# Evaluation and Application of SPME Arrows

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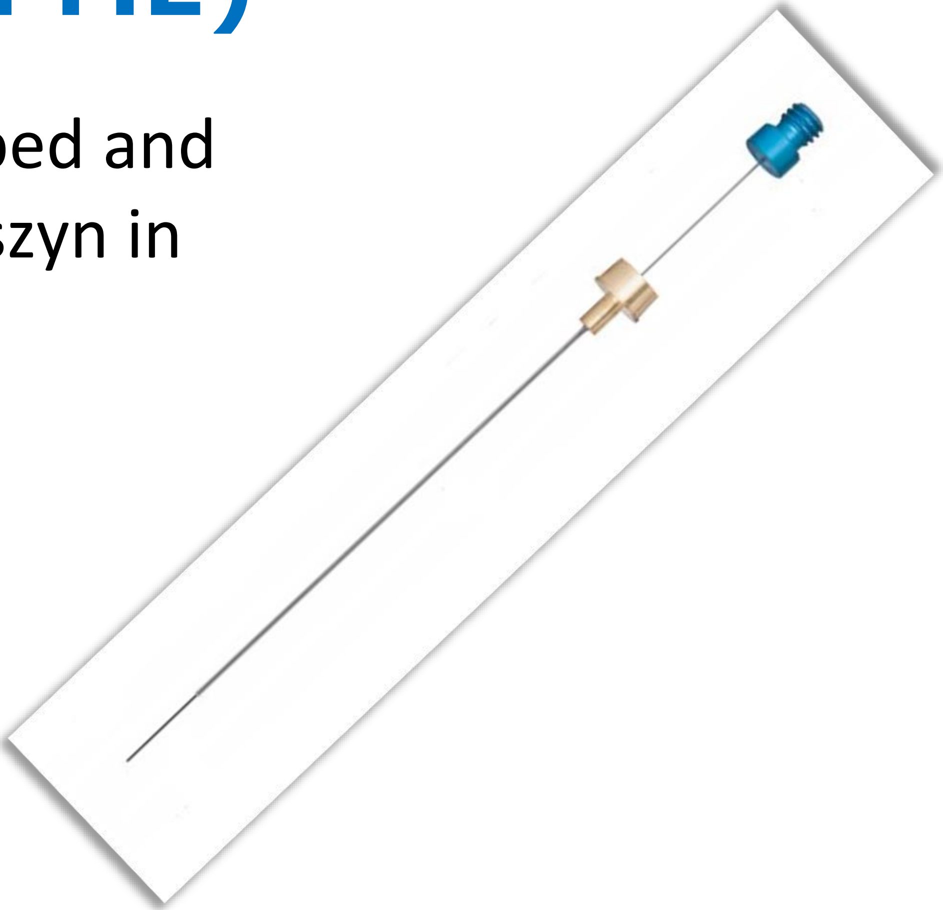
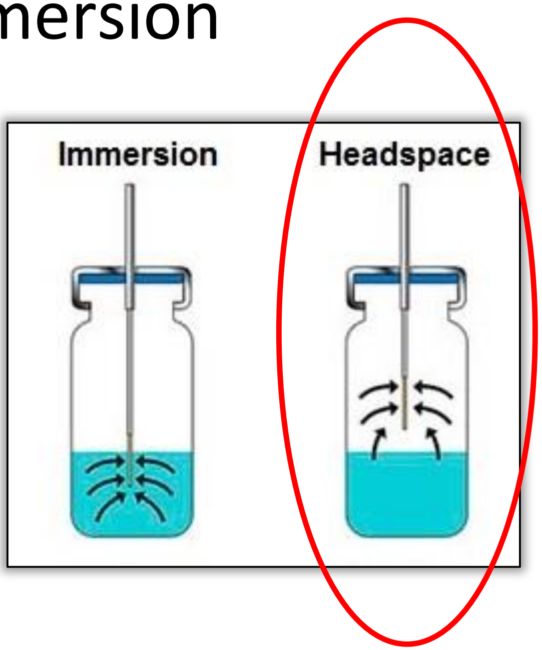
# Solid Phase Microextraction (SPME)

- SPME fibers were developed and patented by Janusz Pawliszyn in 1990
- Subsequently licensed to Supelco until 2014



