Clarus SQ 8™ GC/MS

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Making Semi-Volatile Analysis Safer for our Environment: More Accurate, Precise, Clean and Sensitive

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Outline

- Benefits of reducing sample size
- Experiments with semi-volatile analysis
- Technologies
  - Inlet
  - MS
- Data
  - PAH – GC/MS
  - Pesticdes – GC/ MS
  - Site study EPA method 508 – GC/ECD
  - Site study EPA method 8270 – GC/MS
- Conclusion

Reducing Sample Amount

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Why should we reduce sample amount?

Using 1mL instead of 1L sample equals more profits…

- **By enhancing productivity**
  - Reducing time for extraction
  - Elimination of concentration step increases throughput
  - Able to use faster methods, such as SPE

- **By reducing costs**
  - Save on expensive extraction solvent required for liquid/liquid extractions
  - Save on precious refrigerator space and glassware
  - Save on disposal costs of recovered solvents
  - Save on shipping costs
- **By increasing instrument uptime**
  - Injecting less sample matrix ⇨ cleaner system ⇨ more time running samples
- **By delivering better performance**
  - Meeting and/or achieving enhanced detection limits
  - Enhancing recoveries
  - Optimizing dynamic range

… use less solvent … evaporate less solvent into environment … a "greener" analysis

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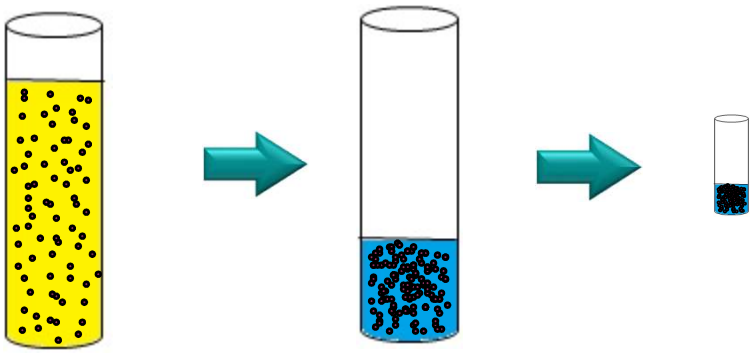
1 mL sample volume

(or 40mL or 100mL)

1 liter liquid/liquid extraction: Disadvantages

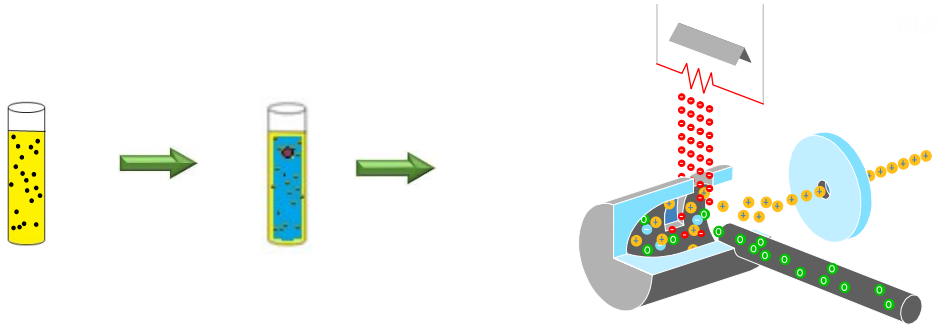
- 1.0 liter of sample (0. 2ug/L detection limit)
- Extract with 300 mL dichloromethane (DCM)
- Separate phases
- Concentrate to 1mL (0.2ug/mL)
- Inject



Disadvantages

- High costs (solvent, glassware, shipping)
- Requires more space
- Laborious sample prep
- Expensive, not efficient
- Environmentally unfriendly

Enhance sample prep time and save on laboratory costs!



- 1mL sample volume (or 40mL)
- Extract with 1mL of DCM
- Separate phases
- Inject organic phase or use SPE
- Inject!

- Advantages:
  - Reduced operating costs
  - Enhanced instrument uptime!
  - Faster sample prep improves lab productivity and efficiency
  - GREENER analysis!!!

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First Experiment

Investigating PAH at varying injection volumes

PAH experiments using 1mL extraction volume

Injection Volume	Acquisition	Lowest Conc Analyzed (µg/L)	Signal to Noise (ave of 16 targets)
1µL	Full Scan	0.20	70 to 1
1µL	SIM	0.20	420 to 1
5µL	Full Scan	0.06	190 to 1
5µL	SIM	0.06	770 to 1
10µL	Full Scan	0.06	440 to 1
50µL	Full Scan	0.01	500 to 1

… data collected in Simultaneous Full Scan/Sim

Matrix injected and reporting limit varying sample amount and inj vol

Sample Amount	Amount Matrix Injected (X)	
	1µL Injection	10µL Injection
1 liter	X	10X
0.1 liter	0.1X	X
0.04 liter	0.04X	0.4X
0.01 liter	0.01X	0.1X
0.001 liter no concentration	0.001X	0.01X

*X represents the amount of matrix injected from a 1L sample volume which was concentrated to 1mL

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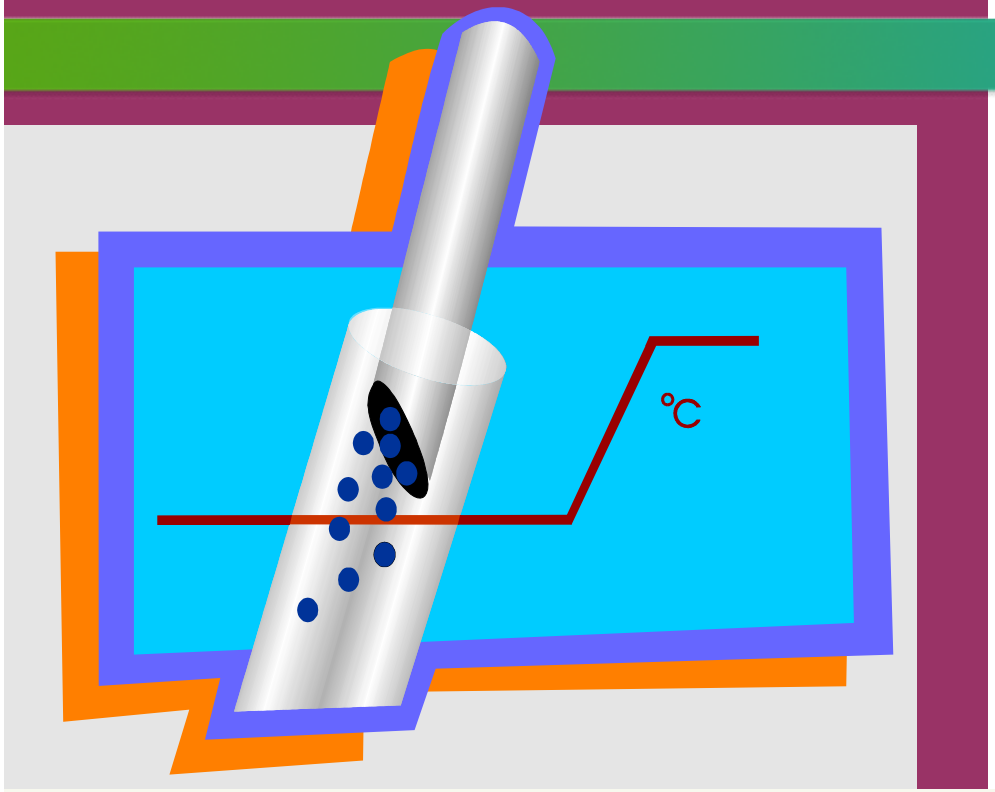
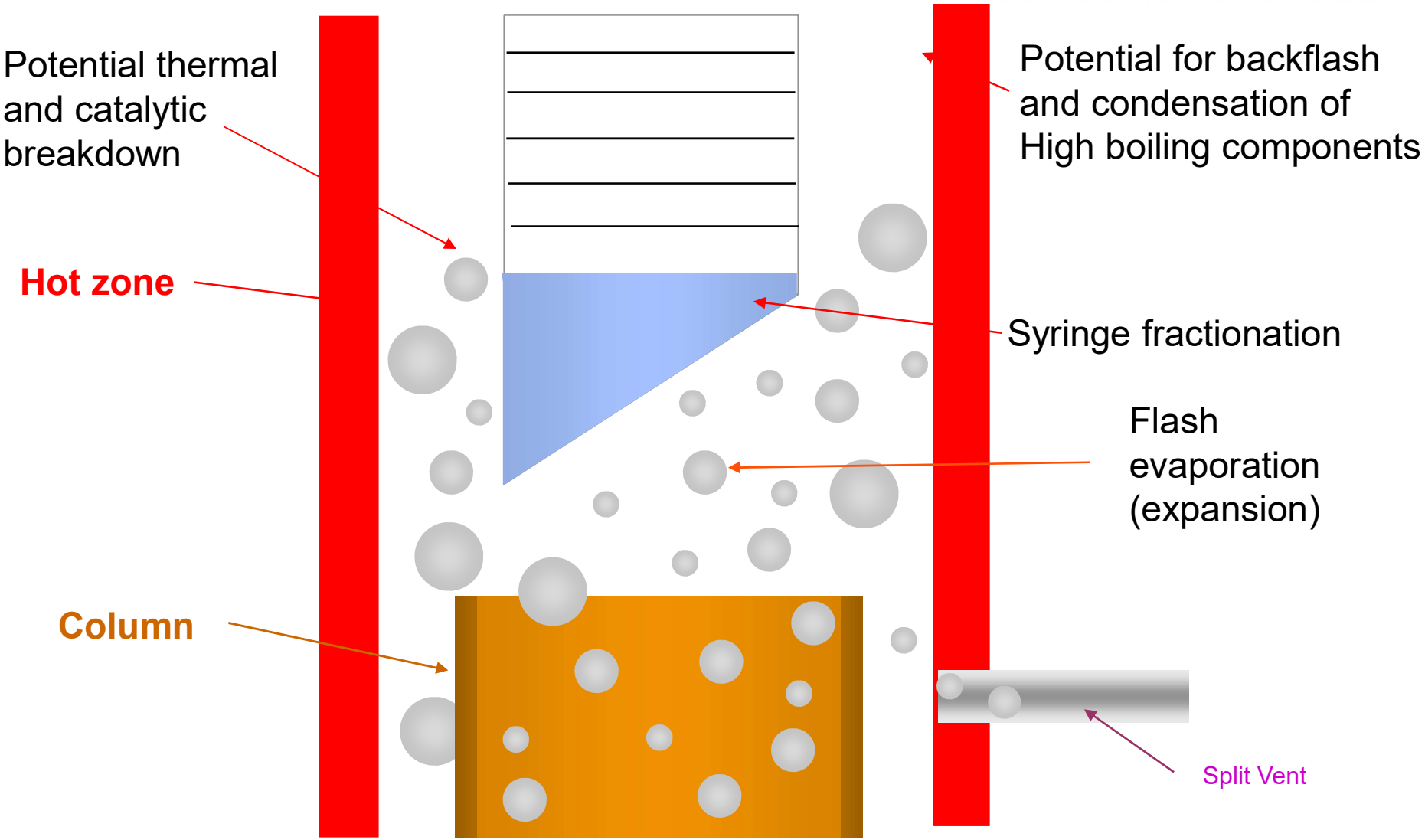


