Weck Laboratories

EPA 625 by SLE and GC-MS/MS

Agustin Pierri, PhD

About our laboratory

A full-service environmental lab

- Metals
- VOCs
- SVOCs
- Anions
- Microbiology
- ~27,000 ft^2
- ~65 analysts

About our laboratory

A full-service environmental lab

- Metals
- VOCs
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- Microbiology
- ~27,000 ft²
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- Semi-volatiles in wastewater
- SLE, fast GC, and MS/MS
- 1,4-dioxane in water
- Solid-phase micro-extraction (SPME)
- PFAS
- Dilute-and-shoot LC-MS/MS

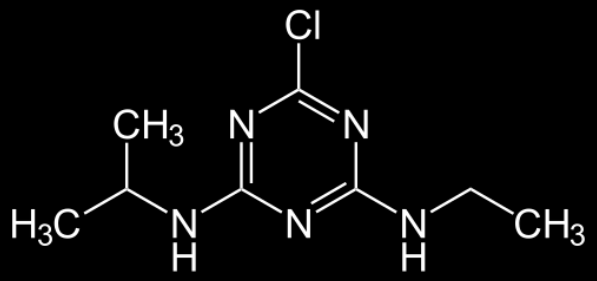
Semi-volatile analysis by SLE, fast GC, and MS/MS

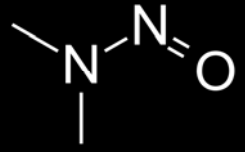
SVOC analysis

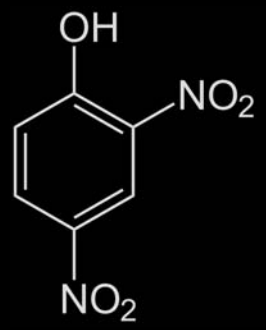
US EPA method 625

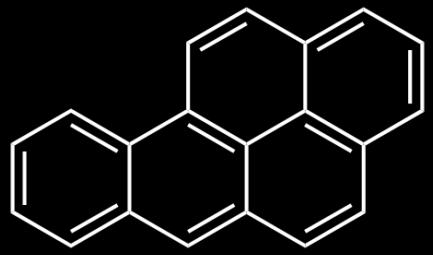
Semivolatiles in industrial discharges

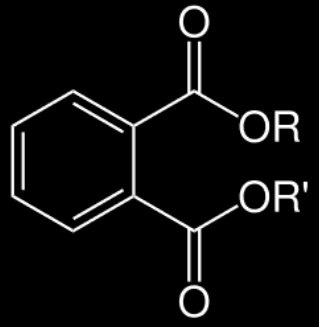
PAHs	Nitrosamines
Phthalates	Pesticides
PCBs	Phenols

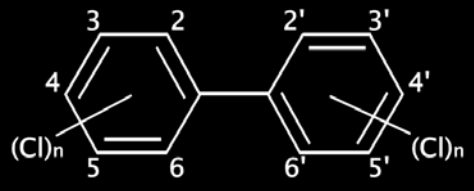










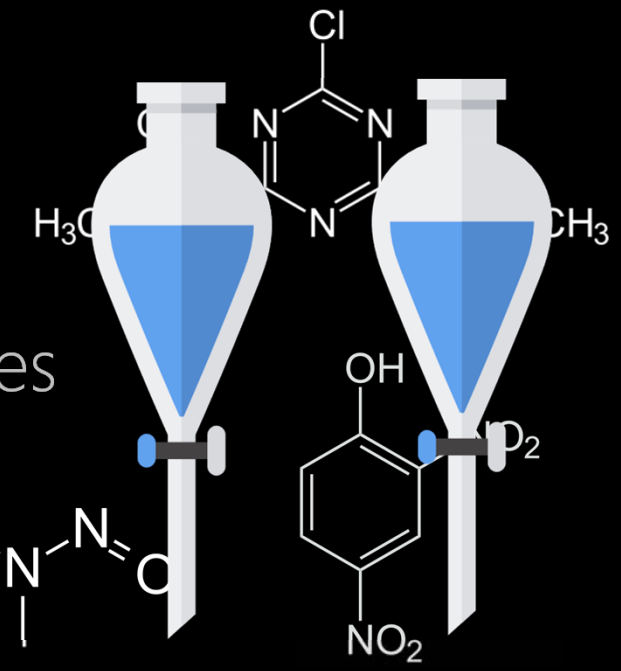


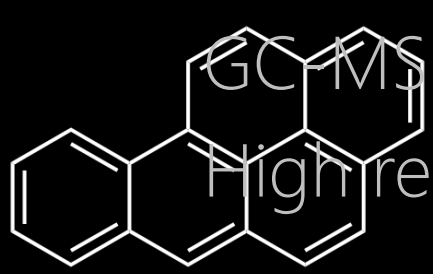
SVOC analysis

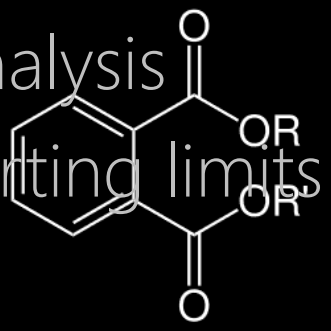
US EPA method 625

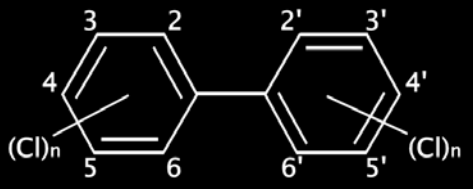
- 1980's method - 1980's technology
- Liquid-liquid extraction (LLE)
- Phthalates
- PCBs
- GC-MS analysis
- High reporting limits

