

Analysis of Organochlorine Pesticides and Semi-Volatile Organics in Water with Semi-Automated Solid Phase Extraction Using EPA Methods 508 and 525.3

Tom Hall
Toxic Report, LLC
Watertown MA

Introduction

- ▶ Organochlorine pesticides are man-made organic chemicals with a history of wide spread use around the world
- ▶ Persistent to degradation, found in drinking water supplies and sediments
- ▶ Some are included in Stockholm Convention (added 2009-2015)
- ▶ EPA method 508

Health risks OCPs

- ▶ Organochlorines have a wide range of both acute and chronic health effects
- ▶ Cancer
- ▶ Neurological effects
- ▶ Birth defects
- ▶ Many OCPs are also suspected endocrine disruptors

Semi Volatiles

- Found in drinking water and waste water
- In US regulated by EPA methods 525 and 625
- Also regulated elsewhere in the world
- Great demand for fast, reliable and reproducible laboratory analysis

Health Effects SVOCs

- ▶ Allergic symptoms
- ▶ Delayed reproductive development
- ▶ Immunotoxicity
- ▶ Cancer
- ▶ Asthma (in dust)
- ▶ Suspected endocrine disruption

Analysis for OCPs/SVOCs

- Many labs analyze drinking and waste water samples
- Liquid-Liquid Extraction (LLE) or Solid Phase Extraction (SPE) can be used
- In both cases organics are transferred from water sample to an organic solvent
- With SPE compounds are first deposited on cartridge or disk, then eluted

Comparison of LLE/CLE vs SPE Methods (1)

LLE/CLE

Open to laboratory background

Uses >360mls solvent

Shaking / Continuous process

Forms emulsions requiring centrifuging

Little Selectivity

Requires water removal

Semi-Automated SPE

Closed system

Uses <60mls solvent

Filtration process

No emulsions formed

Wide Selectivity (adsorbent)

In-line water removal

Comparison of LLE/CLE vs SPE Methods (2)