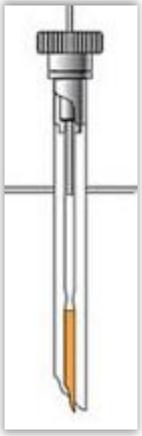
# SPME Sampling/Desorbing

- Target analytes are collected via headspace or immersion




90% of applications

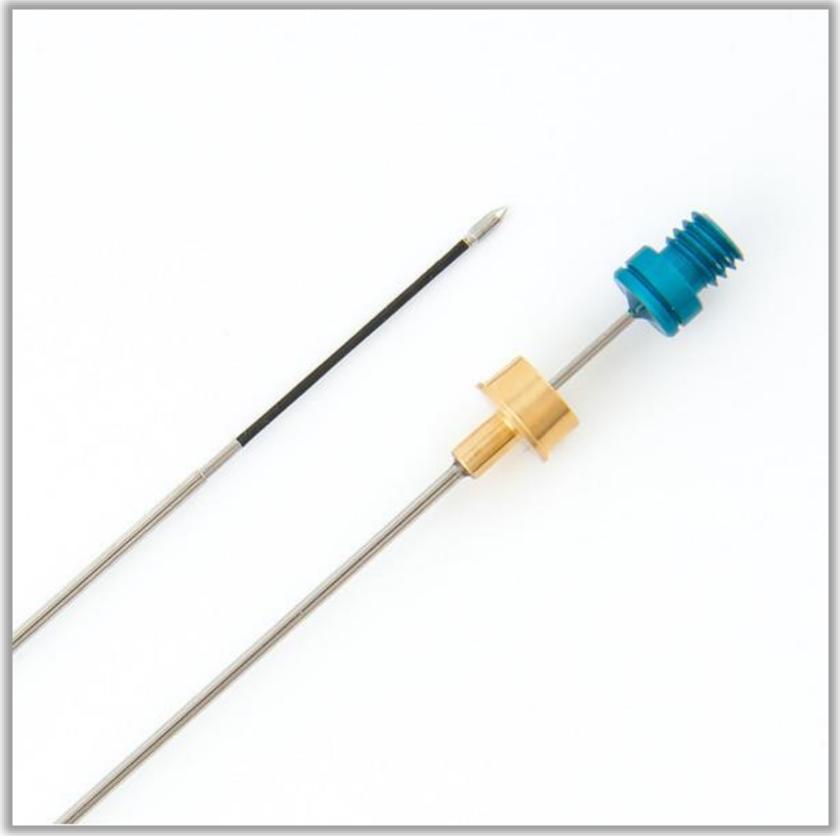
- Desorbed in the GC inlet



# SPME Arrow

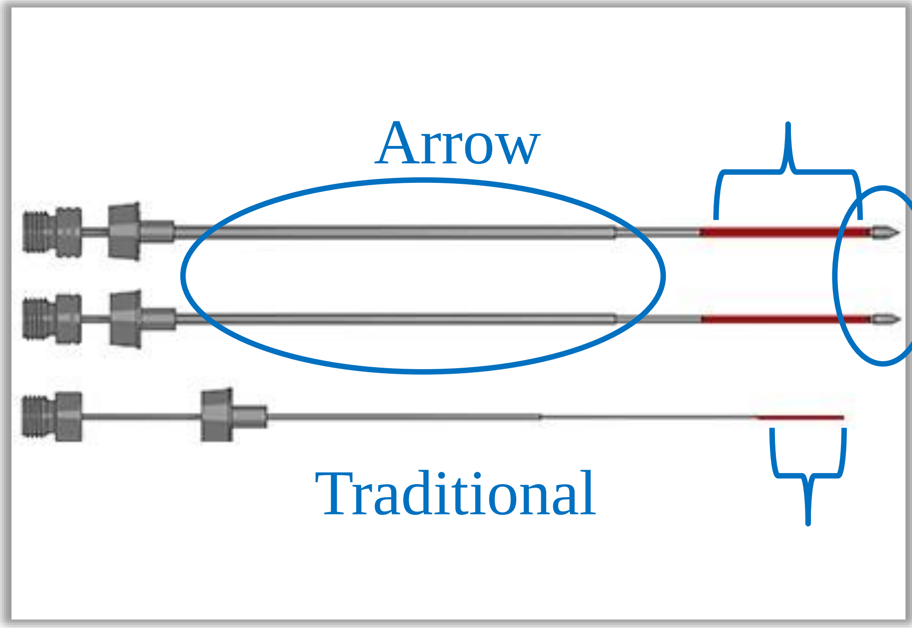
- Developed by CTC Analytics AG
  - PAL Systems (“Rails”)