Why use controlled volatilization (solvent purge) instead of hot splitless injections?

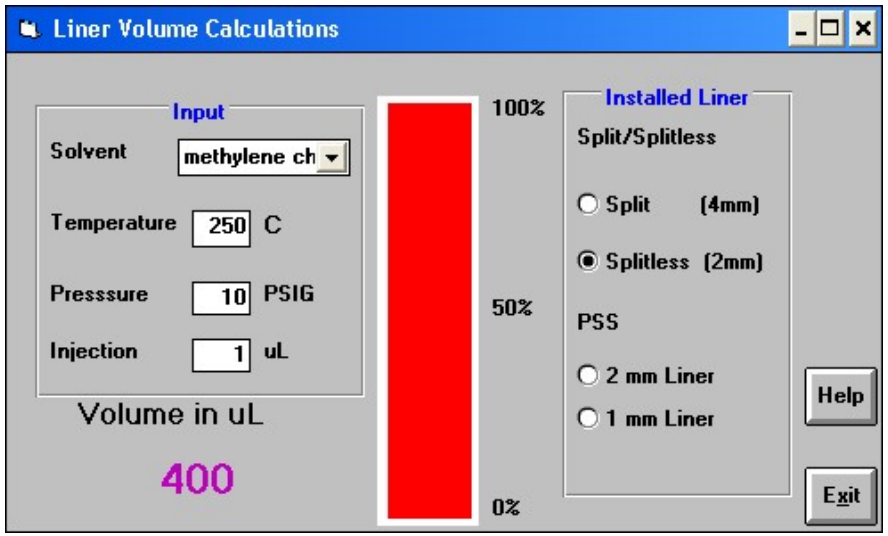
… enhanced precision and accuracy!

Disadvantages to **HOT** (flash-vaporizing) injections



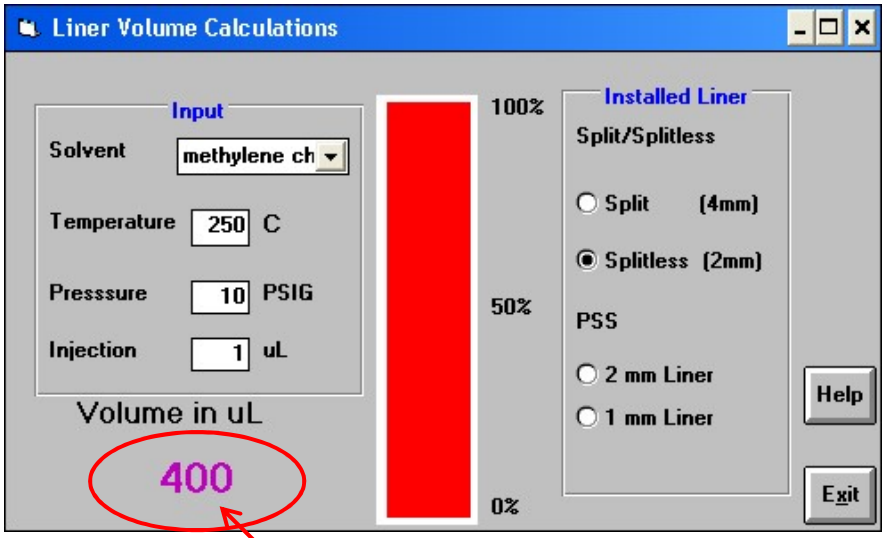
Keeping your analytes in the liner: Problems with backflash

- Backflash of analytes due to vapor expansion volume of solvent in hot injector exceeding the available volume of liner … full injection will not make its way to column.
- Vapor (with sample) can enter pneumatics causing contamination requiring maintenance
- Affect
  - Poor precision and recovery
  - Condensation of high boiling components causing discrimination
  - Carryover into later injections causing “ghost peaks” and poor performance



Why does this happen … ***avoid*** Backflash

- Liner Volume … equation of a cylinder
  - (Liner length)(π) r^2
    - Example for a 4cm x 2mm liner:
    - $(4cm)(0.2cm/2)^2\pi$
- Parameters to consider (V = nRT/P)
  - Injector temperature
  - Injection volume
  - Injector pressure
  - Solvents (have different expansion volumes)