- Semivolatiles discharges
- Liquid-liquid extraction (LLE)
- Acids
- Pesticides
- Bases and neutrals
- Phenols



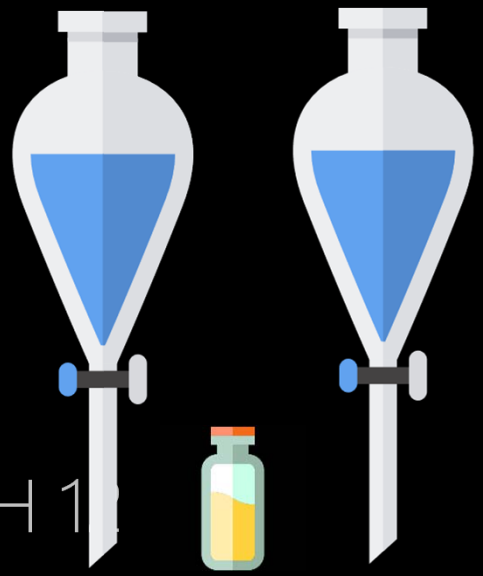






SVOC analysis

- US EPA method 625
  - 1980s method-1980s techniques
    - Liquid-liquid extraction (LLE)
      - Acids
      - Bases and neutrals
    - GC-MS analysis
    - High reporting limits



Acid extractables

Base extrac

LLE pros and cons

Pros:

- Efficient extractions
- Large concentration factor
- Minimal hardware

Cons:

- Efficient extractions
- Emulsions
- Time consuming
  - 10 samples in 8 hrs
- Solvent usage
  - 6 x 60 mL portions
  - ~9 L of $MeCl_2$
- Drying extracts

Semivolatiles by SLE vs LLE

LLE

- Large concentration
  - Lots of matrix
- 40 samples in 16 hours
- Combined extracts
  - One 30 min. run
- 5-10 ug/L MRLs
  - More GC maintenance
- Too much sample handling

