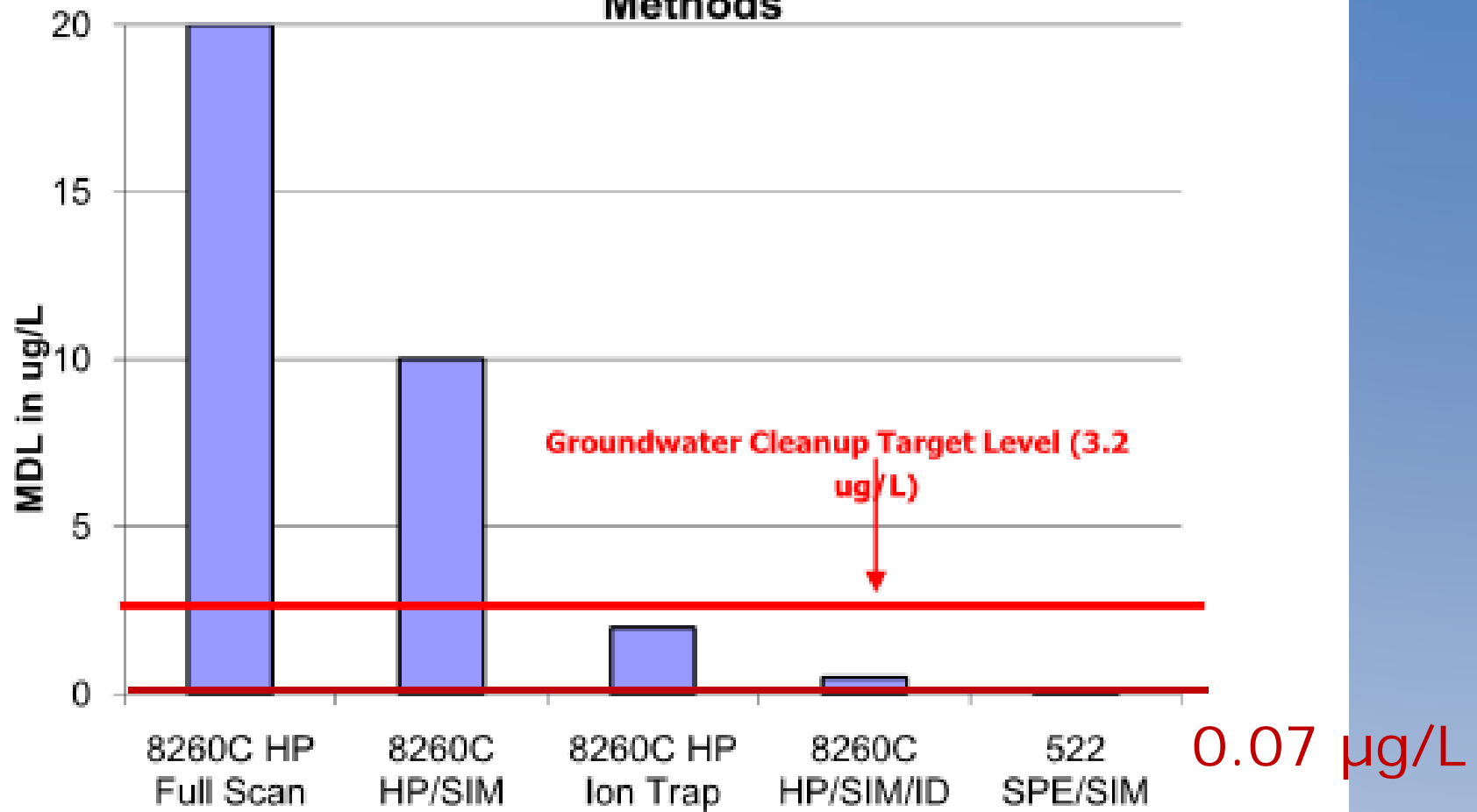


# Use Large Volume Splitless Injection with an Unmodified Split/Splitless GC Inlet to Lower Reporting Limits for 1,4-Dioxane in Drinking Water by EPA Method 522

