acetonitrile | | | | 172% | 169% | | 342 |
| methylene chloride | 48% | 89% | 90% | 72% | 5% | | 58 |
| 2-propenenitrile | 178% | | | 98% | 47% | 11% | 20 |
| 2-butanone | 11% | 6% | 5% | 19% | 3% | 5% | 198 |
| benzene | 15% | 7% | 7% | 6% | 4% | 9% | 602 |
| 2-butenal | | | | | | | 0 |
| methyl isobutyl ketone | 30% | 87% | 92% | | | 176% | 45 |
| toluene | 8% | 13% | 7% | 29% | 21% | 6% | 164 |
| 1,1,2-trichloroethane | | | | | | | 0 |
| 1,1,2,2-tetrachloroethane | 96% | 92% | | 87% | | 12% | 127 |

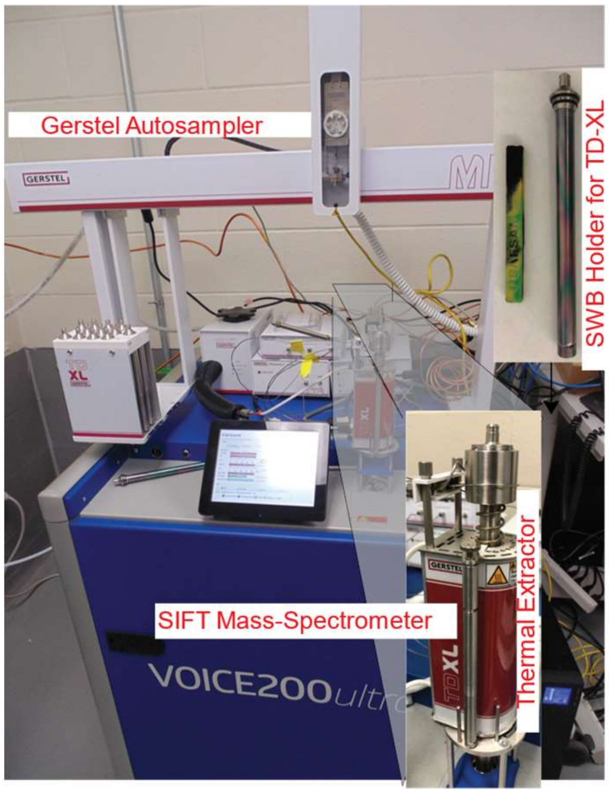
- 2 devices hung at each sampling location onboard submarine
- From each device – 2 technical replicates
- Net = 4 quantitative measurements
- Average and RSD are <u>of those 4</u> measures

## MPS

| | A1 | A2 | A3 | F1 | F2 | F3 | Average ng |
|---|---|---|---|---|---|---|---|
| R114 | | | | | | | 0 |
| acetaldehyde | 20.87% | 23.55% | 6.80% | 98.60% | 7.17% | 6.96% | 5108 |
| ethanol | 11.19% | 9.93% | 0.06% | 26.03% | 7.82% | 19.30% | 600 |
| acrolein | 16.51% | 27.07% | 14.89% | | 7.68% | 24.06% | 37 |
| acetone | 7.89% | 1.33% | 1.94% | 35.38% | 1.27% | 1.27% | 1888 |
| 2-propanol | 10.16% | 7.86% | 6.10% | 41.13% | 8.91% | 13.99% | 3284 |
| acetonitrile | | | | 141.42% | | | 39 |
| methylene chloride | 67.87% | 141.42% | 141.42% | 141.42% | 141.42% | 64.23% | 7 |
| 2-propenenitrile | 20.35% | 9.82% | 9.49% | 74.79% | 3.76% | 27.63% | 53 |
| 2-butanone | 11.89% | 9.40% | 15.03% | 55.80% | 6.78% | 11.71% | 1384 |
| benzene | 13.76% | 9.84% | 3.97% | 47.82% | 5.42% | 15.92% | 13 |
| 2-butenal | | | | | 141.42% | | 20 |
| methyl isobutyl ketone | 11.17% | 7.31% | 9.27% | 70.31% | 3.84% | 13.39% | 1271 |
| toluene | 12.55% | 5.08% | 5.29% | 72.62% | 4.17% | 8.91% | 30 |
| 1,1,2-trichloroethane | | | | | | | 0 |
| 1,1,2,2-tetrachloroethane | | | | | | | 0 |