- To overcome the limited mechanical stability and small phase volumes



# Traditional vs Arrow

- Arrow tip facilitates smooth septa penetration
- Fully protects phase
- Thicker needle is more durable
- Larger phase area/volume for increased sensitivity



# Phase Volumes

- Initial design of up to 6x the area and 20x the volume

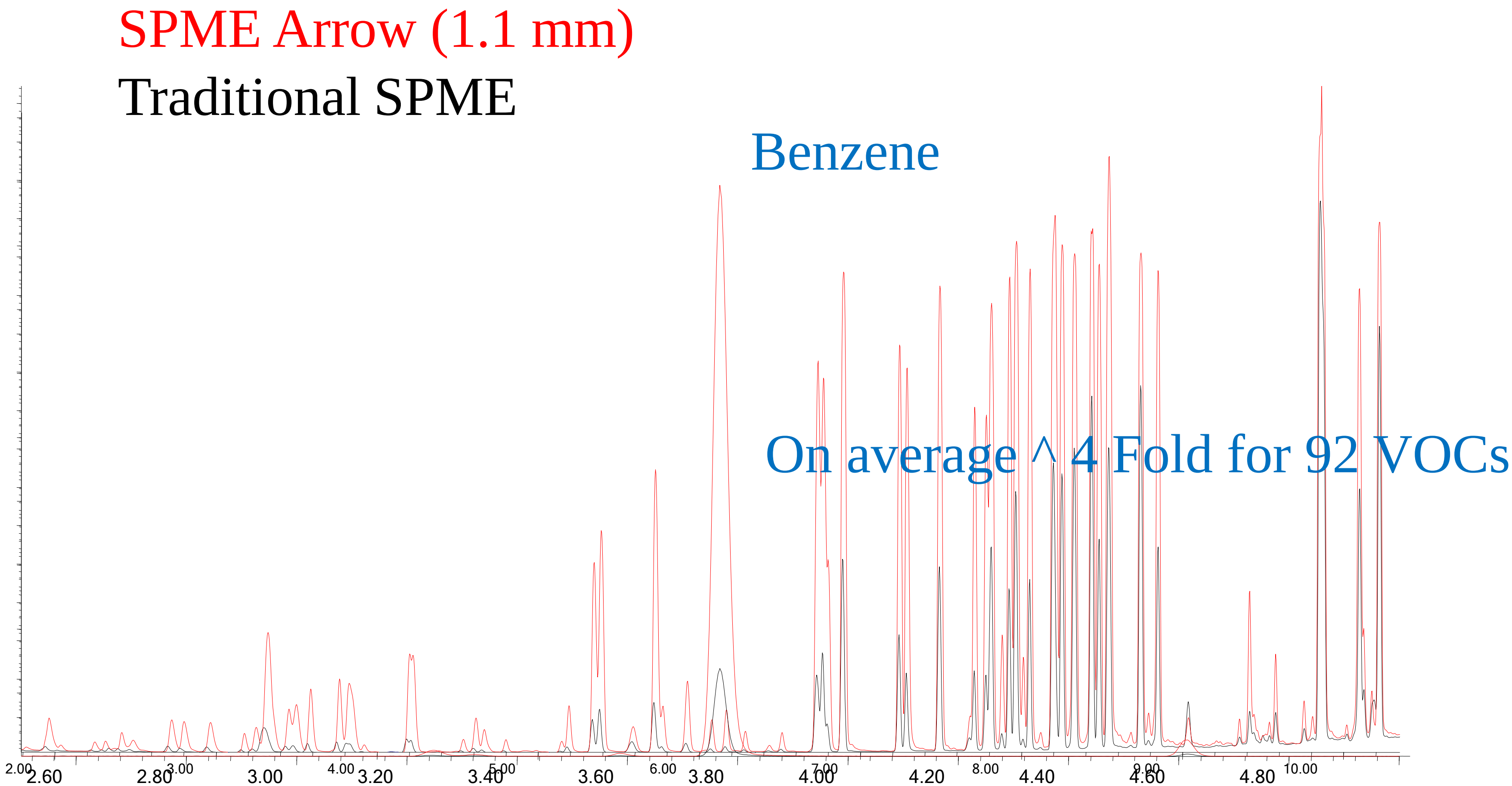
- Our calculations show 17 - 18x the volume