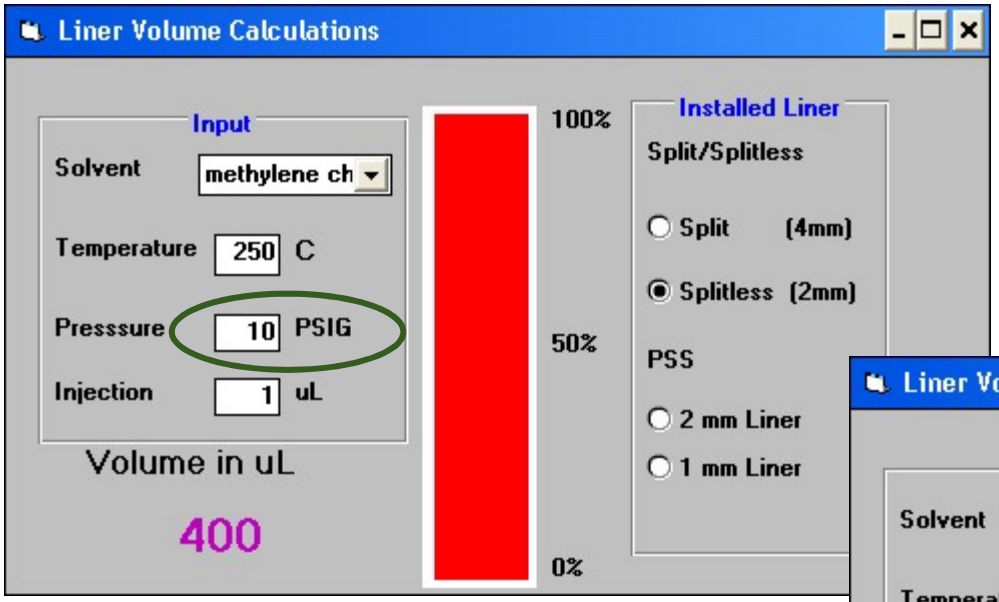


Vapor expansion greater than liner volume

… let's discuss how to eliminate exceeding liner volume via vapor expansion

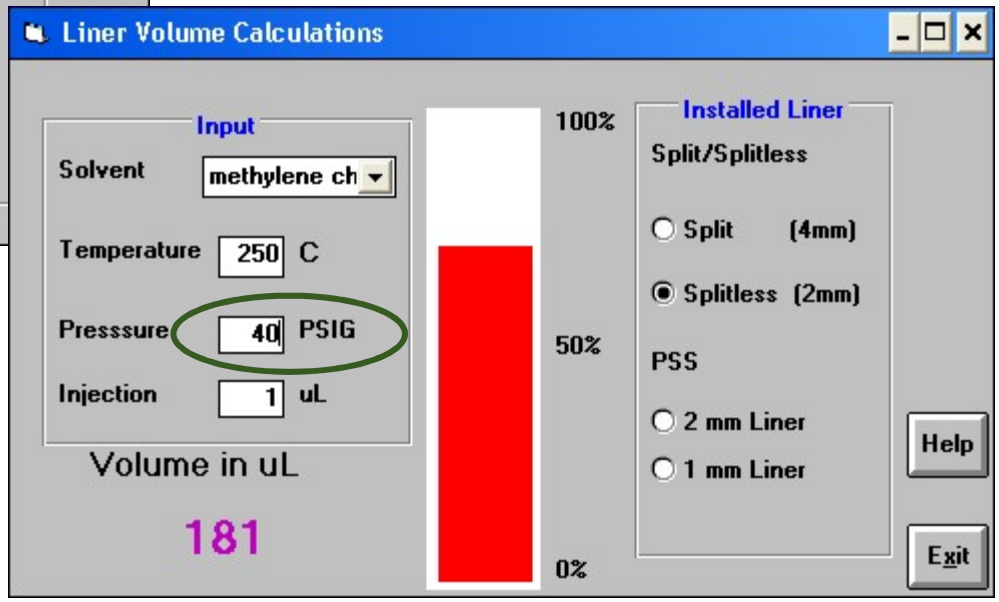
Vapor Expansion: ex. Dichloromethane – 1 uL injection

Effect of Pressure



Advantages to Pressure Pulse

reduce vapor expansion



V=nRT/P.
Increase pressure reduces vapor expansion

Benefits of Controlled Volatilization

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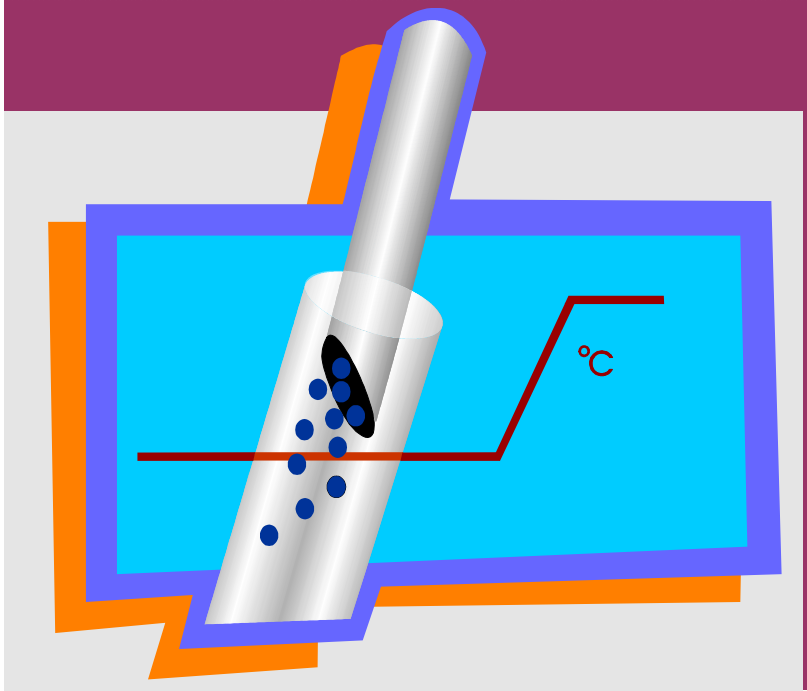


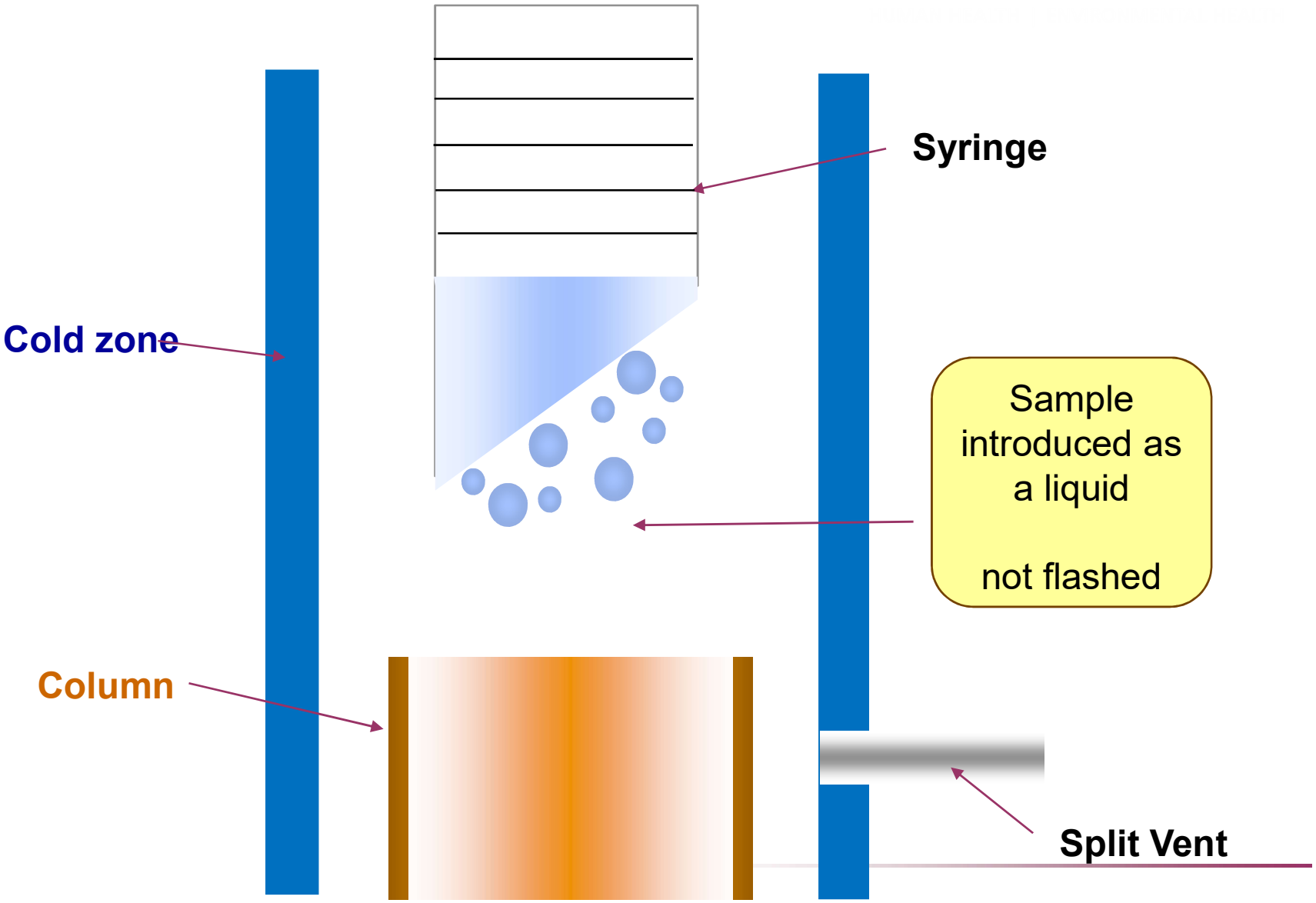
Temperature programmed injection

is superior than

splitless pressure-pulsed (PP)

… better results … improved performance!