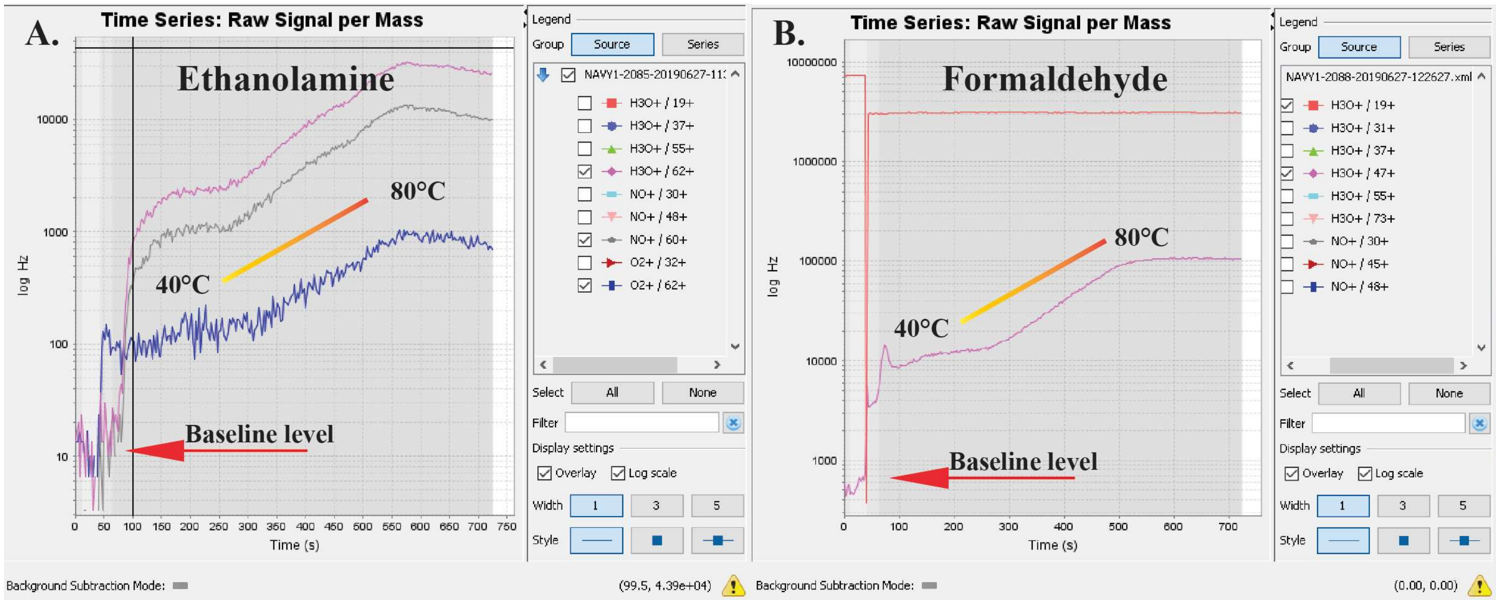
**<u>Sample Key</u>**
**<u>F1</u> – Aux machine room**
**<u>F2</u> – Crew's mess**
**<u>F3</u> – Fan room (aft bh)**
**<u>A1</u> – Engine room LL aft**
**<u>A2</u> – Engine room LL fwd**
**<u>A3</u> – Engine room maneuvering**