- Sensitivity (up to 10x) increase seems intuitive and reasonable

# Sensitivity of HS VOCs in Water

- 10 mL of $H_2O$
- 2.5 ppb of ISO 17943 VOCs
- 3 g NaCl
- 2 min of equilibration @ 60 °C
- 100 µm PDMS traditional and Arrow
- 10 min of headspace extraction @ 60 °C w/ 500 rpm of heatex

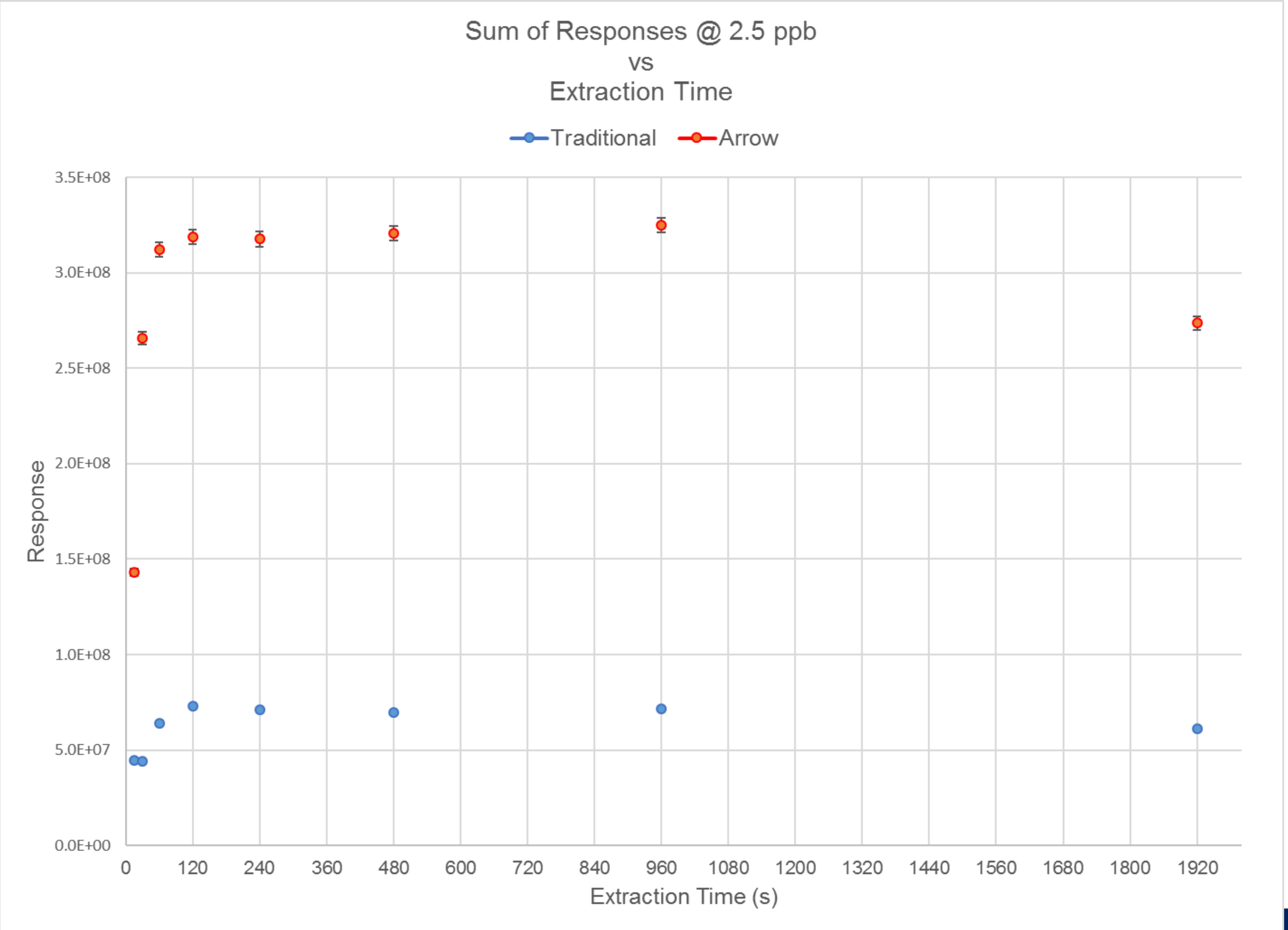
# VOCs in Water



# Response vs Extraction Time

- Goal: utilize the Arrow with shorter extraction times to achieve the same sensitivity as traditional SPME