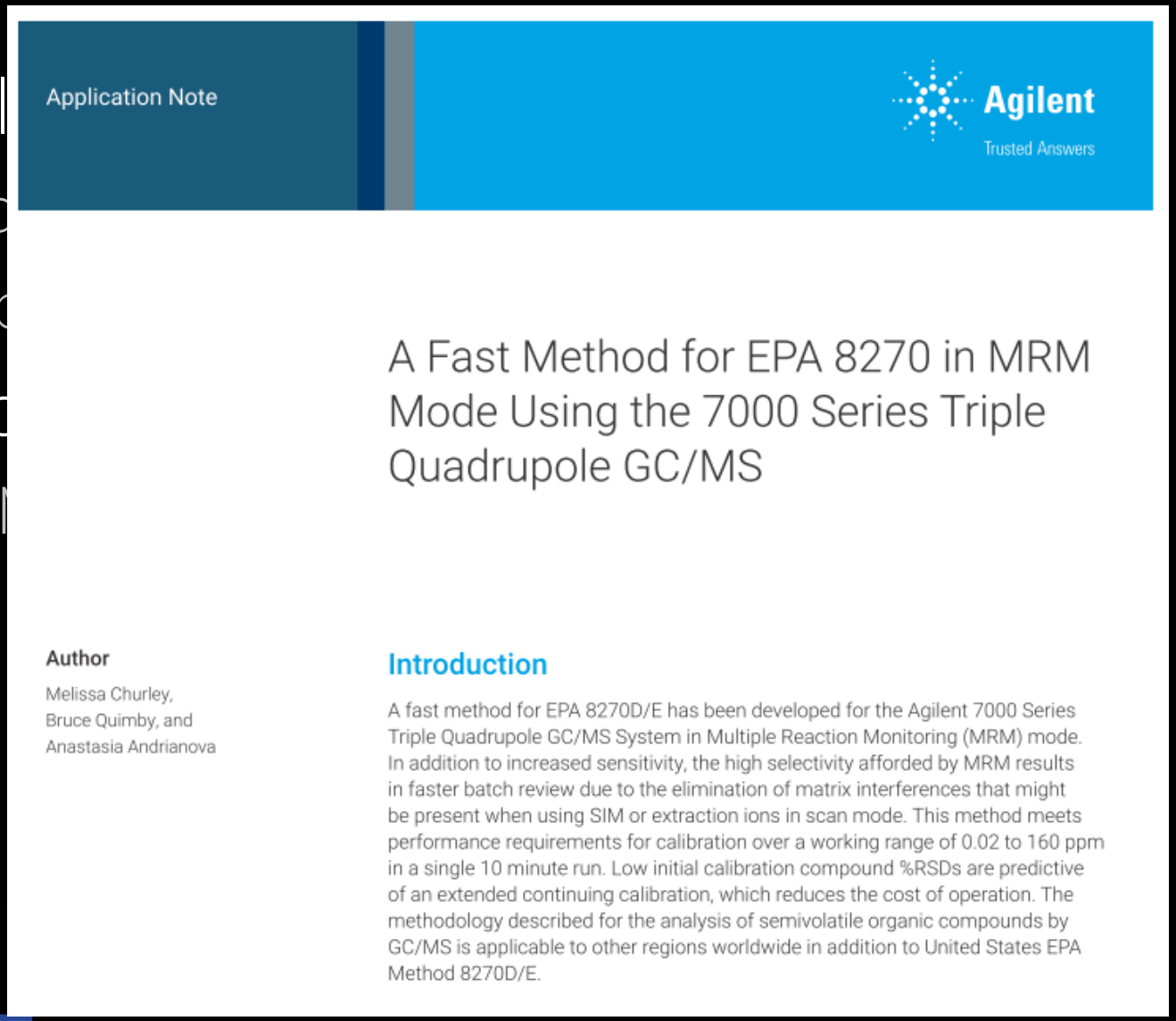
SLE

- Less concentrated ✓
  - Less matrix
- 40 samples in 2 hours ✓
- Two extracts ✓
  - Two 10 min. runs
- 5-10 ug/L MRLs ✓
  - Less GC maintenance
- Minimal sample handling ✓

Improvements for a commercial lab

Simpl
- Solic
- Supp

Impro
- GC-
- Fast



Application Note

Agilent
Trusted Answers

A Fast Method for EPA 8270 in MRM Mode Using the 7000 Series Triple Quadrupole GC/MS

Author

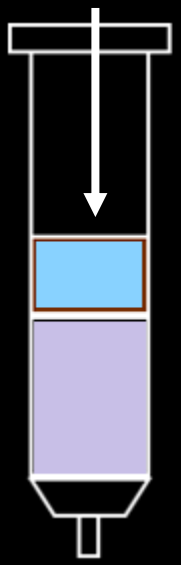
Melissa Churley,
Bruce Quimby, and
Anastasia Andrianova

Introduction

A fast method for EPA 8270D/E has been developed for the Agilent 7000 Series Triple Quadrupole GC/MS System in Multiple Reaction Monitoring (MRM) mode. In addition to increased sensitivity, the high selectivity afforded by MRM results in faster batch review due to the elimination of matrix interferences that might be present when using SIM or extraction ions in scan mode. This method meets performance requirements for calibration over a working range of 0.02 to 160 ppm in a single 10 minute run. Low initial calibration compound %RSDs are predictive of an extended continuing calibration, which reduces the cost of operation. The methodology described for the analysis of semivolatile organic compounds by GC/MS is applicable to other regions worldwide in addition to United States EPA Method 8270D/E.

Supported Liquid Extraction

Add aqueous sample



Hold 5 min

Add solvent

Gravity elute

Supported Liquid Extraction

Improved workflow

- <10 minutes per sample
- Batch processing
- 40 samples in 2 hours
- Cleaner extracts

Drawbacks

- Two extractions
- Less concentration

SLE: 2x concentration

LLE: 1000x concentration

LLE: 8 hours

LLE: 8 hours

SLE: 2 hours

SLE procedure—base/neutrals

Spike 125 mL sample volume with surrogate standards

Adjust sample aliquot to pH 12 with NH_4OH

Load 2 mL of sample onto Chem Elute SLE cartridge (2 mL capacity)

Allow to soak for 5 minutes

Load 5 mL $MeCl_2$, soak for 3 minutes, collect under gravity

Gravity elute 2 x 5 mL of $MeCl_2$, combining extracts

Evaporate extract to 1 mL, add internal standard and prepare for analysis

SLE procedure—acid extractables

Spike 125 mL sample volume with surrogate standards

Adjust sample aliquot to pH 12 with formic acid

Load 2 mL of sample onto Chem Elute SLE cartridge (2 mL capacity)