# Novel MOTS Instrumentation – TE-SIFT-MS



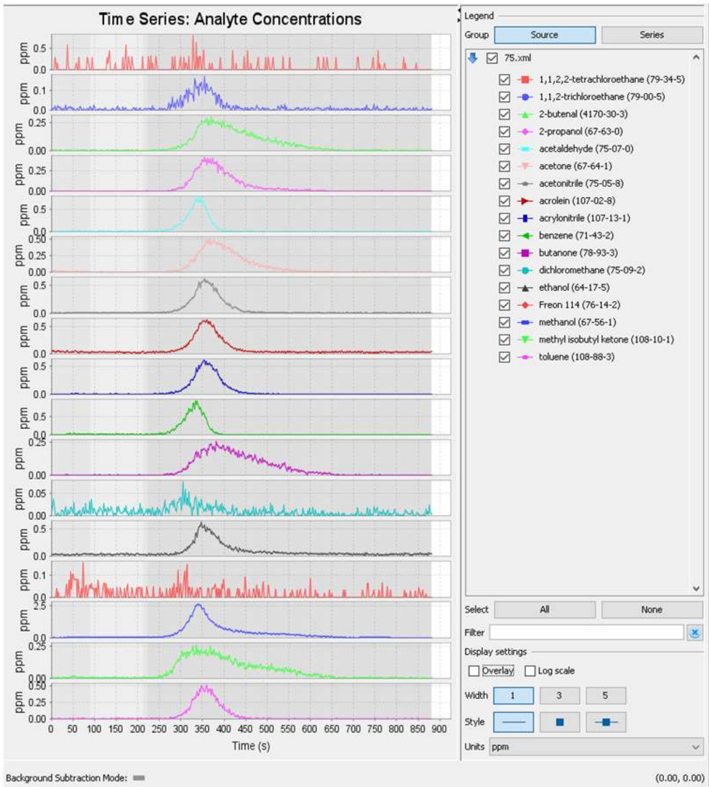

- Custom Gerstel autosampler and thermal extractor
- Fully automated thermal extraction and analysis of up to 30 samples
- Rapid thermal gradient (120°C/min)
- Analysis ~ 10-15 min/sample
- SIFT-MS amenable to methanol and formaldehyde analysis
- No limitations for polar/non-polar compounds

# Example SIFT-MS Analysis

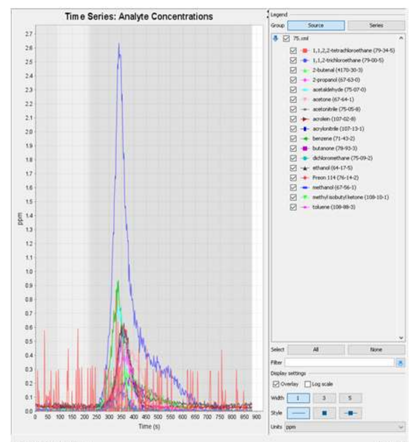



- Permeation tubes introduced VOCs via thermal extractor
- Thermal gradient demonstrates emission increase as function of temperature
- Emission ranges from 30-200ng/min over gradient

# Simultaneous Analysis of 17 Targets vis SIFT-MS




- Mixture of 17 compounds* loaded to Xplosafe sorbent token
- Token desorbed using TD-XL system
- Simultaneous SIM scan of targets




**SIFT-MS uses unique reaction chemistries to provide target ID confirmation and qualitative info for unknowns**

*Xcel+ tokens appear to have poor affinity for R-114 and 1,1,2,2-TCA

# Summary

- Current (gold-standard) samplers are bulky and require multiple, independent analyses to yield data
- New methods developed to prepare 2 novel sorbents for passive sampling of VOCs
- Novel sorbents used for sampling onboard submarine
- Collection of multiple classes of organic compounds on single media
- Both sorbents differentiated between sampling locations while underway
- Good agreement between novel sorbents and legacy device
- Development of new analytical technologies to allow analysis of multiple classes of analytes using one instrument/method

# Acknowledgments


- Work was funded by Defense Health Agency Funds
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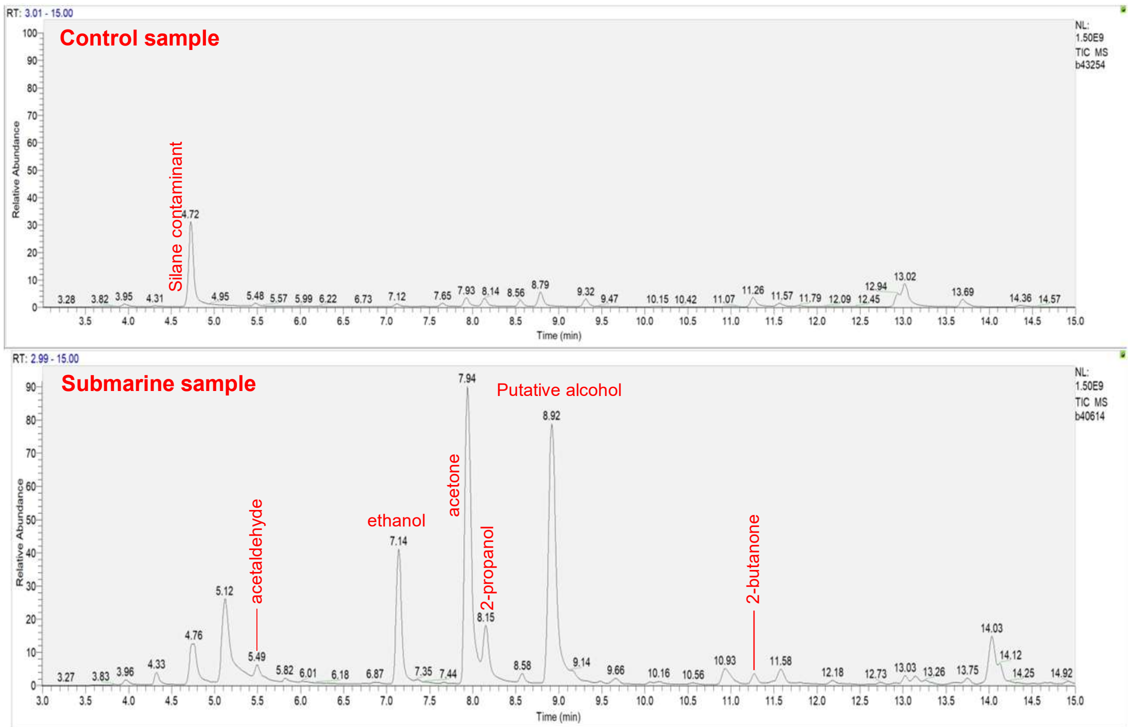
  - Defense Health Program (Joint Program Committee 5, Military Operational Medicine Research Program, work unit F1604)