Chris Rattray, Jack Cochran,  
Chris English

Figure 1. MDLs for 1,4-Dioxane by Various EPA Methods



# Lowering Detection Limits

1. Extract more sample

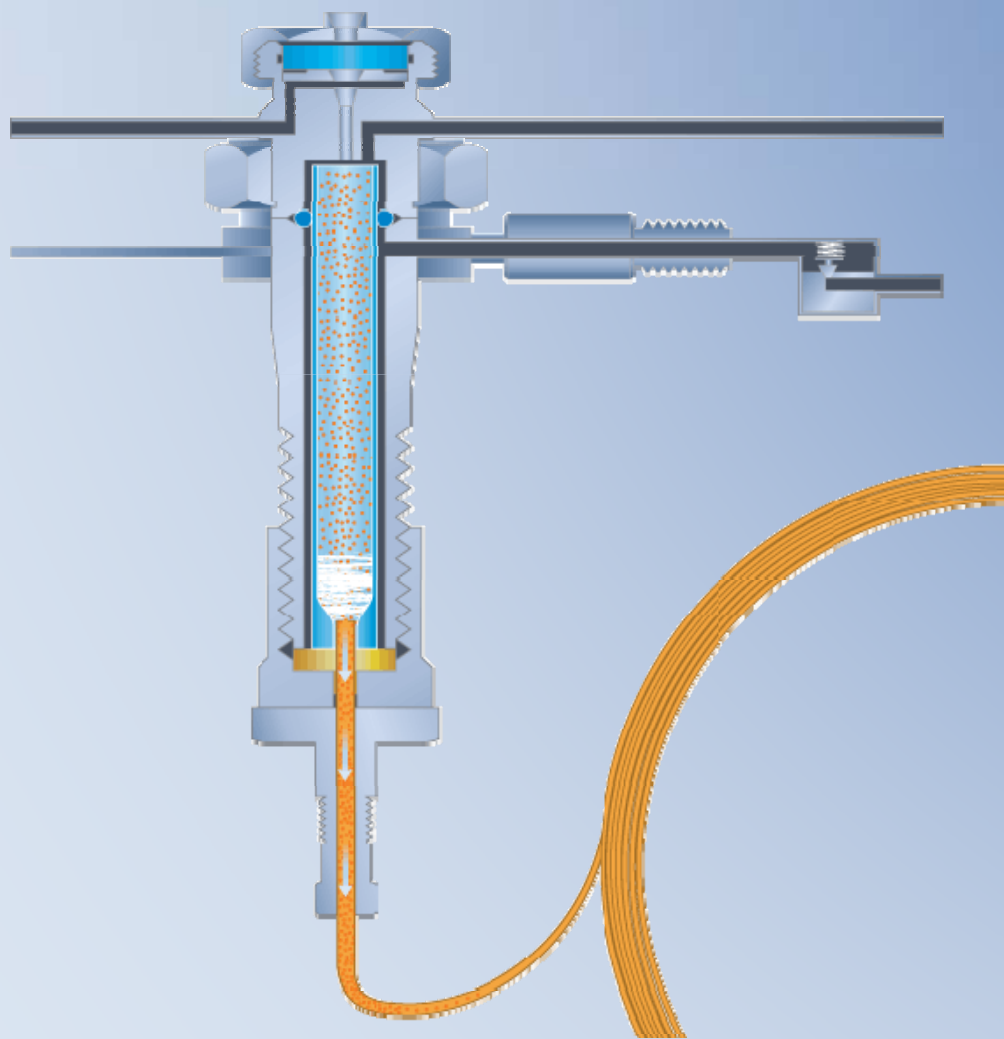
# Lowering Detection Limits

1. Extract more sample
2. Concentrate extract