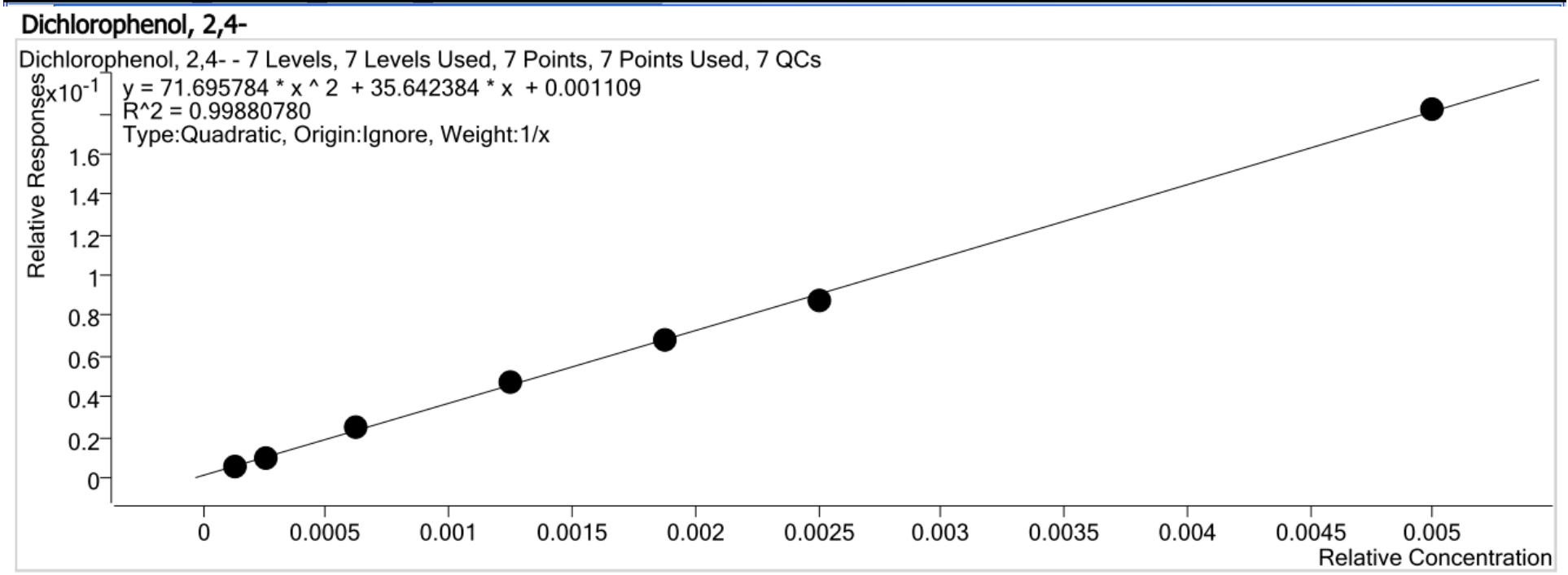
Allow to soak for 5 minutes

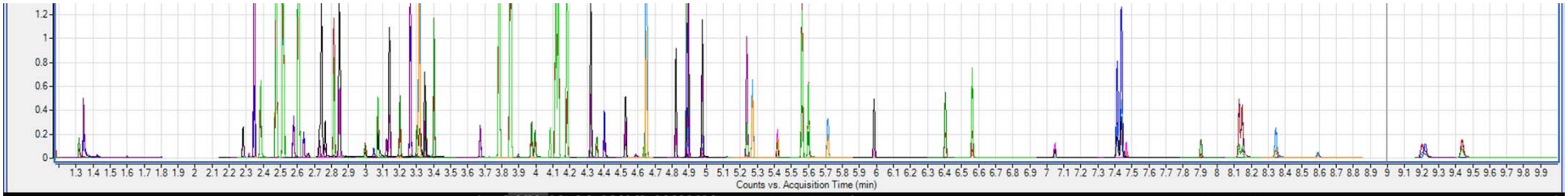
Load 5 mL $MeCl_2$, soak for 3 minutes, collect under gravity