LLE/CLE

No Separation of waste

More volume to evaporate

Massive solvent emission

CLE uses a lot of solvent

Requires lots of solvent for cleaning

Semi-Automated SPE

Separates Aqueous and Organic Waste

<60mls solvent to evaporate

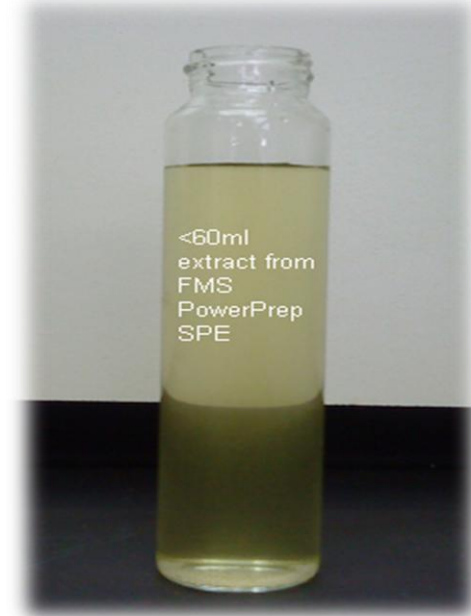
6 times less solvent emission

Easily Capture Solvent

Lower solvent costs

Lower Disposal Costs

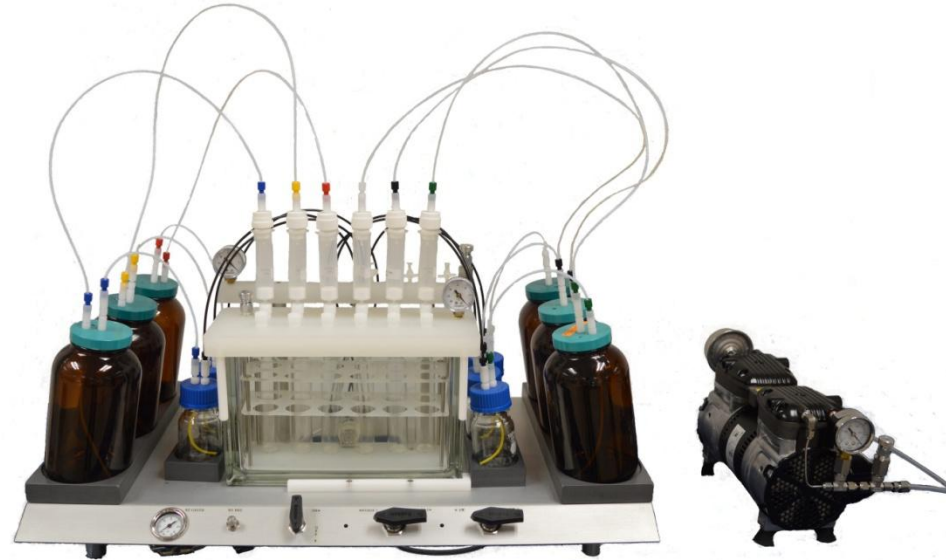
Reduced Solvent Usage



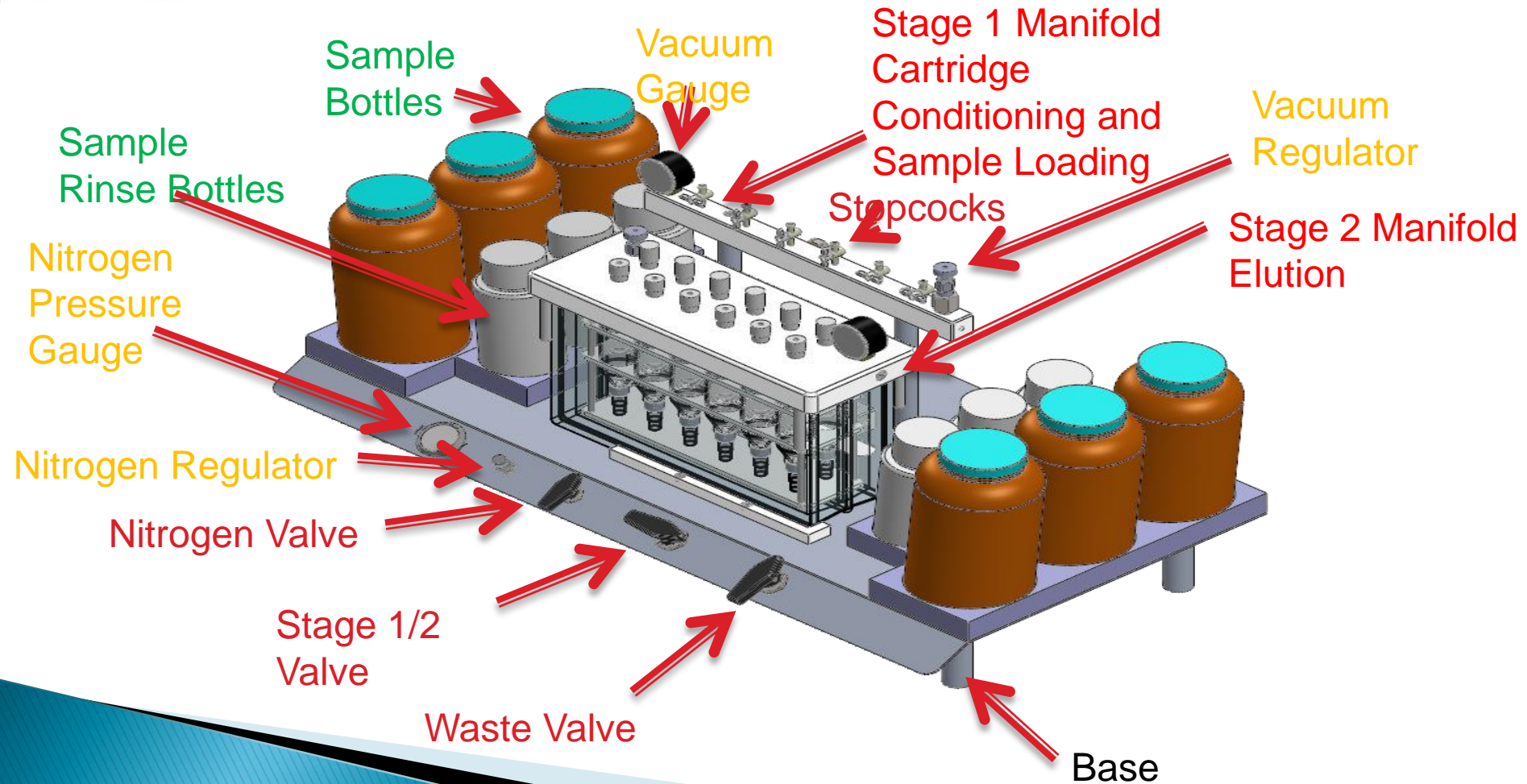
Semi-Automated SPE

- ▶ Semi-automated SPE done by many labs around the world
- ▶ Cheaper than fully automated systems
- ▶ Important that system is reliable and fast
- ▶ Should be able to use variety of cartridges

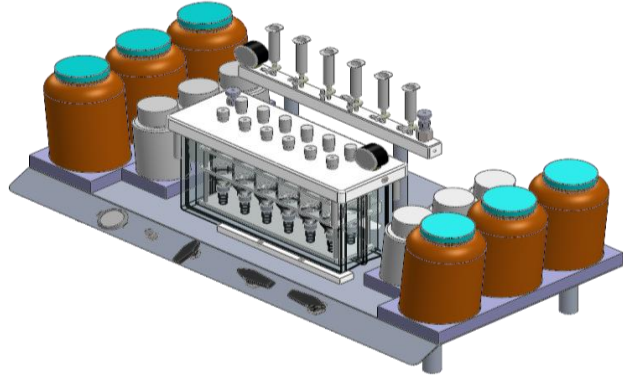
Semi-Automated FMS System (EZSpe™)