# Lowering Detection Limits

1. Extract more sample
2. Concentrate extract
3. Inject more extract

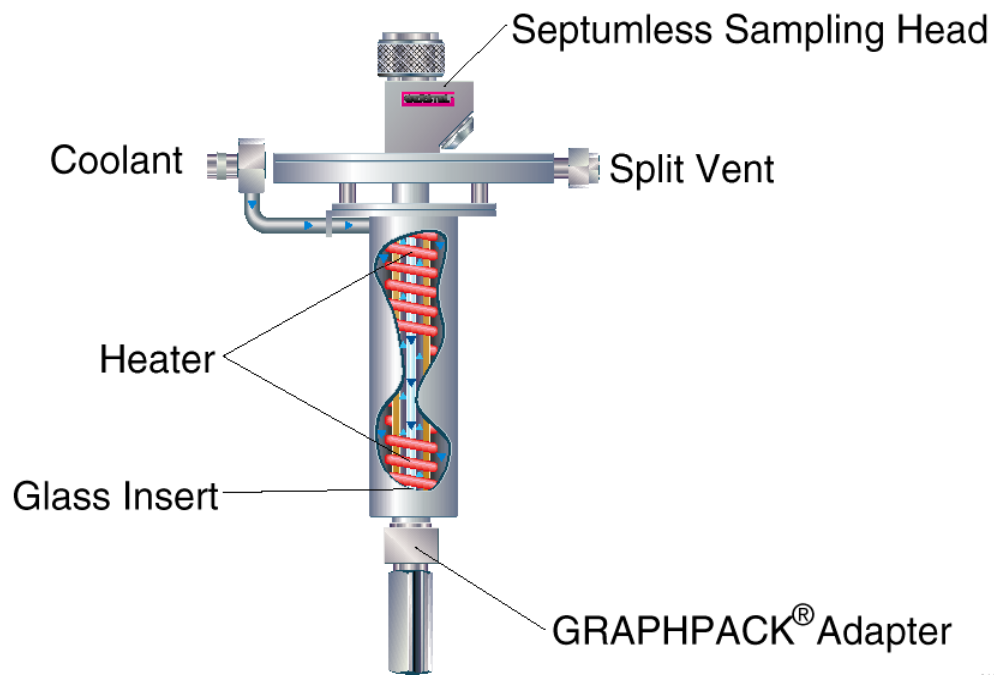
# Standard Splitless Injection



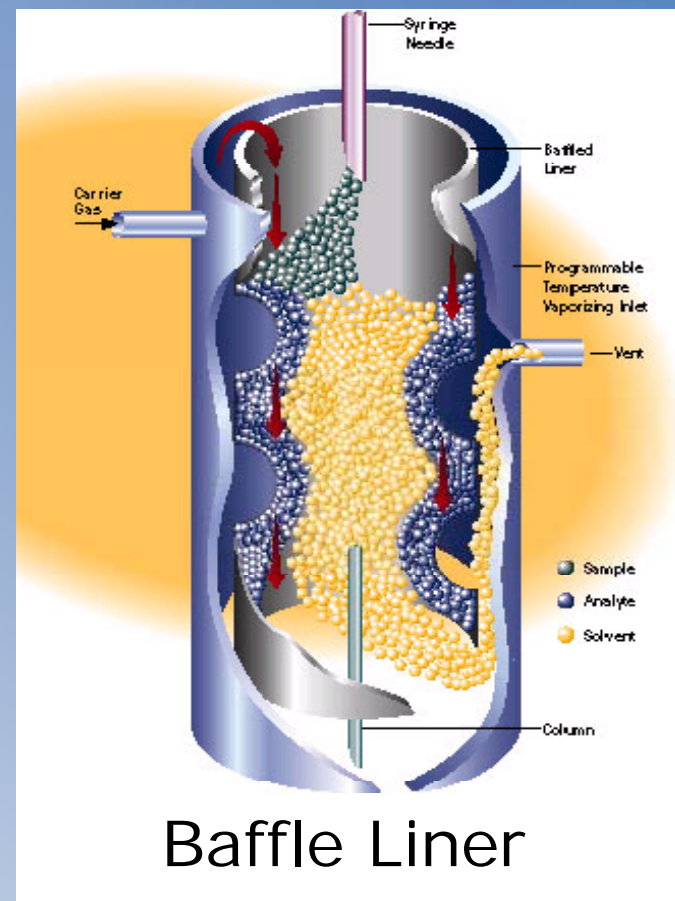
# Programmed Temperature Vaporization (PTV) Injector