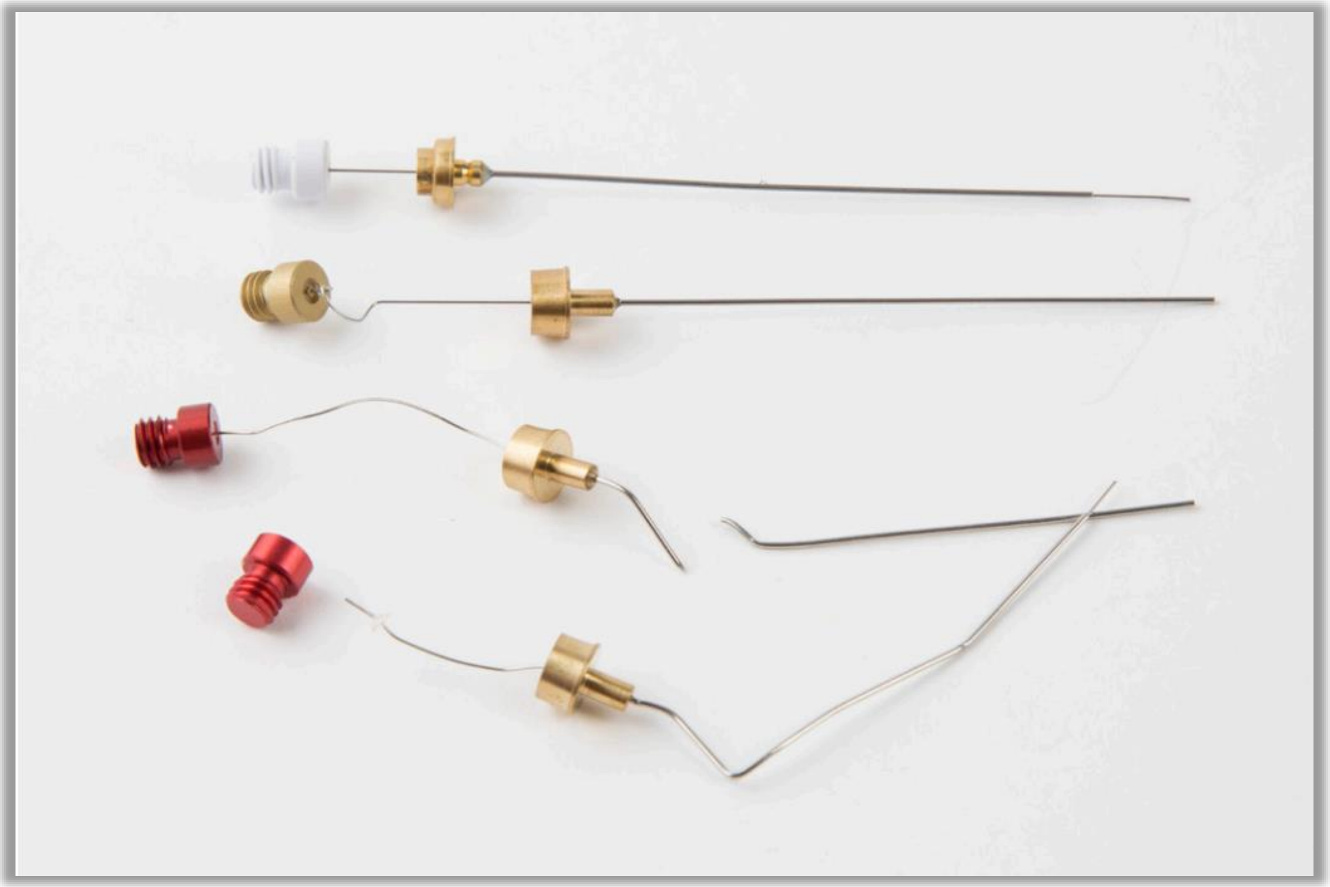
- Evaluated traditional and Arrow for:
  - 15, 30, 60, 120, 240, 480, 960, and 1920 s


Sum of Responses @ 2.5 ppb
vs
Extraction Time
Traditional
Arrow
Response
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
0
120
240
360
480
600
720
840
960
1080
1200
1320
1440
1560
1680
1800
1920
Extraction Time (s)