Advantages of a Programmed Injection



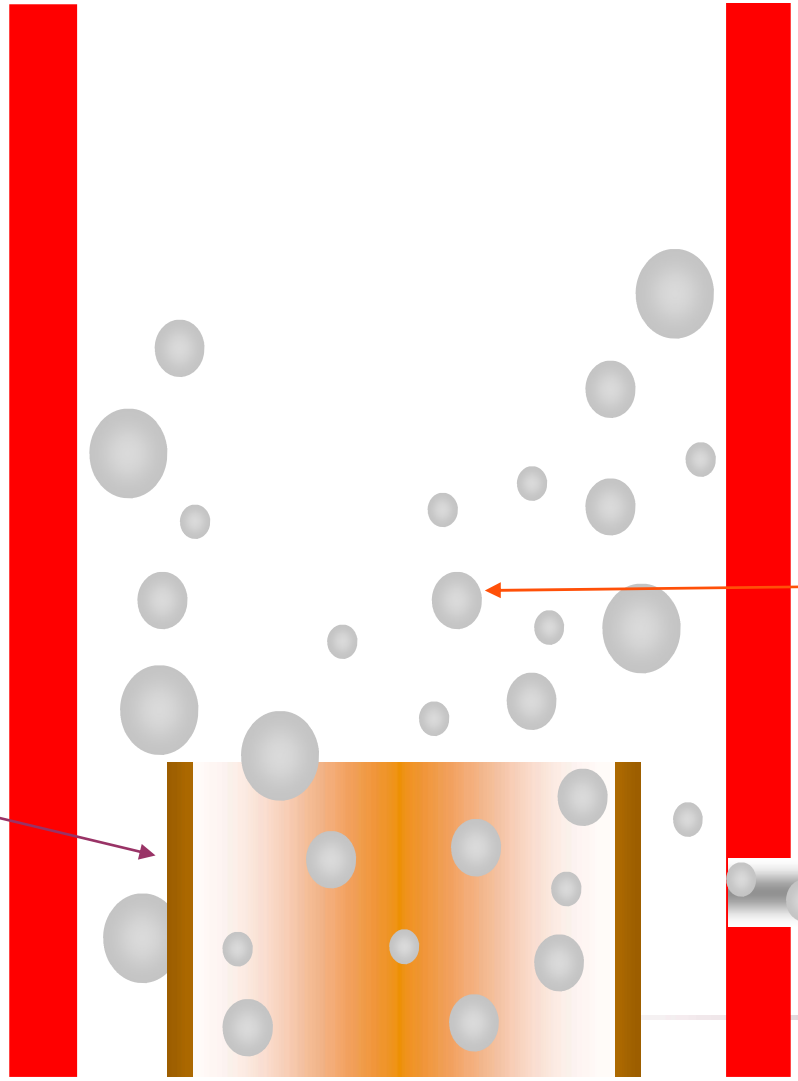
Programmed Evaporation Takes Place after the Syringe is Removed

Enhance recoveries by significantly minimizing high boiler condensation

Enhance recoveries by reducing or preventing thermal and catalytic breakdown of thermally labile and active targets

Eliminate problems associated with backflash

Enhance accuracy by preventing discrimination caused By syringe fractionation



Controlled Volatilization

Column

Split Vent

Do we want even better detection limits?

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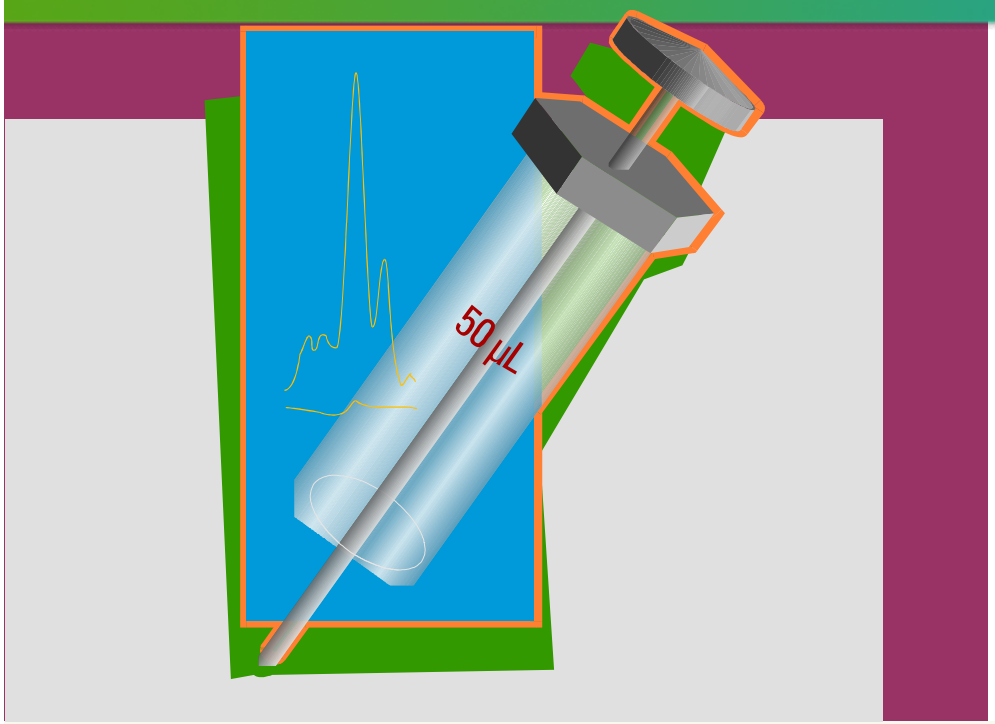


The Technique of Solvent Purge

for semi-volatile analysis

Enhanced Solvent Purge Injections

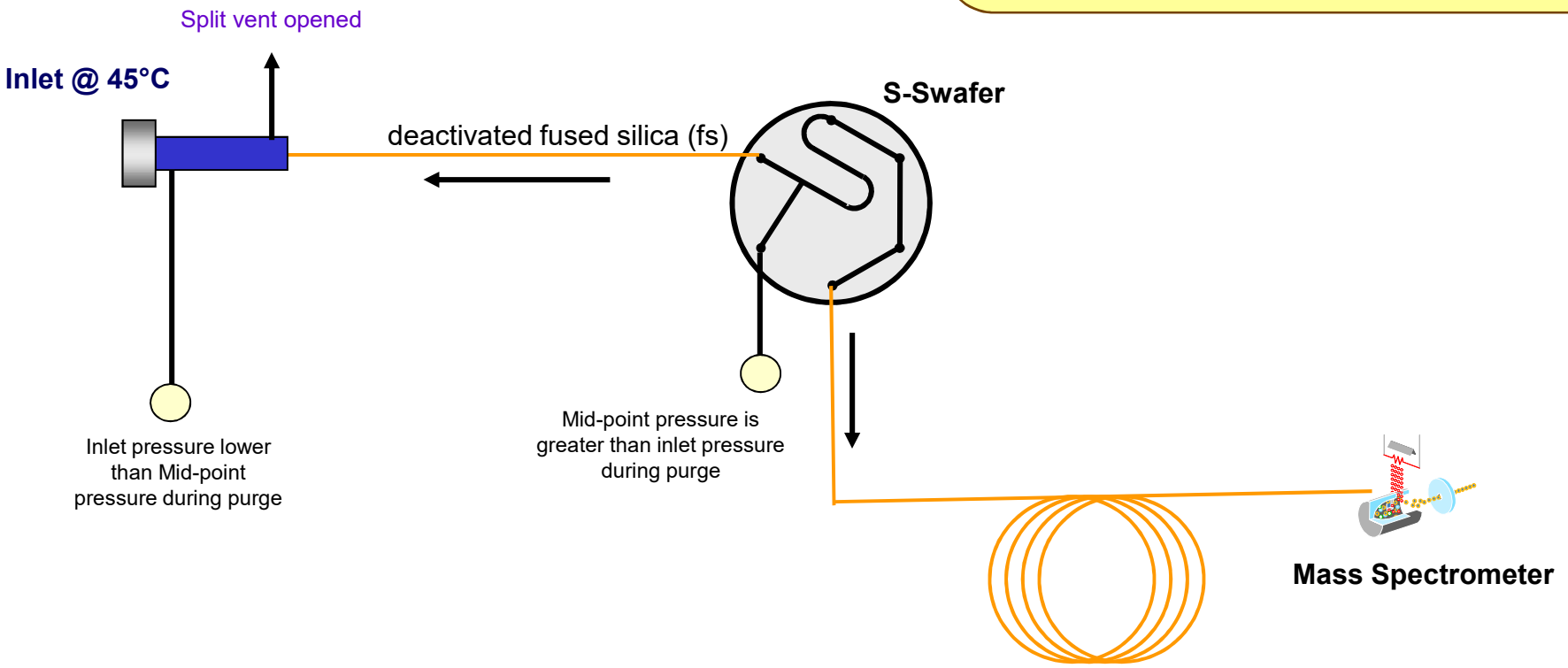
Purge Pneumatics with Swafer – **Solvent Purge Step**