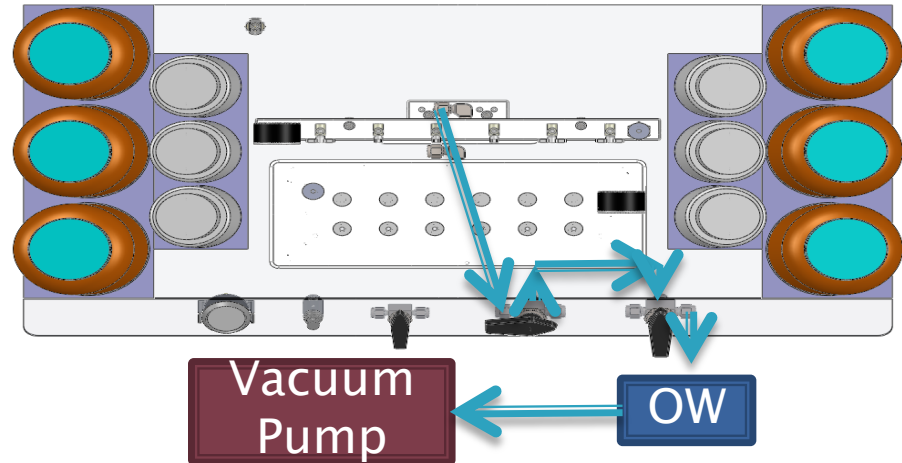
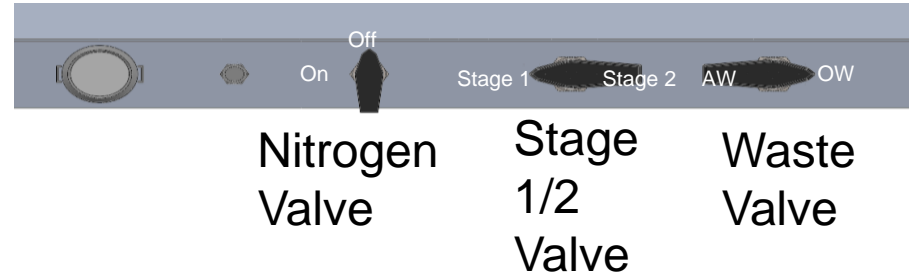
System Layout



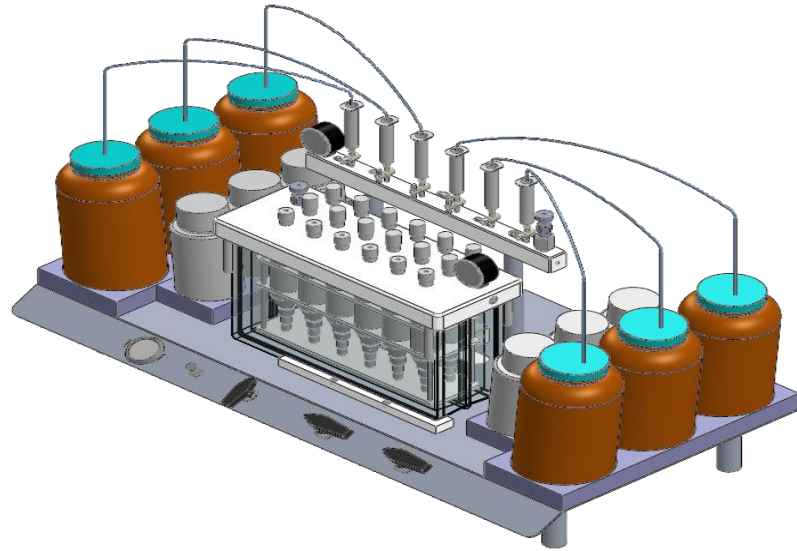
Cartridge Conditioning (Stage 1, Organic Waste)



Flow
Path



Sample Loading (Stage 1, Aqueous Waste)



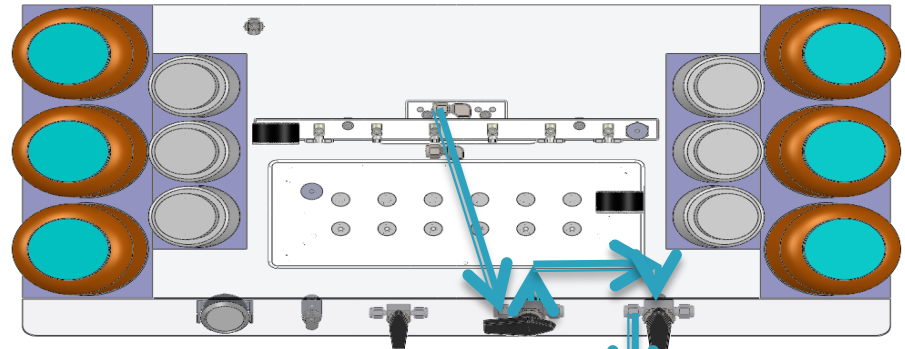
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