Gravity elute 2 x 5 mL of $MeCl_2$, combining extracts

Evaporate extract to 1 mL, add internal standard and prepare for analysis

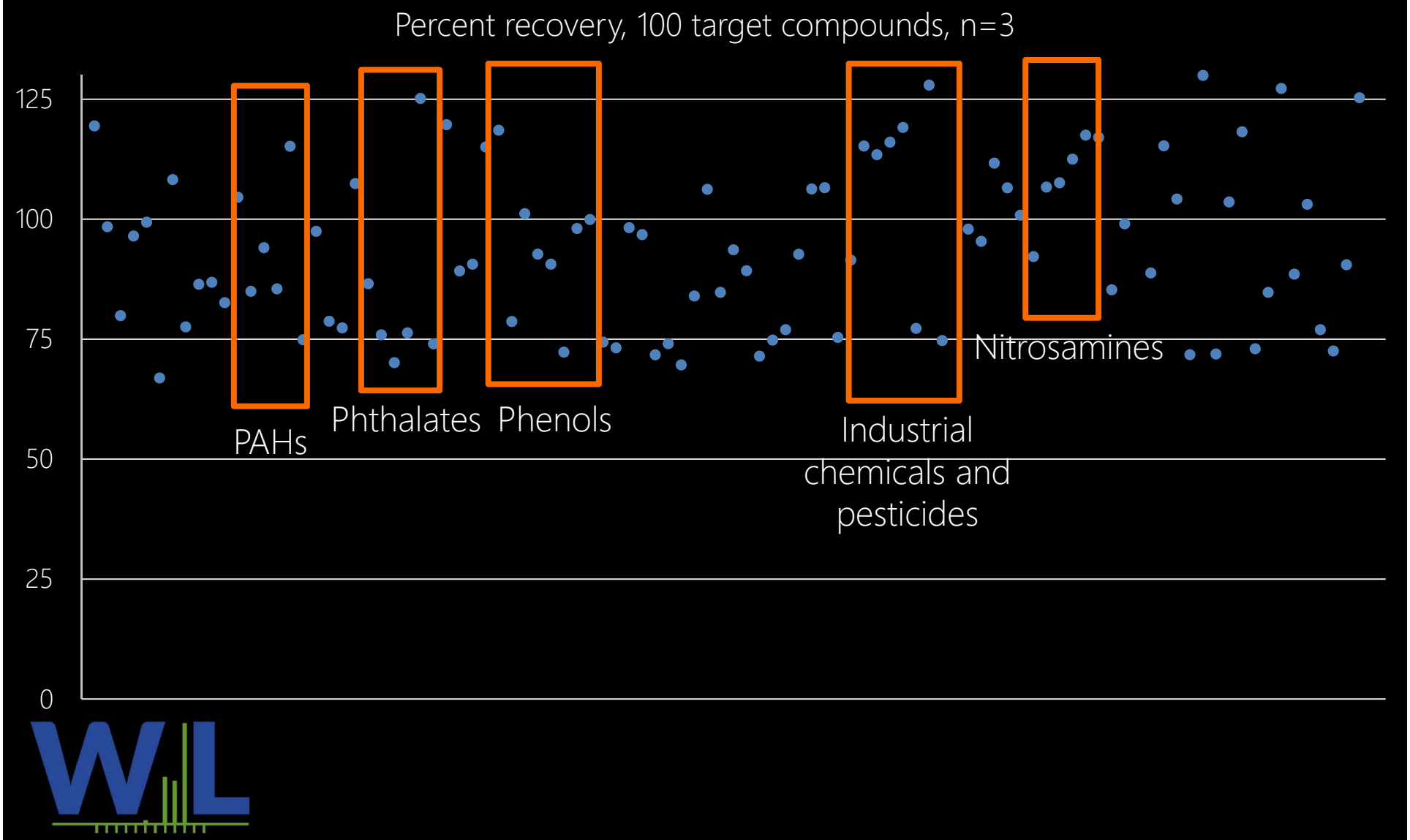
GC-MS/MS analysis



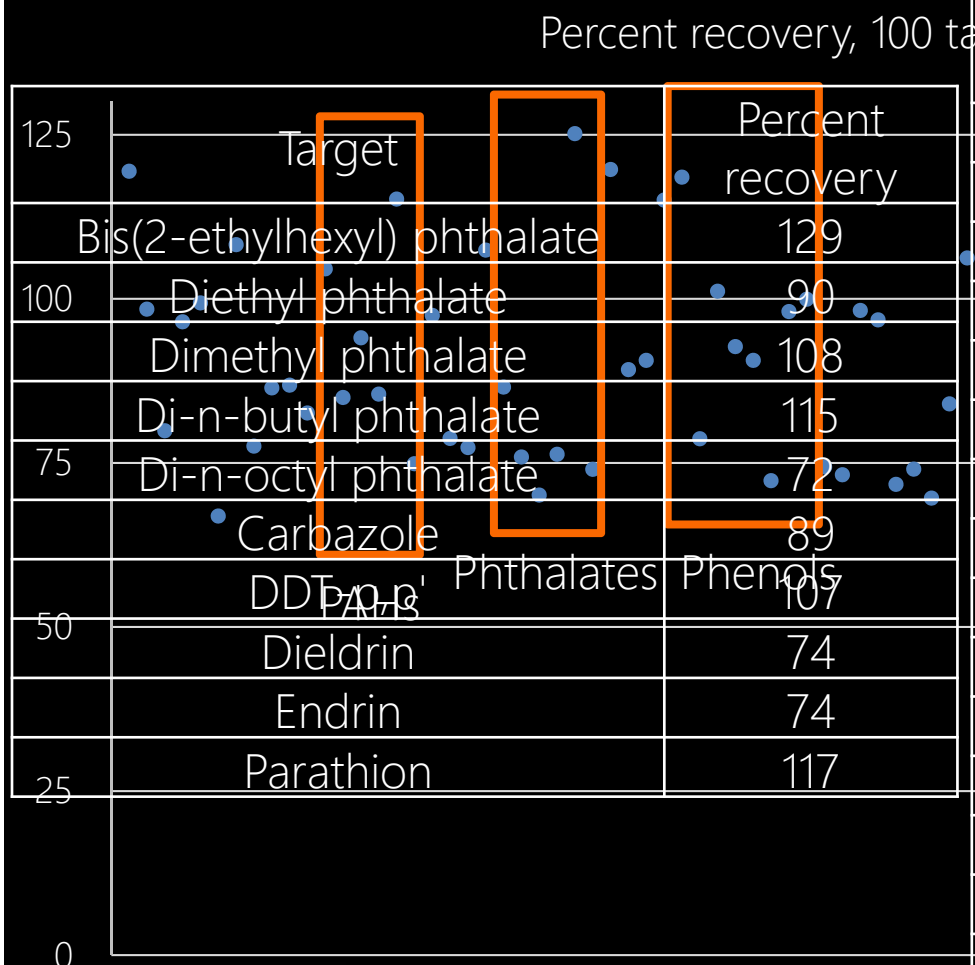


Oven Temperature	40 °C to 320 °C at 35 °C/min, hold for 2 minutes
Carrier Gas	Helium, constant flow at 1.2 mL/min
Transfer Line Temperature	320 °C
Run Time	10 minutes

Average recoveries



Average recoveries



Target	Percent recovery
Bis(2-ethylhexyl) phthalate	129
Diethyl phthalate	90
Dimethyl phthalate	108
Di-n-butyl phthalate	115
Di-n-octyl phthalate	72
Carbazole	89
DDT-o,p'	107
Dieldrin	74
Endrin	74
Parathion	117