Temperature programmable (PSS) inlet

- Purge solvent while maintaining semi-volatiles in inlet
- Enables enhanced detection limits
- Prevents thermal breakdown and flashback (controlled volatilization)

Swafer™ (micro channel splitter)

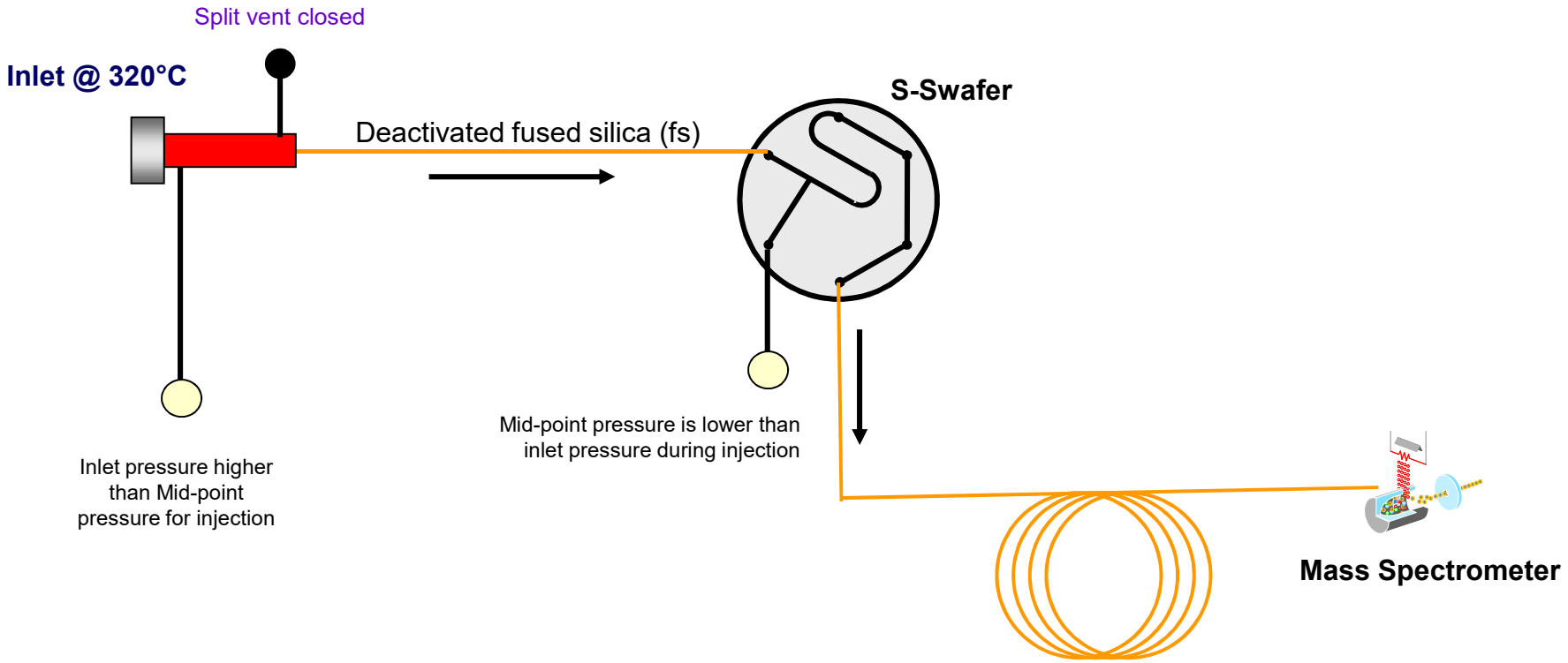
- Allows for the easy, automated control of effluent stream for many applications
- Inert
- For this application, it is used to isolate injector from column and detector



Elite-5 … 30m x 0.25mm x 0.25um

Injection Step

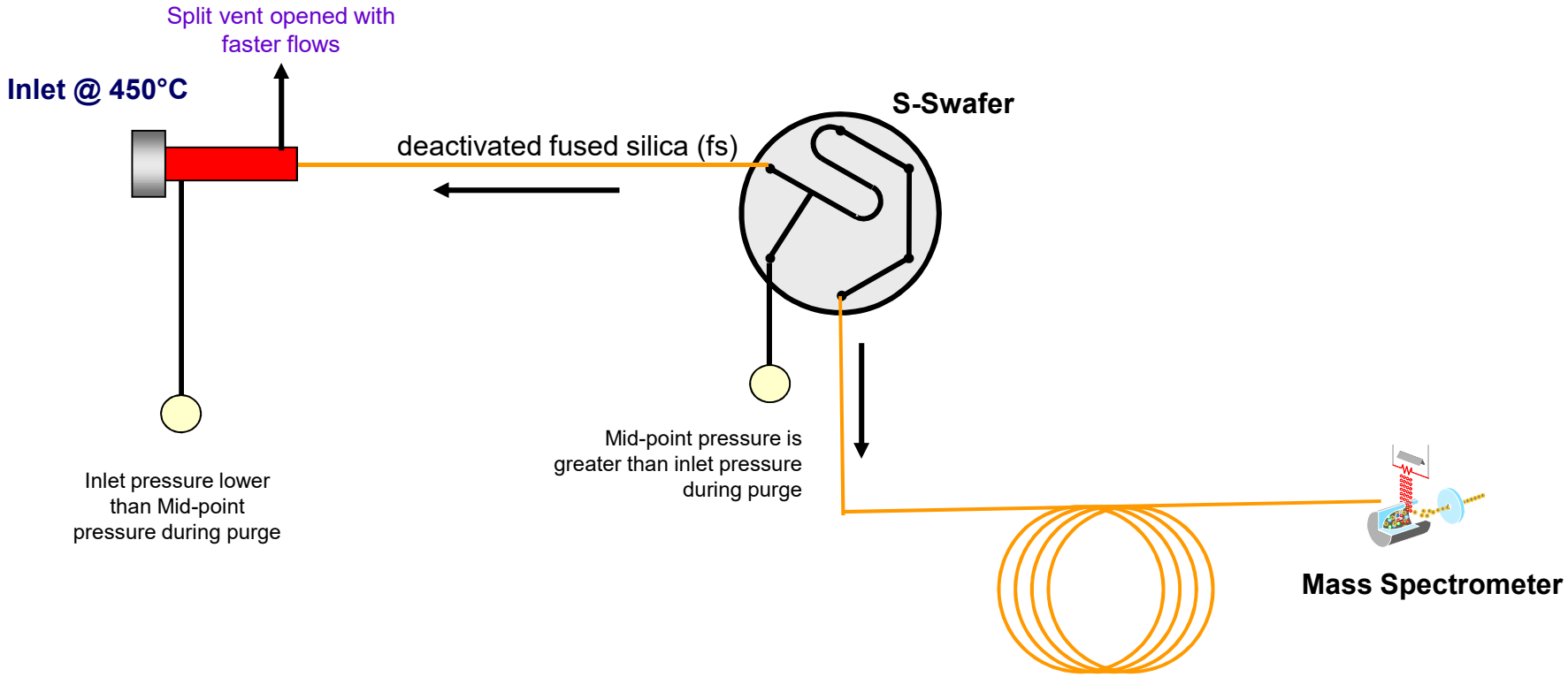
- Close Split Vent (splitless injection of targets)
- Increase inlet pressure so it is the carrier source
- Heat up inlet to desired final temperature



Elite-5 … 30m x 0.25mm x 0.25um

Bake Step

- After targets elute from pre-column, reduce inlet pressure so mid-point pressure is source for carrier
- Increase inlet temperatre
- Increase split vent
- Bake inlet during chromatography