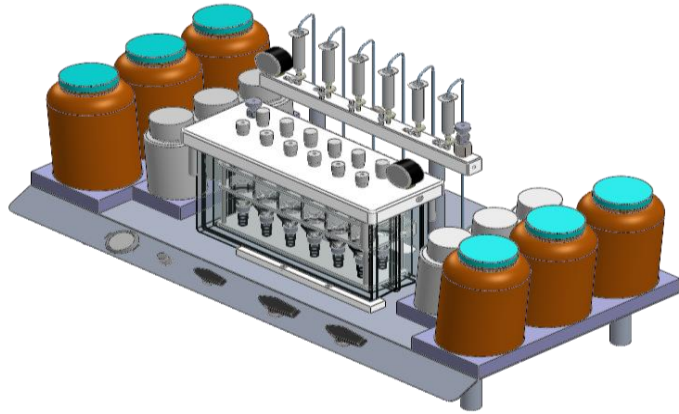
Waste
Valve



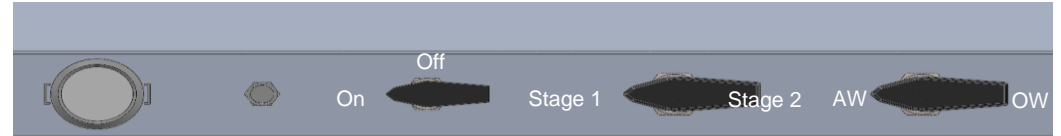
Vacuum
Pump

AW

Cartridge Drying- Nitrogen/Vacuum



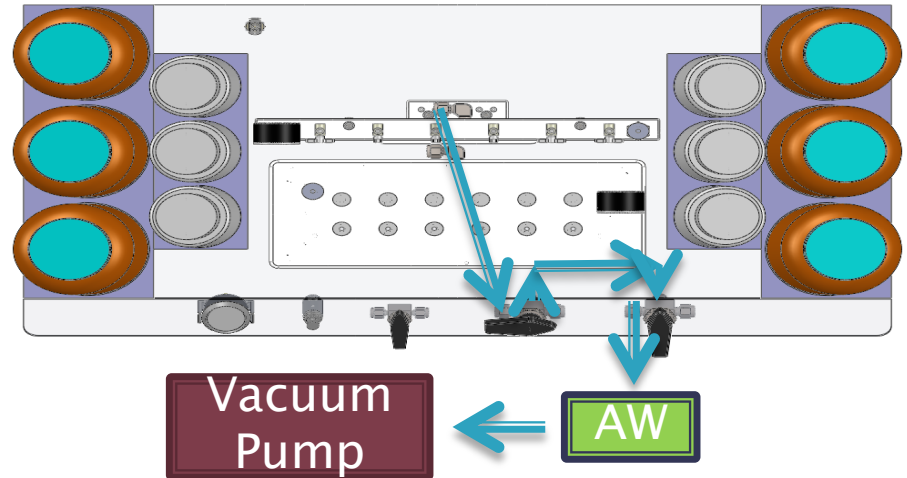
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