Target	Percent recovery
Acenaphthene	77
Acenaphthylene	83
Benzo[a]pyrene	86
Fluoranthene	84
Naphthalene	98
Benzyl alcohol	100
Chlorophenol, 2-	108
Nitrophenol, 2-	104
Phenol	95
Phenol, 4-chloro-3-methyl-	100
Nitrosodiethylamine, N-	98
Nitrosodimethylamine, N-	95
Nitrosodi-n-butylamine, N-	112
Nitrosodi-n-propylamine, N-	107
Nitrosodiphenylamine, N-	101

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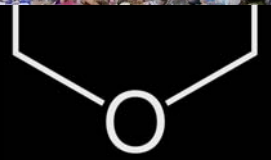
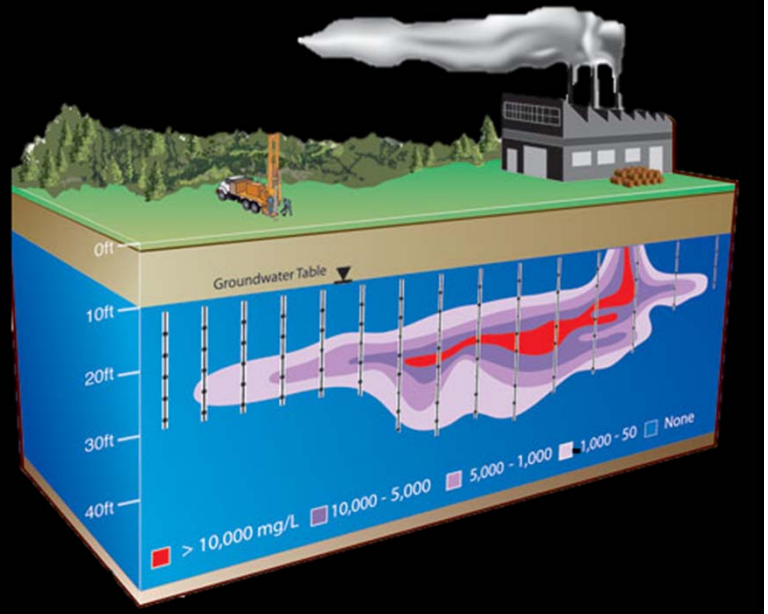
1,4-dioxane

Background

- Versatile aprotic solvent
- By-product of personal care products
- IARC classified as a Group 2B carcinogen
- Extremely water soluble and leads to contamination
  - Groundwater supplies
  - Landfill leachate
  - Industrial waste