Elite-5 … 30m x 0.25mm x 0.25um

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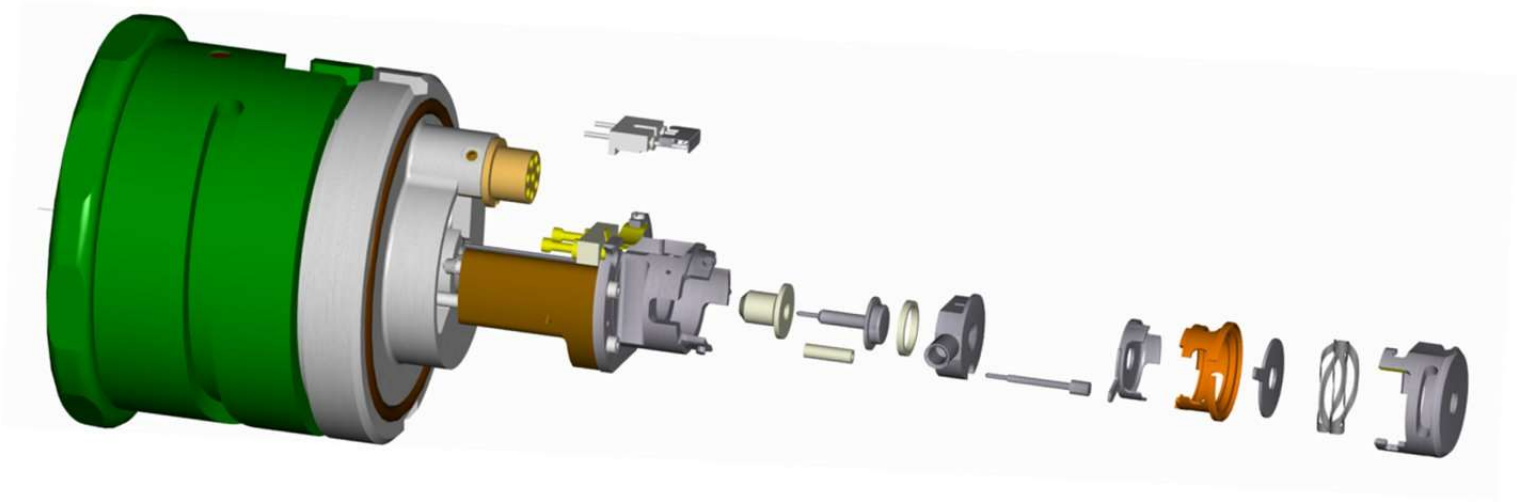
Technology Advancements

Getting more from your GC/MS!

Enhancing detection limits and performance!

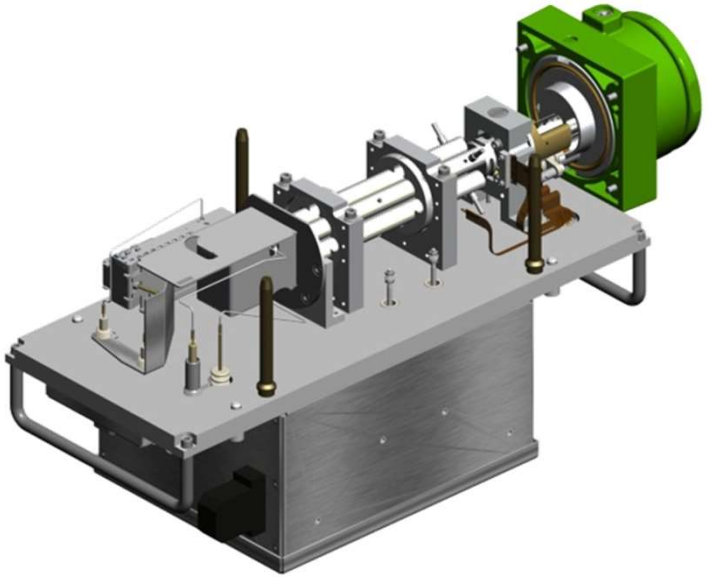
Easy to Use and Maintain … **SMARTSource**

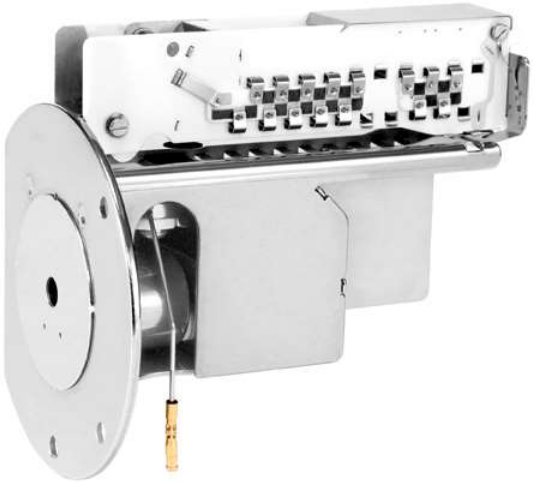
Now it is “Plug and Play” with a twist no wires to remove



Change source components in under 5 minutes **with no tools**

- Clarifi Detector
  - Enhance Sensitivity
  - Increase Operating Range
  - More Flexibility
  - Longer Life – Less Downtime
  - Enhance Library Matches





… improve detection limits and robust (increase throughput)!

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Data

PAH water matrix

Pesticides water matrix – MS detection

Pesticides EPA method 508 (site study)

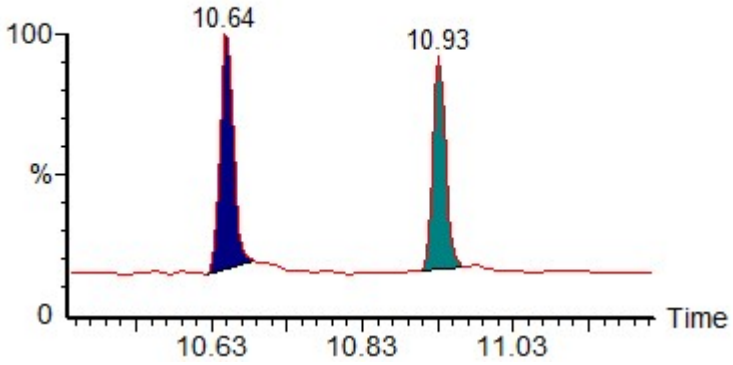
Method 8270 (site study)