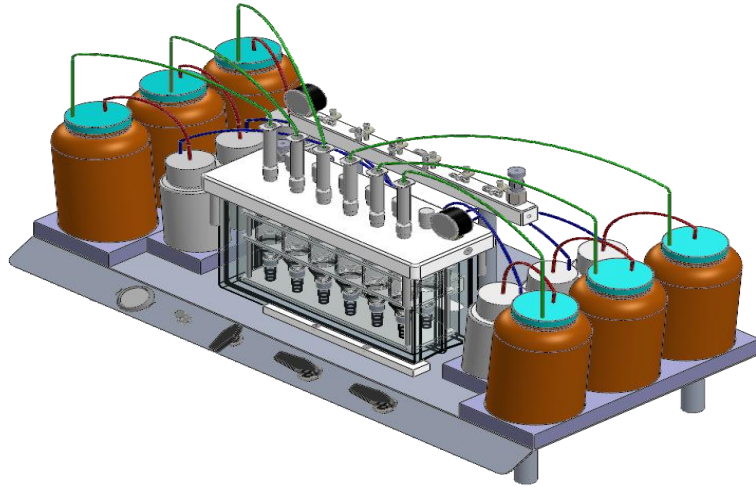
Waste
Valve



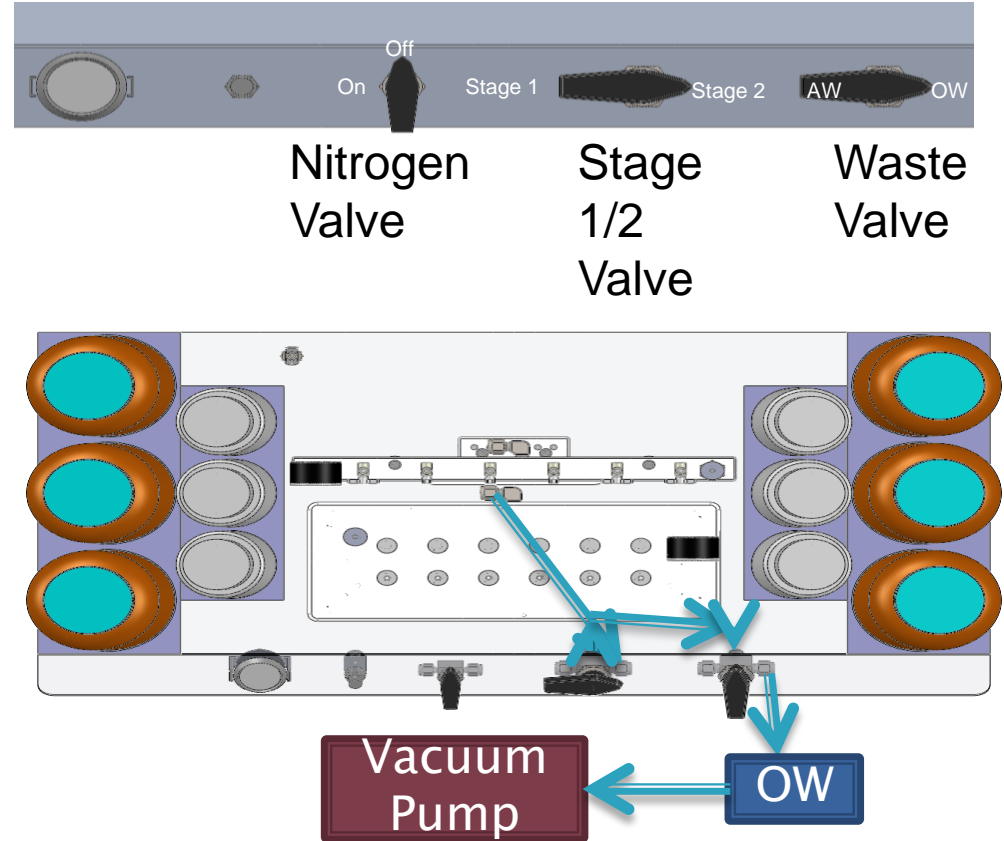
Vacuum
Pump

AW

Sample Elution (Stage 2)




Flow
Path



Attributes EZSpe (1)

- ▶ Simple to Operate No Computer or Electronics
- ▶ Fast Runs 6 Samples in 20 ~ 50 min (depending on sample size)
- ▶ High Throughput Runs 6 Samples in Parallel
- ▶ Flexible Uses All SPE Cartridge Sizes
- ▶ Semi Automated Vacuum Sample Loading & Valve Selection for Separating Aqueous and Organic Waste

Attributes EZSpe (2)

- ▶ Quality Consumables Guaranteed Certified Cartridges
 - ▶ Bottle Rinse Automated Bottle Rinse
 - ▶ In-Line Drying Elution In-line Extract Drying
 - ▶ Reliable No Maintenance Required
 - ▶ Zero Cross-Contamination No Shared Tubing & Fittings
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Procedure (1)

- ▶ 6 samples (1L water each) are prepared and acidified with 1 mL HCl till pH \sim 2
- ▶ Add 5-10 mL methanol and spike with relevant standards
- ▶ Put sample bottles in place and fill dichloromethane
rinse bottles with 25 mL solvent
- ▶ Cartridges are installed in each of the six positions.

Procedure (2)

Stage 1:

- ▶ Vacuum is turned on
- ▶ Cartridges are conditioned with 5 mL dichloromethane, methanol and water
- ▶ Samples are loaded across cartridges under vacuum
- ▶ Cartridges are dried with nitrogen for 10 min
- ▶ Sample bottles are automatically rinsed from the rinse bottles with 25 mL dichloromethane

Procedure (3)

Stage 2:

- ▶ Dichloromethane from sample bottles is loaded across the C18 cartridges and sodium sulfate cartridges
- ▶ Eluent is collected for analysis into Direct to GC Vial Collection Vessels