1,4-dioxane analysis

Offline SPE

500 mL extra

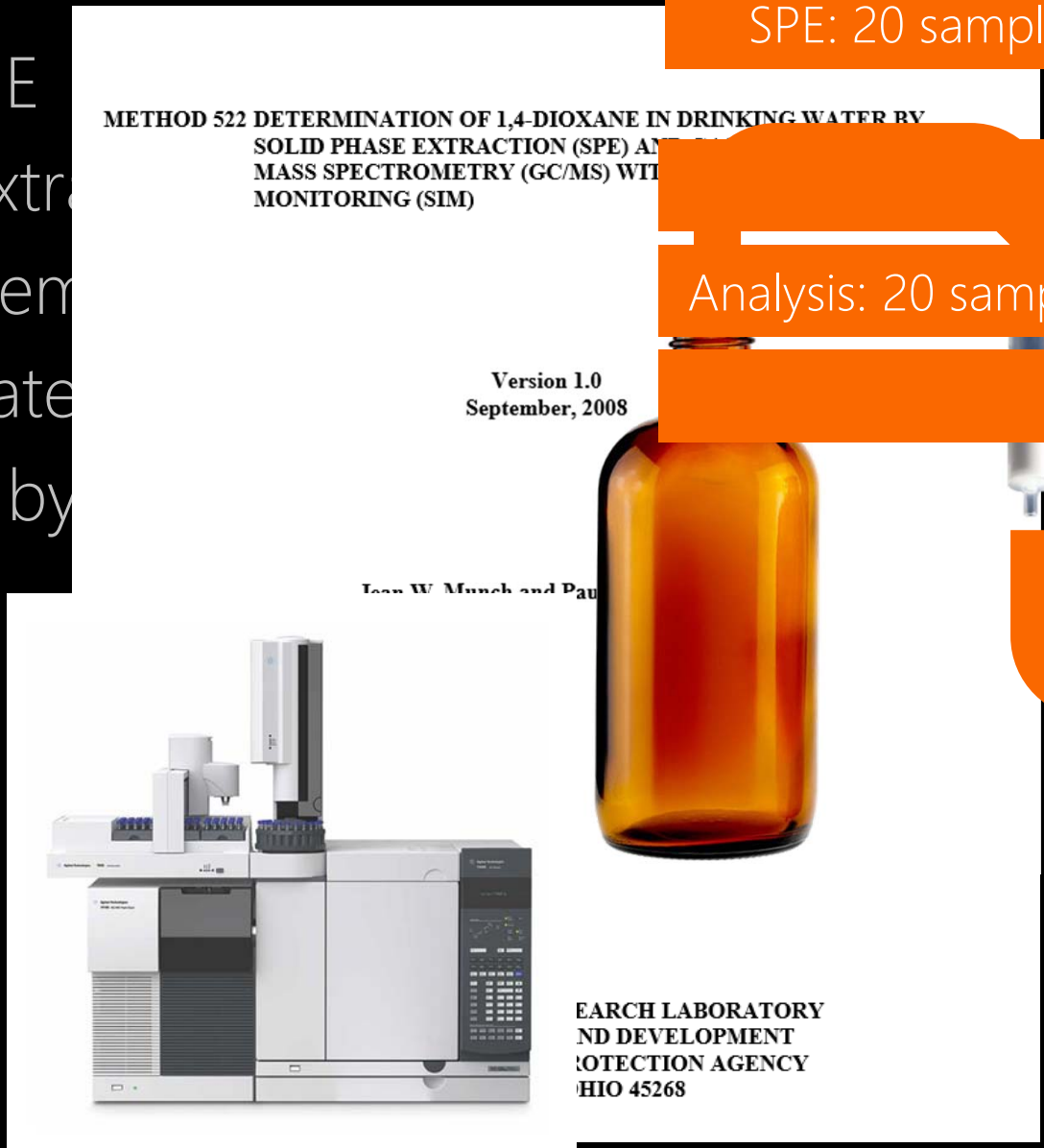
Dried to rem

Concentrate

Analyzed by

SPE: 20 samples in 4 hours

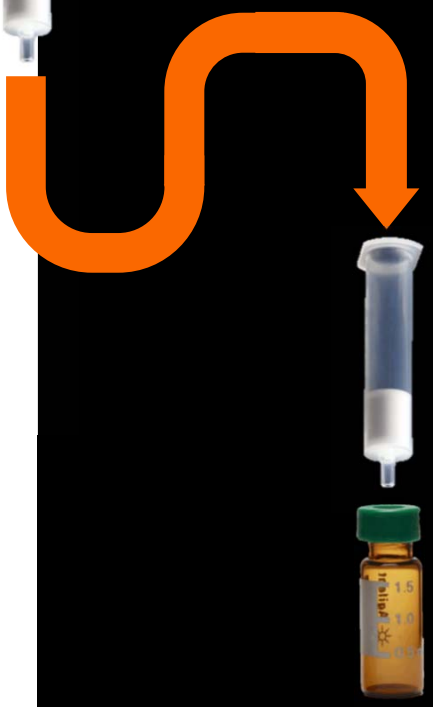
Analysis: 20 samples in 12 hours


METHOD 522 DETERMINATION OF 1,4-DIOXANE IN DRINKING WATER BY
SOLID PHASE EXTRACTION (SPE) AN
MASS SPECTROMETRY (GC/MS) WIT
MONITORING (SIM)

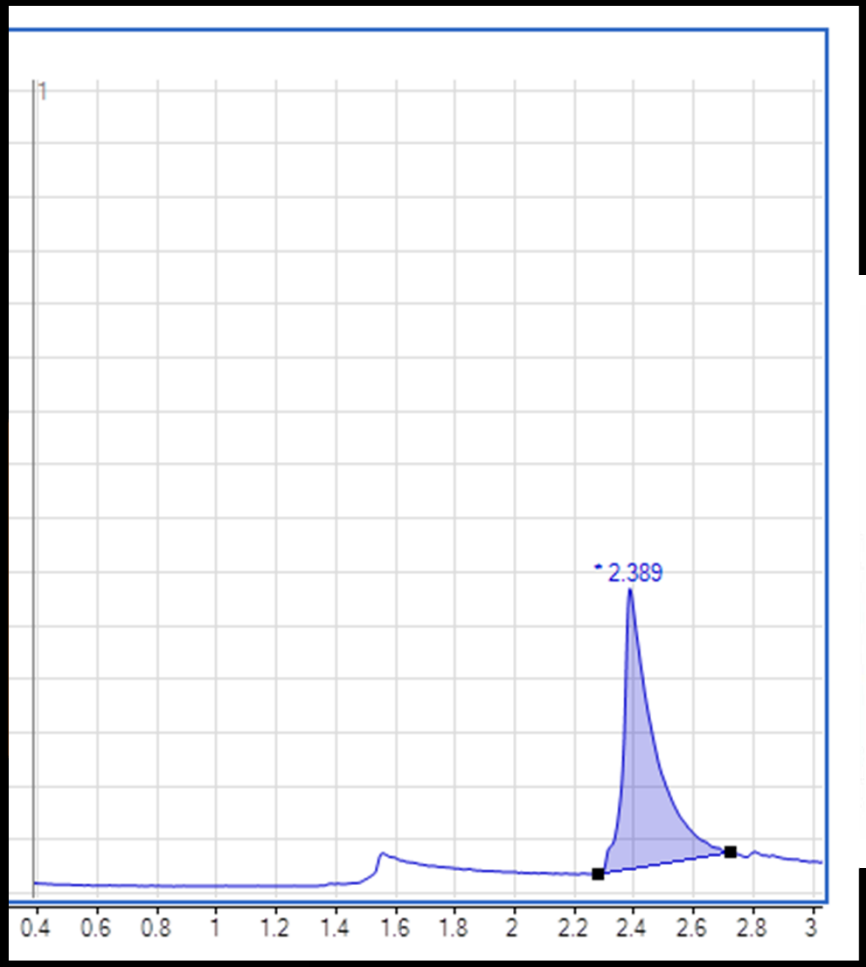
Version 1.0
September, 2008

Jean W. Munch and Pau

EARCH LABORATORY
ND DEVELOPMENT
ROTECTION AGENCY
HIO 45268



Solid-phase micro-extraction



- Add 10 mL sample
- Spike with IS (1,4-dioxane-d_8)
- Add 3 g of salt (NaCl)
- Incubate 15 sec. at 65°C
- Agitate 60 sec at 350 RPM
- Extract 1200 sec. at 65°C
- Analyze by GC-MS