Pyrene Calibration from 0.06 to 50 ppb (10uL injection) SIM

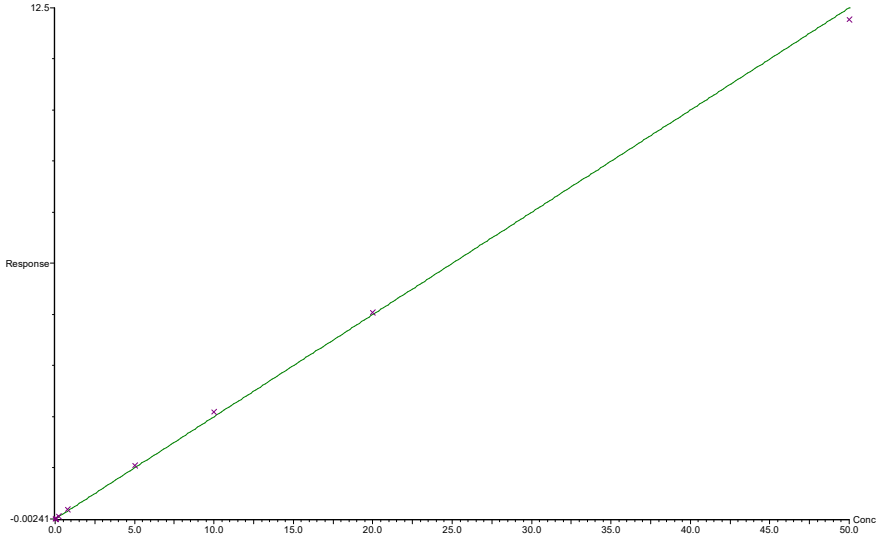
Extraction Volume: 1mL

Concentration: 0.06 µg/L

Fluoranthene and Pyrene



r^2: 0.9992



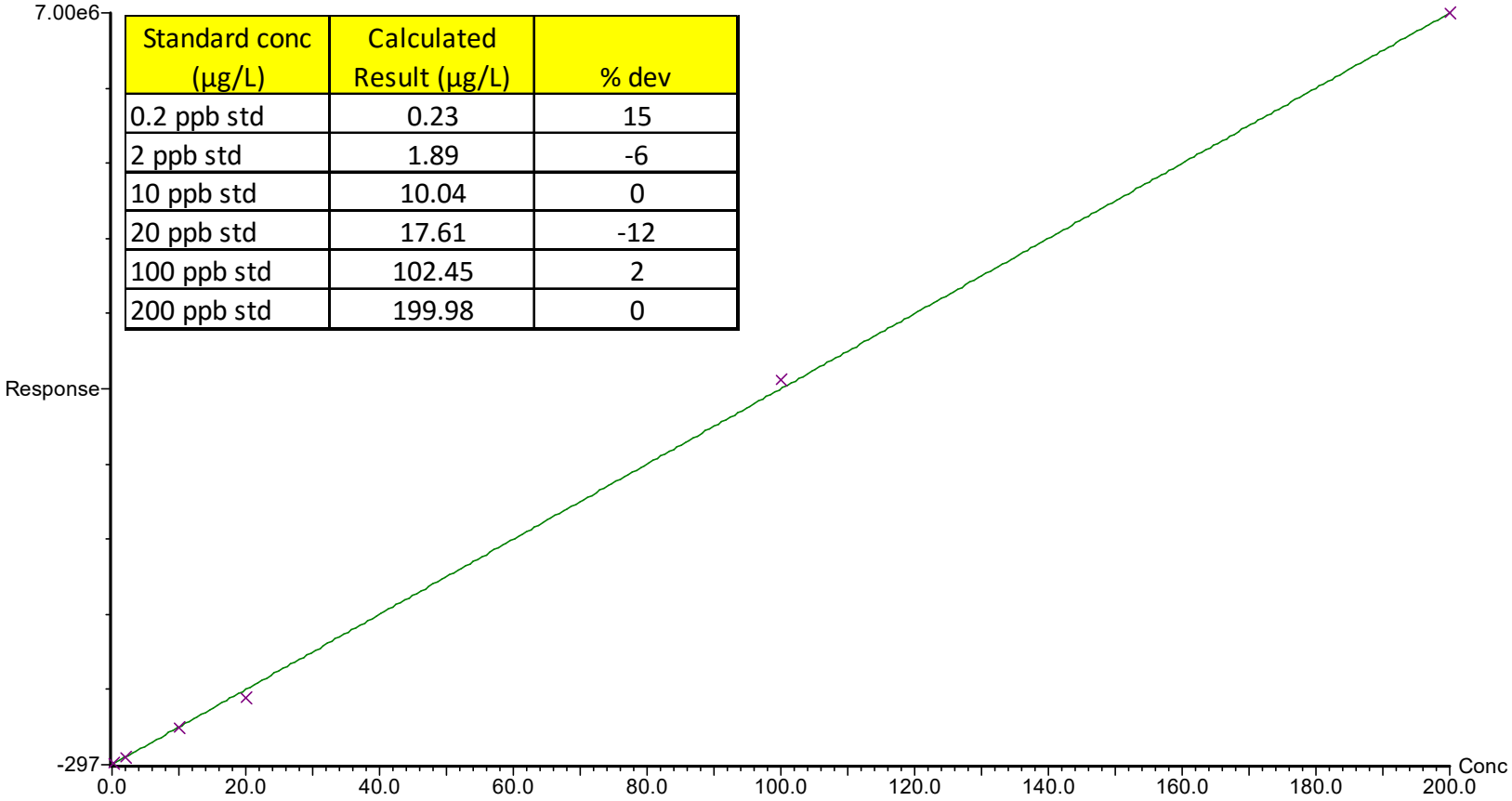
7 level Calibration – Full Scan processing from FS/SIM Acquisition

Chlordane – 0.2 ppb to 200 ppb

Extraction Volume: 1mL

Compound 8 name: Chlordane
Coefficient of Determination: 0.999640
Calibration curve: 34983.8 * x + -297.362
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

Standard conc (µg/L)	Calculated Result (µg/L)	% dev
0.2 ppb std	0.23	15
2 ppb std	1.89	-6
10 ppb std	10.04	0
20 ppb std	17.61	-12
100 ppb std	102.45	2
200 ppb std	199.98	0



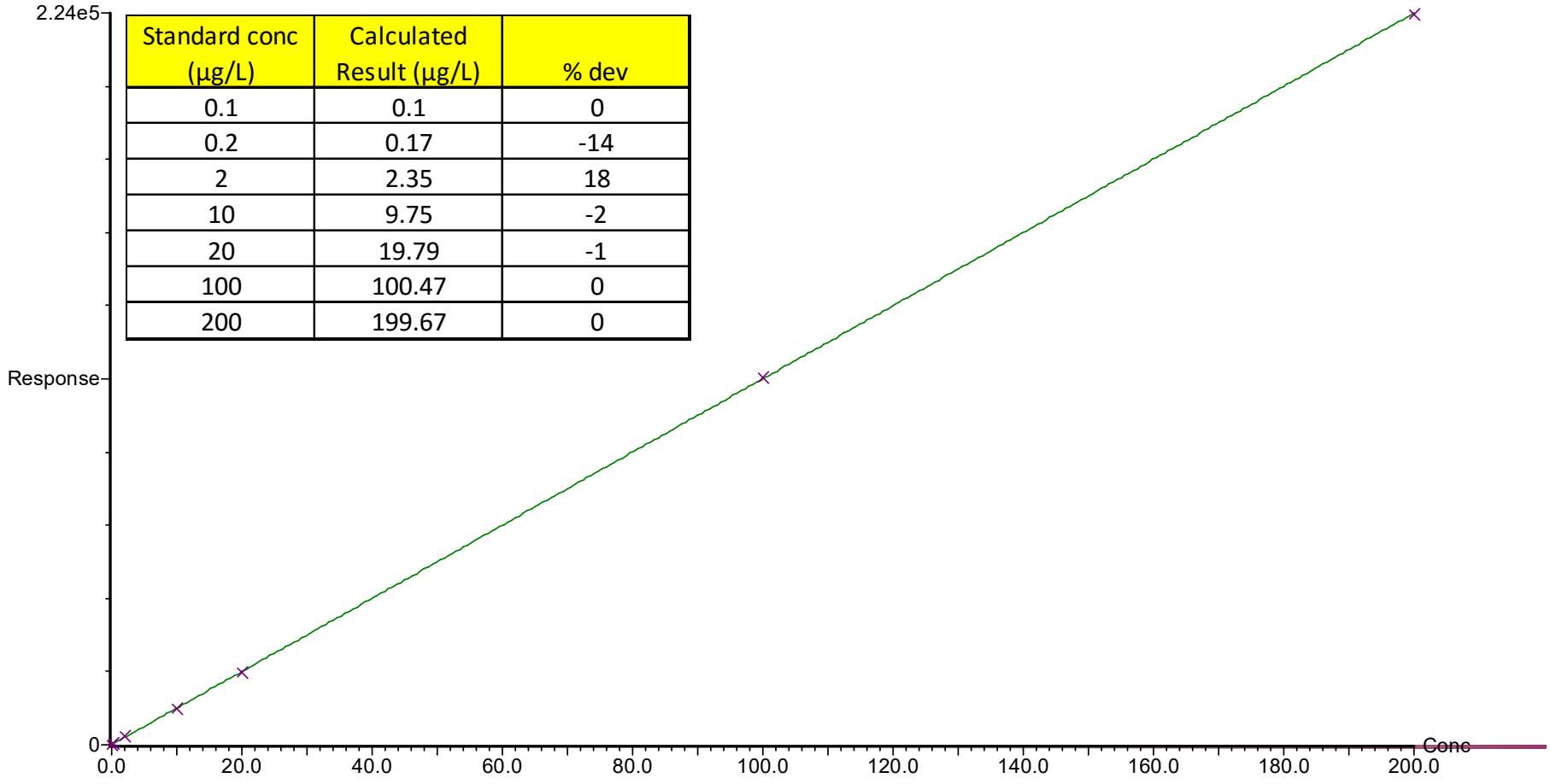
7 level Calibration – SIM processing from FS/SIM Acquisition

Aldrin – 0.1 ppb to 200 ppb

Extraction Volume: 1mL

Compound 6 name: Aldrin
Coefficient of Determination: 0.999984
Calibration curve: 1119.20 * x + 41.5440
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

Standard conc (µg/L)	Calculated Result (µg/L)	% dev
0.1	0.1	0
0.2	0.17	-14
2	2.35	18
10	9.75	-2
20	19.79	-1
100	100.47	0
200	199.67	0



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Experiment and Results Method 508

Experiments performed in environmental lab on Long Island. Since samples did not contain pesticides (☺) relied upon surrogate comparison and matrix spike

Experiment # 1: One liter sample size

- Extract pesticides with 300mL of DCM prescribed by method
- Exp 1a: Remove 1mL aliquot of this extract. Inject 40uL
  - Omit concentration step. Was able to achieve detection limits without concentration.
  - Omit solvent exchange step. System is configured in inlet isolation mode so that the methylene chloride is purged through split vent in “cool” inlet (refer to slide 21).
- Exp 1b: Process the remaining 299mL as prescribed by method
  - Concentrate to 5mL
  - Solvent exchange to hexane.
  - Inject 2uL