12 position evaporator 50 mLs



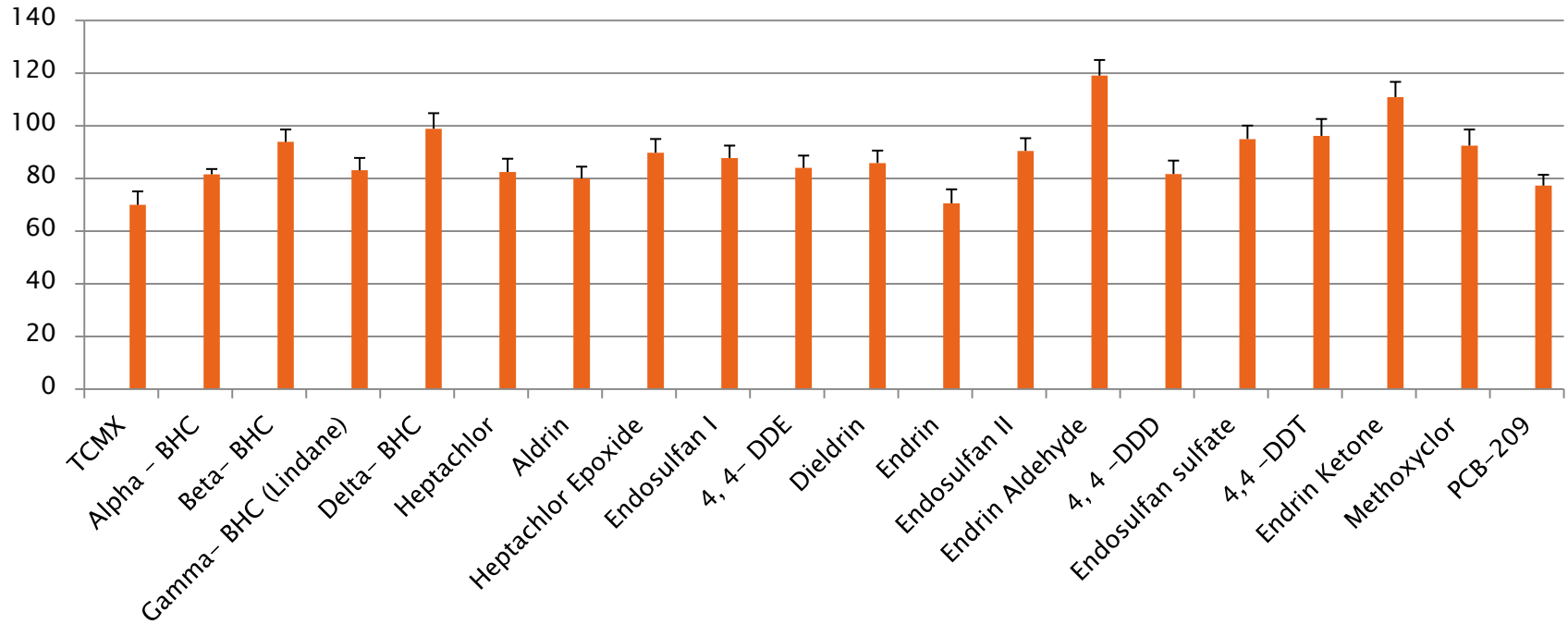
SuperVap Features

- ▶ 6 (250mL) and 12 (50mL) position models for extractions.
- ▶ Dry bath heating element
- ▶ Independent secondary heater for extract nipple (can be disabled).
- ▶ Sensor controlled
- ▶ Savable temperature log capability.

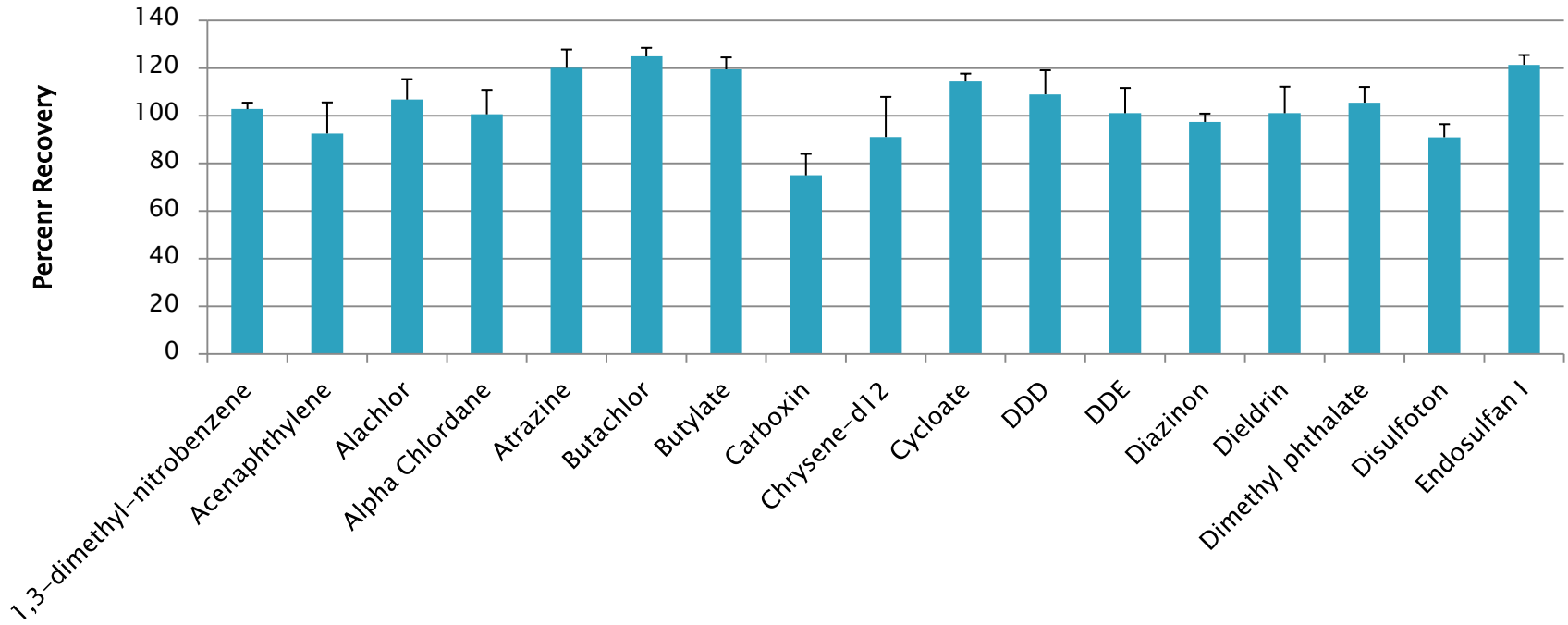
Analysis

- ▶ Samples reduced to 1 mL under nitrogen flow
- ▶ Samples analyzed in 1 mL DCM
- ▶ OCPs analyzed with ECD
- ▶ Semi-Volatiles analyzed with low resolution GC/MS (full scan)