- Special thanks for the on-going collaboration among government and industrial partners
  - Gerstel
  - SYFT Technologies, Inc.
  - XploSafe
  - MyExposome

AFRL

USS Connecticut (SSN-22) departing on her first scheduled deployment on 1 May 2002

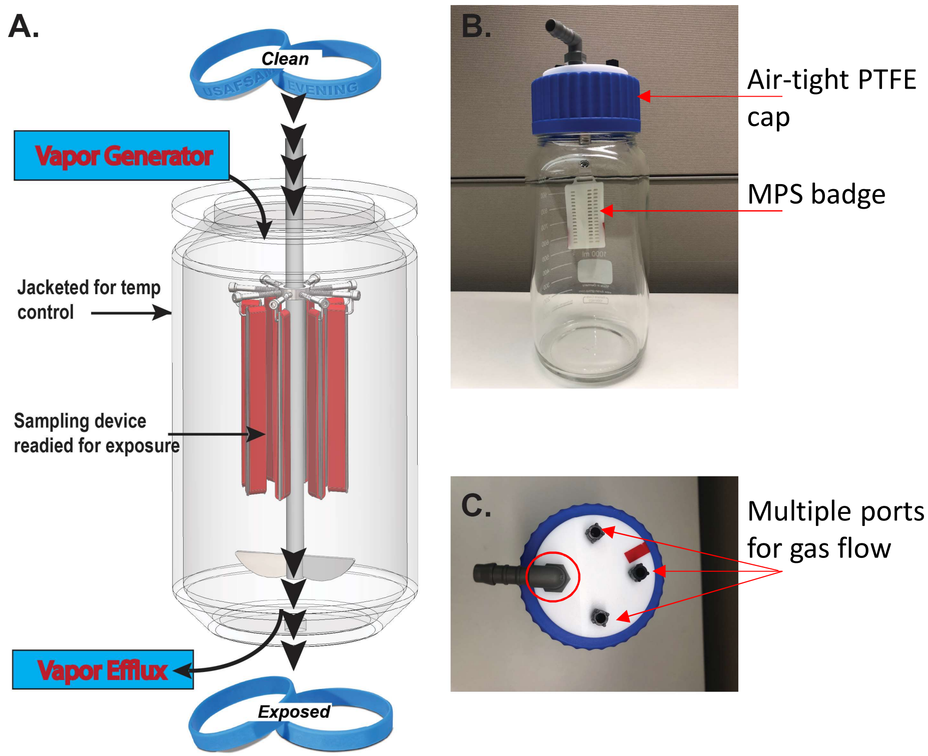
# SWB Extract – Comparing Control to Submarine Sample




## SWB Control Sample:

| | SWB |
|---|---|
| acetaldehyde | 1551 |
| ethanol | 2521 |
| acrolein | 685 |
| acetone | 13383 |
| 2-propanol | 9787 |
| acetonitrile | 195 |
| methylene chloride | 16 |
| 2-propenenitrile | 31 |
| 2-butanone | 723 |
| benzene | 2204 |
| 2-butenal | 0 |
| methyl isobutyl ketone | 3 |
| toluene | 69 |
| 1,1,2,2-tetrachloroethane | 0 |
| | *Values in ng |

# Determine Rate of Absorption




**Dosing Process**

1. Dosimeter(s) enclosed in chamber
2. Chamber purged with pure $N_2$
3. Timed application of:
   -Continuous flow of VOCs <u>or</u>
   -Static VOCs concentration
4. Chamber purged with $N_2$
   -Collect remaining VOCs by TD for mass-balancing
5. Sample extraction and analysis