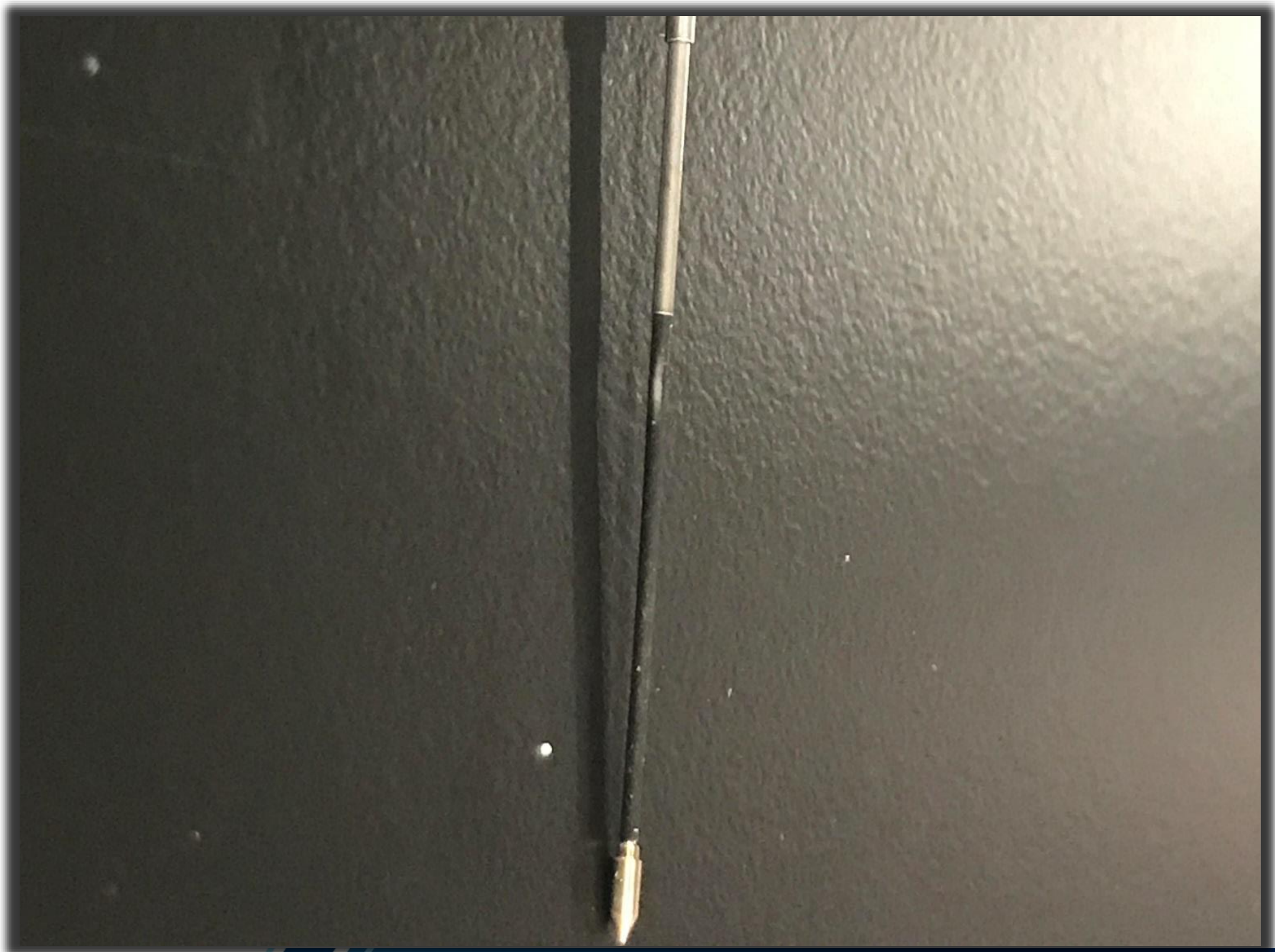
# Ruggedness/Lifetime

- Rack up a traditional fiber and Arrow
- Run 24 to 48 samples / day
  - Same # of runs on each SPME
- Evaluate responses everyday
- First to 50% collection efficiency or a mechanical failure loses

# A far too common outcome…



# Real Ruggedness Example



# SPME Methods

- ASTM D 6520, 2000
  - Standard Practice for the SPME of Water and its Headspace for the Analysis of Volatile and Semi-Volatile Organic Compounds
- ASTM D 6889, 2003
  - Standard Practice for Fast Screening for Volatile Organic Compounds in Water Using Solid Phase Microextraction (SPME)
- EPA Method 8272, 2007
  - Parent and Alkyl PAHs in Sediment Pore Water by SPME-GC/MS
- ISO 27108 (DIN 38407-34), 2013
  - Determination of selected plant treatment agents and biocide products - Method using SPME followed by GC-MS
- ISO 17943 (DIN 38407-41)
  - Determination of VOCs in water - GC-MS after HS-SPME