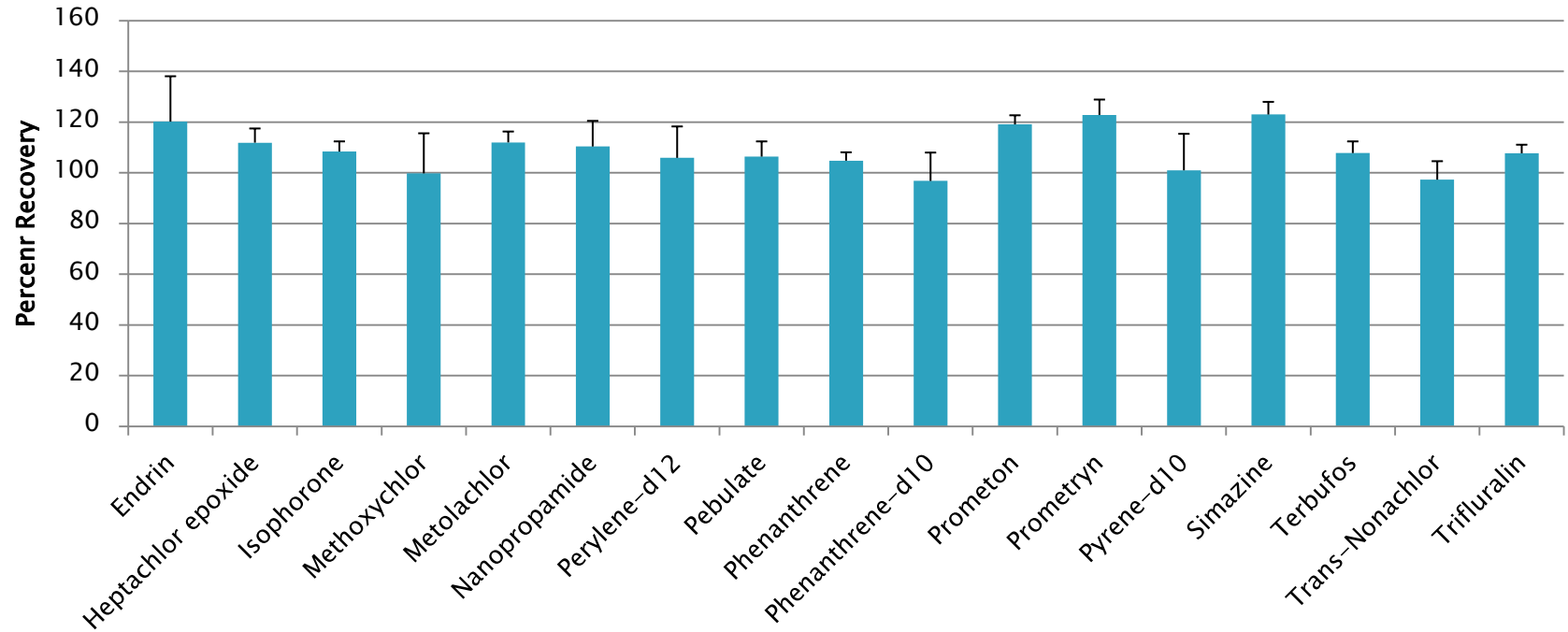
EZSpe data for OCPs (Drinking Water)



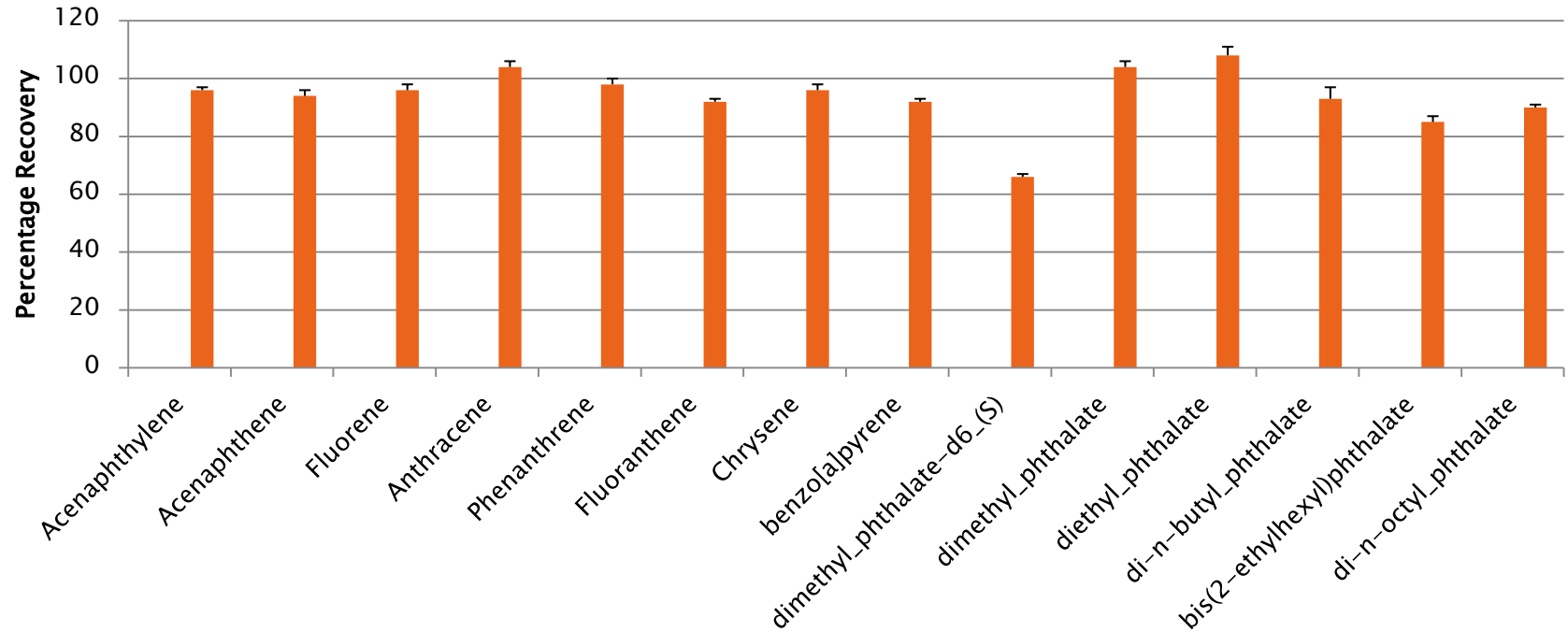
EZSpe data for SVOCs (Drinking Water, 1)