Surrogate Recoveries on nine samples

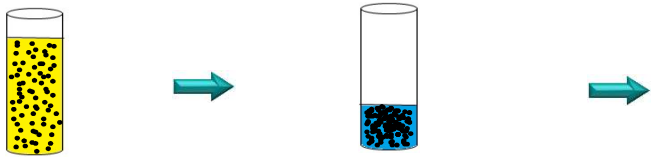
Sample Name	Exp 1a: SURR=0.067µg/L 40µL Solvent Purge		Exp 1b: SURR=20µg/L 2µL Splitless	
	TCX	DCB	TCX	DCB
LFB	86	73	77	70
BLANK ON 3-25	91	79	80	71
9607600	97	94	77	80
9607980	87	90	77	88
9607581	92	78	79	88
9607497	94	98	74	83
9607490	92	93	77	87
9607601	96	88	78	81
9607632	97	61	79	56
9607670	92	82	81	76
9607671	90	90	78	88

Experiment # 2: comparing a 10mL matrix spike to a 1 liter spike

- 10 mL matrix spike extraction
- 1 liter matrix spike extraction

- **Exp 2a**: 10mL matrix spike at detection limit (0.02µg/L)
  - Extract with 3mL MeCl2. Inject 40µL
- **Exp 2b**: 1L matrix spike at detection limit
  - Extract with 300mL of MeCl2. Remove 1mL aliquot. Inject 40µL solvent purge
- **Exp 2c**: The remaining 299mL of exp 2b extract was concentrated to 5mL volume and then solvent exchanged into hexane (same procedure as exp 1b)
  - Inject 2µL splitless

Sample size decrease to 10mL



Enhance productivity and profits

- 10 mL of Sample
- Extract with 3 mL of $MeCl_2$
- Inject !!!

Decrease solvent use and cost

Enhance instrument uptime

Less storage space for smaller containers

Meet criteria!

Eliminate laborious extractions

Environmentally friendlier ☺

Check Standard spike

	Exp 2a	Exp 2b	Exp 2c
	10 mL Extract	1L Extract (3/10 Conc)	1L Extract (conc 1000x)
	40 uL Solvent Purge	40 uL Solvent Purge	2uL Splitless
TCX (surrogate)	77	88	77
Gamma- BHC (Lindane)	72	71	70
HEPTACHLOR	79	70	72
ALDRIN	76	77	76
HEPTACHLOR EPOXIDE	83	81	83
GAMMA CHLORDANE	94	87	90
DIELDRIN	77	75	83
ENDRIN	86	80	79
METHOXYCHLOR	106	81	87
DCB (surrogate)	66	77	70

3 Point Calibration for of Mix A (solvent purge)

Components	Average Response Factor (%RSD)	Correlation Coefficient (r^2)
TCX (Surrogate)	2.5	0.9999
alpha-BHC	16.0	0.9997
gamma-BHC	12	0.9999
HEPTACHLOR	4	0.9999
ENDOSULFAN I	1.4	0.9999
DIELDRIN	5.2	0.9999
ENDRIN	2.7	0.9999
4,4' DDD	4.5	0.9995
4,4' DDT	4.8	0.9999
METHOXYCHLOR	16.0	0.9983
DCB (Surrogate)	11.0	0.9997

3 Point Calibration of Mix B (solvent purge)

Components	Average Response Factor (%RSD)	Correlation Coefficient (r^2)
TCX (Surrogate)	2.5	0.9995
beta-BHC	4.0	0.9997
delta-BHC	19	0.9994
ALDRIN	11	0.9997
HEPT. OXIDE	2.2	0.9999
gamma-CHLORDANE	2.0	0.9999
alpha-CHLORDANE	1.6	1.0000
4,4' DDE	7.4	0.9998
ENDOSULFAN II	2.1	0.9998
ENDRIN ALDEHYDE	7.9	0.9994
ENDO. SULFATE	7.1	0.9999
ENDRIN KETONE	2.9	0.9995
DCB (Surrogate)	9.5	0.9998

Enhancing Instrument uptime for

EPA Method 8270

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Injecting less matrix extends maintenance interval! More Clocks!

Increase profits by running more samples

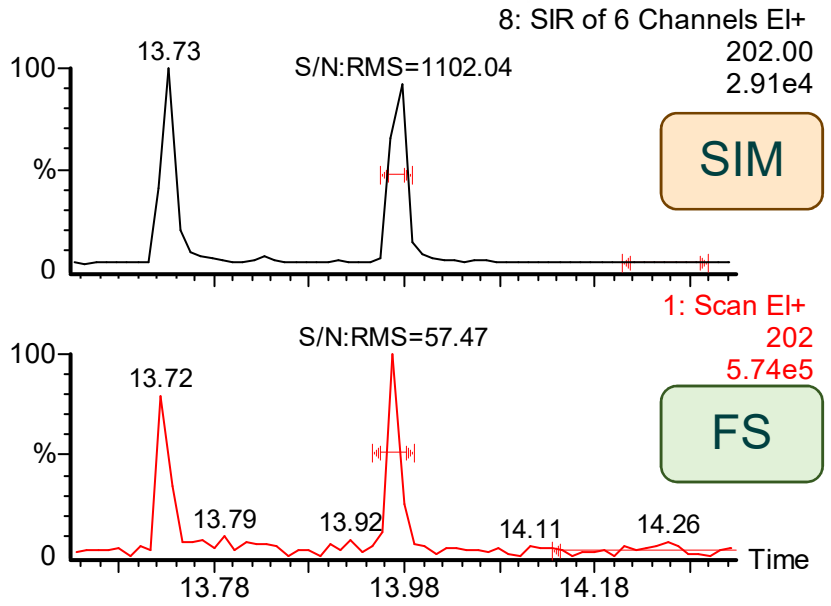
100mL sample volume

Collected at an Environmental Testing lab

Experiments performed in 2003 … older MS

Results Comparing 1L to 100mL

- Detection limit significantly improved over regulated detection limits for all targets
- More Clocks achieved than 1L extract because less matrix being injecting
- 1.0uL splitless injection



From Matrix spike

Pyrene – 0.025 ppb (actual concentration)

100mL extract conc to 5mL

Increasing Productivity, Efficiency and Performance

- Meet required reporting limits while using less sample
  - New detector technology
  - SIFI (simultaneous full scan / SIM detection)
  - Larger injection volumes
- Inject less matrix – cleaner system means enhanced instrument uptime increasing productivity
- Extract less sample – reduce operating costs (less solvent, less glassware and less storage space required)
- Adds up to faster return on investment and a more productive laboratory with improved recoveries

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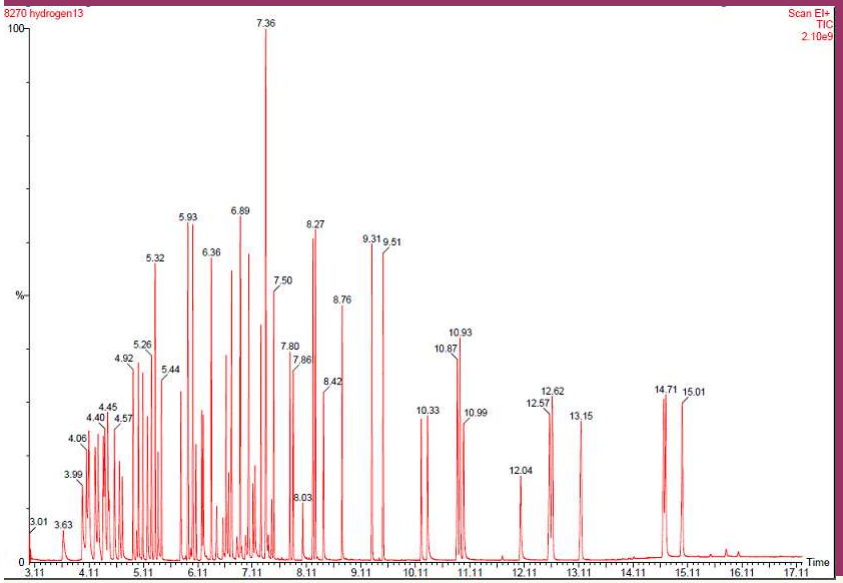

Hydrogen vs Helium

Semi-Volatile Analysis

Passing Criteria

- All targets quant and qualifying ions were compared in hydrogen versus helium and met criteria
- DFTPP criterion was met
- All other criteria were met

Acknowledgement: Thank you to Miles Snow for doing the work verifying hydrogen for 8270 criteria.

The PerkinElmer
Clarus SQ8 GC/MS

Thank you

????

Contact Information

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