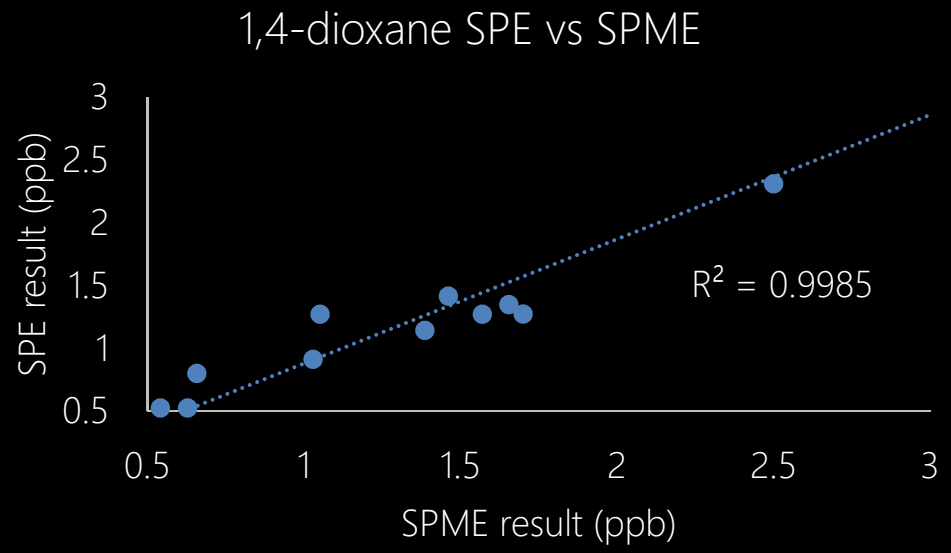
SPME optimization

Conc.	Response	Fiber
100 ppb	1992	Polydimethylsiloxane (PDMS)
100 ppb	950	Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS)
100 ppb	5962	Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)
100 ppb	2764470	Carboxen/Polydimethylsiloxane (CAR/PDMS)

Salt	Response
0 g / 10 mL of water	5403
1 g / 10 mL of water	8219
2 g / 10 mL of water	15088
3 g / 10 mL of water	17475

SPME performance vs SPE

SPE (ppb)	SPME (ppb)	% difference
17.95	17.71	1%
2.5	2.31	8%
1.7	1.27	29%
1.65	1.35	21%
1.57	1.27	21%
1.46	1.41	3%
1.39	1.14	19%
1.05	1.27	-19%
1.03	0.91	12%
0.66	0.80	-19%
0.63	0.52	18%
0.54	0.52	4%
Average		8%



	MDL (ppb)	MRL (ppb)
SPME	0.17	0.5
SPE	0.04	0.5

SPE: 20 samples in 4 hours

SPME:

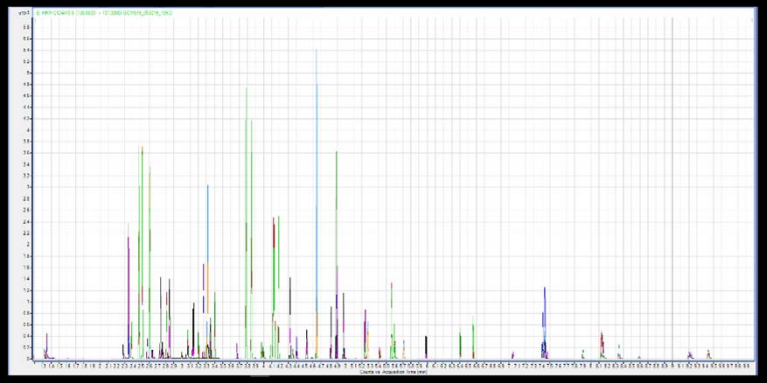
Automated extraction + analysis

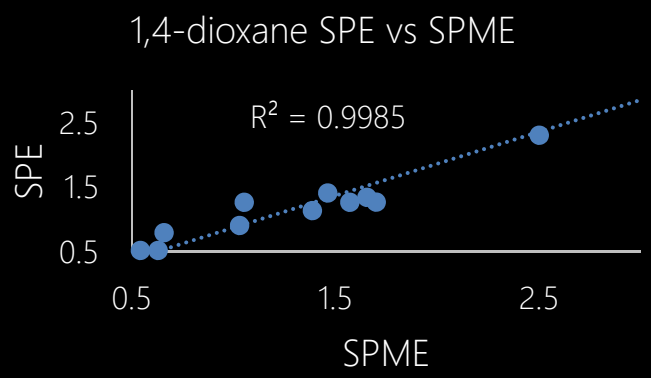
20 samples in 15 hours

Conclusion

Semi-volatiles in wastewater

SLE, fast GC, and MS/MS





Weck Laboratories

Thank you!

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