# ISO 17943

- We evaluated 92 VOCs. ISO 17943 only list 63 VOCs.
- Calibration linearity, precision, and detection limits were obtained from:
  - 10 mL of drinking water
  - With only a 2 minute headspace extraction @ 60 °C
  - With a 1 minute desorption @ 250 °C

| Compound | $r^2$ (0.0025 - 166 µg/L) | %RSD (n = 7 @ 250 ng/L) | MDL (ng/L) |
|---|---|---|---|
| Dichlorodifluoromethane (CFC-12) | 0.992 | 3.16 | 8.73 |
| Chloromethane | 0.997 | 12.3 | 135 |
| Vinyl chloride | 0.997 | 7.51 | 24.2 |
| Bromomethane | 0.999 | 18.8 | 47.3 |
| Chloroethane | 0.994 | 30.1 | 102 |
| Trichlorofluoromethane (CFC-11) | 0.991 | 1.97 | 2.75 |
| Diethyl ether | 0.998 | 5.11 | 11.1 |
| 1,1-Dichloroethene | 0.998 | 3.09 | 7.25 |
| Carbon disulfide | 0.997 | 2.11 | 8.52 |
| Trichlorotrifluoroethane (CFC-113) | 0.992 | 6.73 | 8.08 |
| Iodomethane | 0.997 | 3.29 | 5.61 |
| Allyl chloride | 0.998 | 1.53 | 3.17 |
| Methylene chloride | 0.998 | 2.92 | 54.0 |
| Acetone | 0.996 | 5.76 | 1137 |
| trans-1,2-Dichloroethene | 0.999 | 1.91 | 7.78 |
| Methyl tert-butyl ether (MTBE) | 0.999 | 5.51 | 11.2 |
| tert-Butanol (TBA) | 0.999 | 6.97 | 28.5 |
| Diisopropyl ether (DIPE) | 0.999 | 14.1 | 39.7 |
| Acetonitrile | 0.999 | 3.01 | 169 |
| Chloroprene (2-chloro-1,3-Butadiene) | 0.999 | 3.18 | 17.4 |
| 1,1-Dichloroethane | 0.999 | 3.17 | 7.03 |
| Acrylonitrile | 0.999 | 3.18 | 17.4 |
| Ethyl-tert-butyl ether (ETBE) | 0.999 | 4.36 | 9.34 |
| cis-1,2-Dichloroethene | 1.000 | 2.48 | 8.69 |
| 2,2-Dichloropropane | 0.998 | 3.07 | 53.0 |
| Bromochloromethane | 0.999 | 2.51 | 5.69 |
| Chloroform | 1.000 | 1.00 | 22.6 |
| Methyl acrylate | 0.989 | 3.42 | 47.1 |
| Carbon tetrachloride | 1.000 | 13.3 | 29.4 |
| Tetrahydrofuran | 0.978 | 13.2 | 1456 |
| 1,1,1-Trichloroethane | 1.000 | 2.66 | 6.74 |
| 2-Butanone (MEK) | 0.954 | 4.86 | 2843 |
| 1,1-Dichloropropene | 1.000 | 2.21 | 10.8 |
| Benzene | 0.999 | 3.20 | 31.3 |
| Propionitrile | 0.989 | 4.64 | 88.6 |
| Methacrylonitrile | 1.000 | 7.04 | 33.1 |
| tert-Amyl methyl ether (TAME) | 0.998 | 4.50 | 13.6 |
| 1,2-dichloroethane | 1.000 | 2.87 | 10.6 |
| Isobutyl alcohol | 0.992 | 5.77 | 1702 |
| Trichloroethene | 1.000 | 1.37 | 16.3 |
| Dibromomethane | 0.996 | 2.25 | 5.3 |
| 1,2-Dichloropropane | 0.997 | 4.96 | 15.9 |
| Bromodichloromethane | 0.999 | 2.33 | 11.6 |
| Methyl methacrylate | 0.999 | 6.24 | 30.1 |
| 1,4-Dioxane | 0.987 | 3.76 | 386 |
| 2-Chlorethyl vinyl ether | 0.999 | 4.16 | 16.2 |
| 2-Chloropropanol | 0.999 | 6.83 | 407 |
| cis-1,3-Dichloropropene | 1.000 | 1.93 | 11.2 |
| Toluene | 0.995 | 1.88 | 83.6 |
| 2-Nitropropane | 0.990 | 4.26 | 101 |
| 2-Hexanone | 1.000 | 4.66 | 26.9 |
| trans-1,3-Dichloropropene | 0.990 | 2.34 | 34.0 |