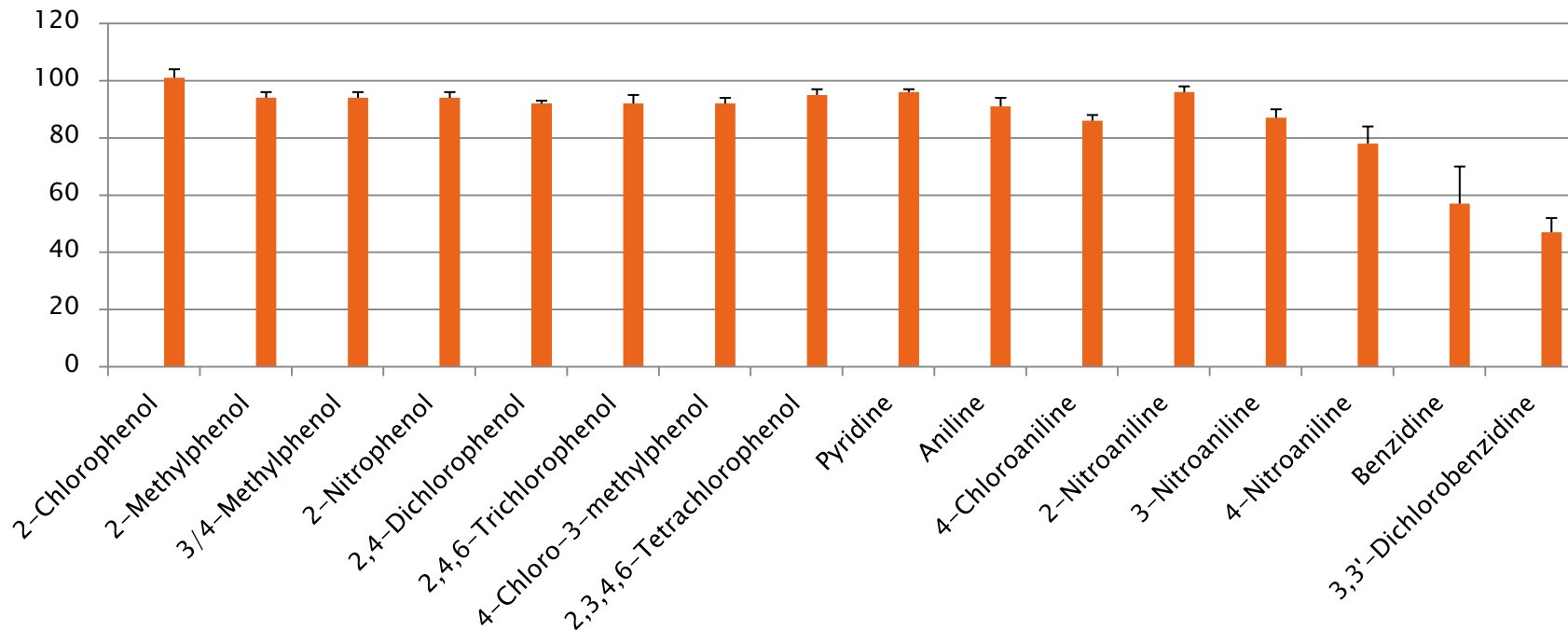
EZSpe data for SVOCs (Drinking Water, 2)



PAHs and phthalates (Waste Water)



Phenols and Ion Exchangers (Waste Water)



Conclusions

- ▶ EZSpe delivers excellent recoveries for Organochlorine Pesticides and Semi-Volatiles
- ▶ Runs 6 samples in parallel
- ▶ Gets data in under 2h
- ▶ No maintenance required
- ▶ No separate water removal step needed (in-line drying)
- ▶ Other applications are beverages, milk and serum

Questions

Contact us at:

raddink@fms-inc.com (Ruud Addink)

thall@fms-inc.com (Tom Hall)

nkaurin@fms-inc.com (Nem Kaurin)