| Tetrachloroethene | 0.997 | 2.74 | 49.5 |
| Ethyl methacrylate | 0.994 | 3.69 | 39.7 |
| 1,1,2-Trichloroethane | 0.999 | 3.59 | 14.6 |
| Dibromochloromethane | 1.000 | 3.14 | 14.0 |
| 1,3-Dichloropropane | 1.000 | 3.54 | 16.0 |
| 1,2-Dibromoethane | 1.000 | 3.35 | 15.3 |
| 4-Methyl-2-pentanone (MIBK) | 0.999 | 5.44 | 29.8 |
| Ethylbenzene | 0.989 | 2.34 | 115 |
| Chlorobenzene | 0.999 | 2.37 | 24.7 |
| 1,1,1,2-Tetrachloroethane | 1.000 | 4.59 | 43.0 |
| m-Xylene | 0.981 | 2.47 | 50.8 |
| p-Xylene | 0.981 | 2.47 | 50.8 |
| o-Xylene | 0.989 | 2.93 | 38.1 |
| Styrene | 0.999 | 3.14 | 31.0 |
| Bromoform | 0.993 | 4.18 | 26.9 |
| Isopropylbenzene | 0.989 | 3.87 | 56.3 |
| cis-1,4-Dichloro-2-butene | 0.999 | 6.22 | 70.7 |
| n-Propylbenzene | 0.985 | 2.48 | 42.4 |
| 1,1,2,2-Tetrachloroethane | 0.997 | 4.10 | 31.5 |
| Bromobenzene | 0.996 | 2.17 | 26.2 |
| 1,3,5-Trimethylbenzene | 0.986 | 2.74 | 41.5 |
| 2-Chlorotoluene | 0.996 | 2.11 | 24.9 |
| trans-1,4-Dichloro-2-butene | 0.997 | 2.79 | 30.2 |
| 1,2,3-Trichloropropane | 1.000 | 3.51 | 30.6 |
| 4-Chlorotoluene | 0.996 | 2.11 | 24.9 |
| tert-Butylbenzene | 0.990 | 2.69 | 34.9 |
| 1,2,4-Trimethylbenzene | 0.987 | 2.19 | 31.8 |
| Pentachloroethane | 0.998 | 5.14 | 41.1 |
| sec-Sutylbenzene (1-methylpropyl) | 0.987 | 3.30 | 53.7 |
| p-Isopropyltoluene | 0.990 | 3.29 | 47.7 |
| 1,3-Dichlorobenzene | 1.000 | 2.33 | 22.8 |
| 1,4-Dichlorobenzene | 1.000 | 1.70 | 16.4 |
| n-Butylbenzene | 0.995 | 1.95 | 110 |
| 1,2-Dichlorobenzene | 1.000 | 3.81 | 33.6 |
| 1,2-Dibromo-3-chloropropane | 0.985 | 5.50 | 31.1 |
| Hexachlorobutadiene | 0.999 | 3.30 | 30.0 |
| Nitrobenzene | 0.971 | 28.9 | 198 |
| 1,2,4-Trichlorobenzene | 0.999 | 1.27 | 10.4 |
| Naphthalene | 0.998 | 3.39 | 33.0 |
| 1,2,3-Trichlorobenzene | 0.998 | 2.80 | 21.6 |
| **Median** | **0.998** | **3.24** | **30.0** |

# ISO 17943

- Calibration
  - 3 nines or better for most compounds at 2.5 ppt to 150 ppb
- Precision
  - 3 % RSDs, which are well below method requirements
- MDLs
  - ~30 ng/L
- All from a 2 minute extraction!!!

# Implications

- SPME Arrow is more sensitive and sturdy than traditional SPME fibers
- Demonstrated excellent linearity, precision, and detection limits
- However, limited method applicability in the U.S.

# SPME Arrow Application

- Fast screening!!!
  - ASTM D 6889, 2003
    - Standard Practice for Fast Screening for Volatile Organic Compounds in Water Using Solid Phase Microextraction (SPME)

- A 2 minute extraction and 4 minute GC-MS screening run could prevent hours of purge-and-trap instrument down time from a hot sample

# Thank You!

- Colton Myers
- Co-authors
- CTC Analytics AG