Cooled Injection System  
CIS 4

GERSTEL



CIS-1-4



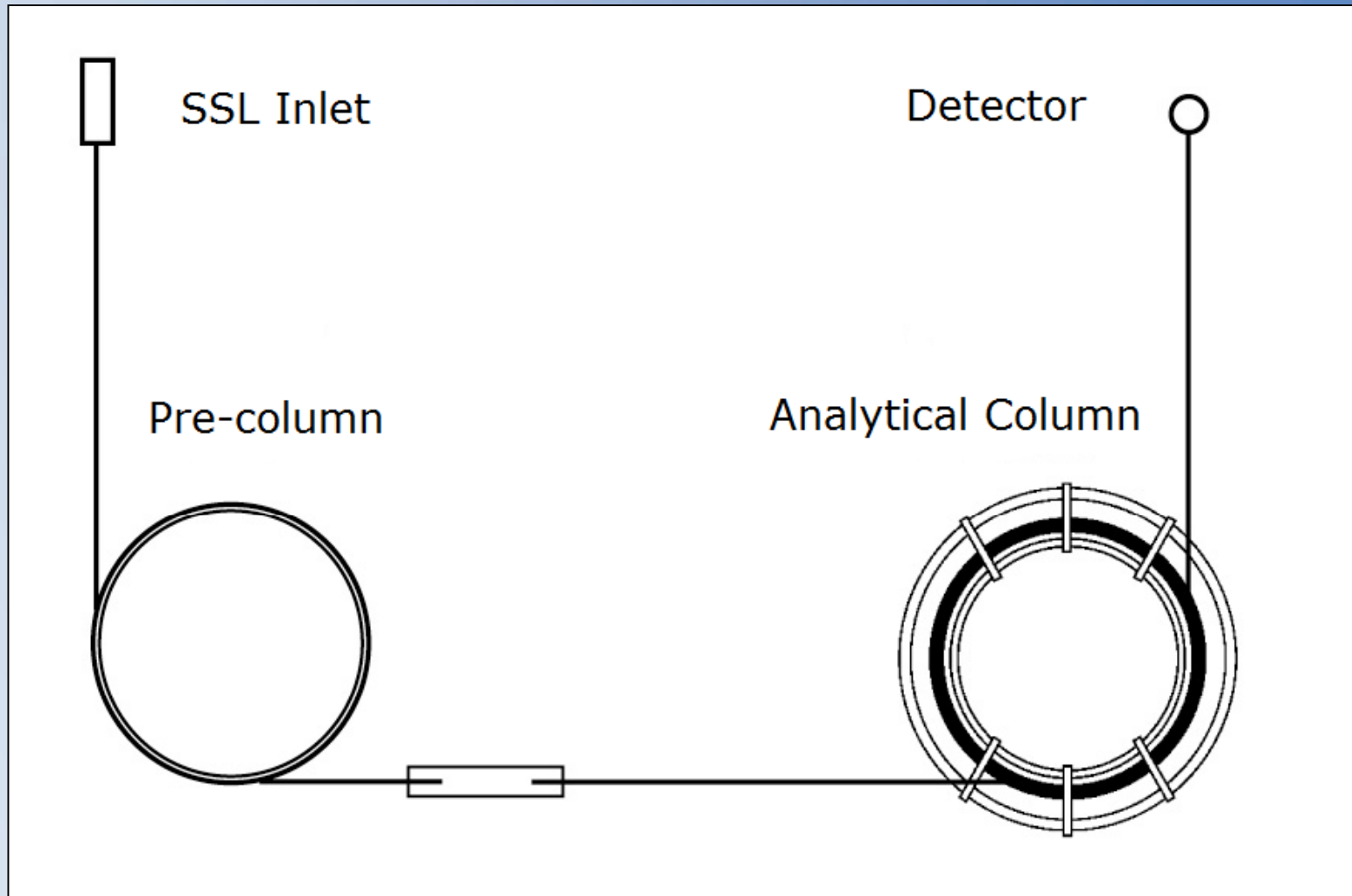
Baffle Liner

# Another Option

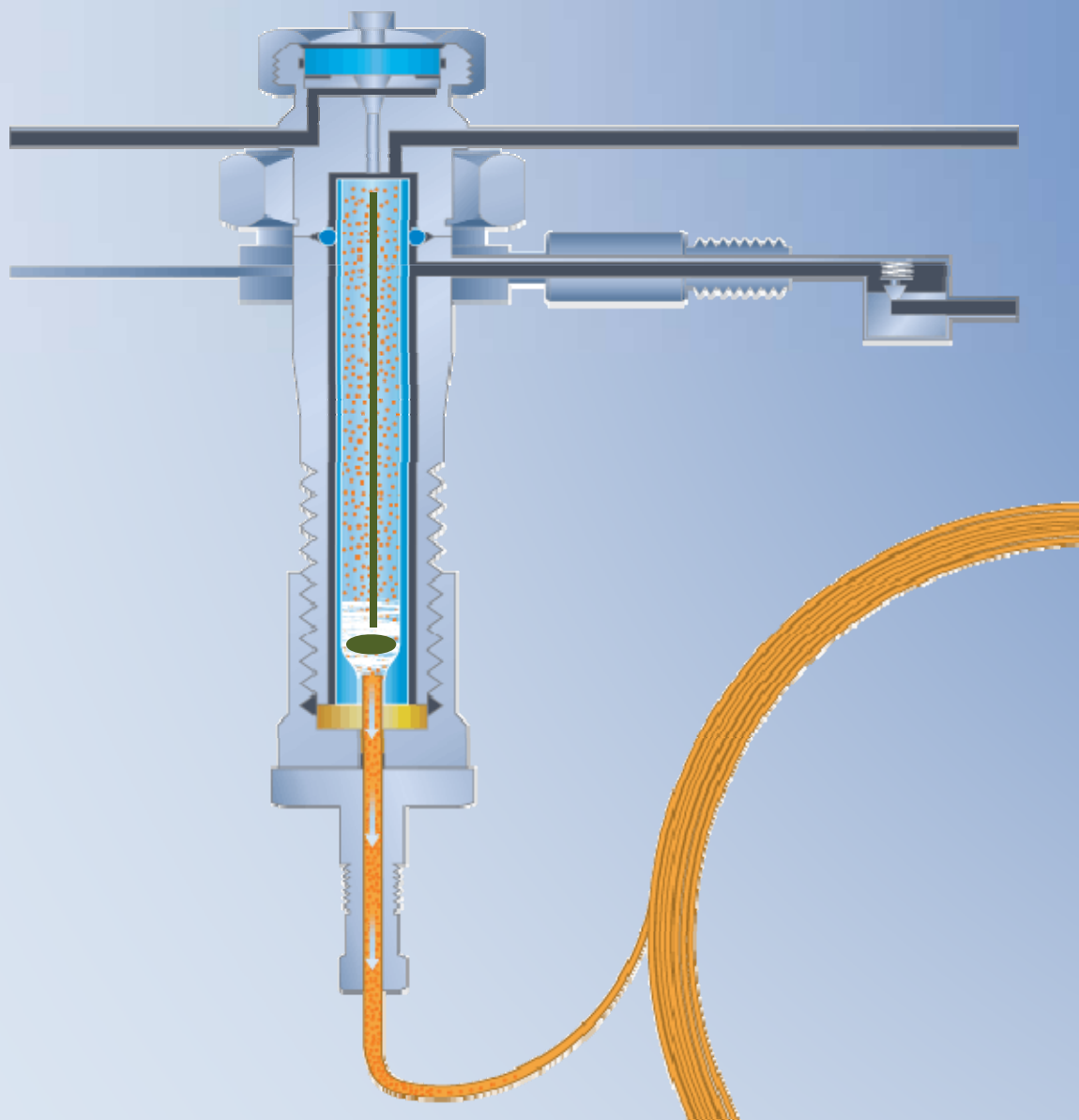
- Concurrent Solvent Recondensation – Large Volume Splitless Injection
- Unmodified Agilent Split/Splitless GC Inlet



# CSR-LVSI Setup

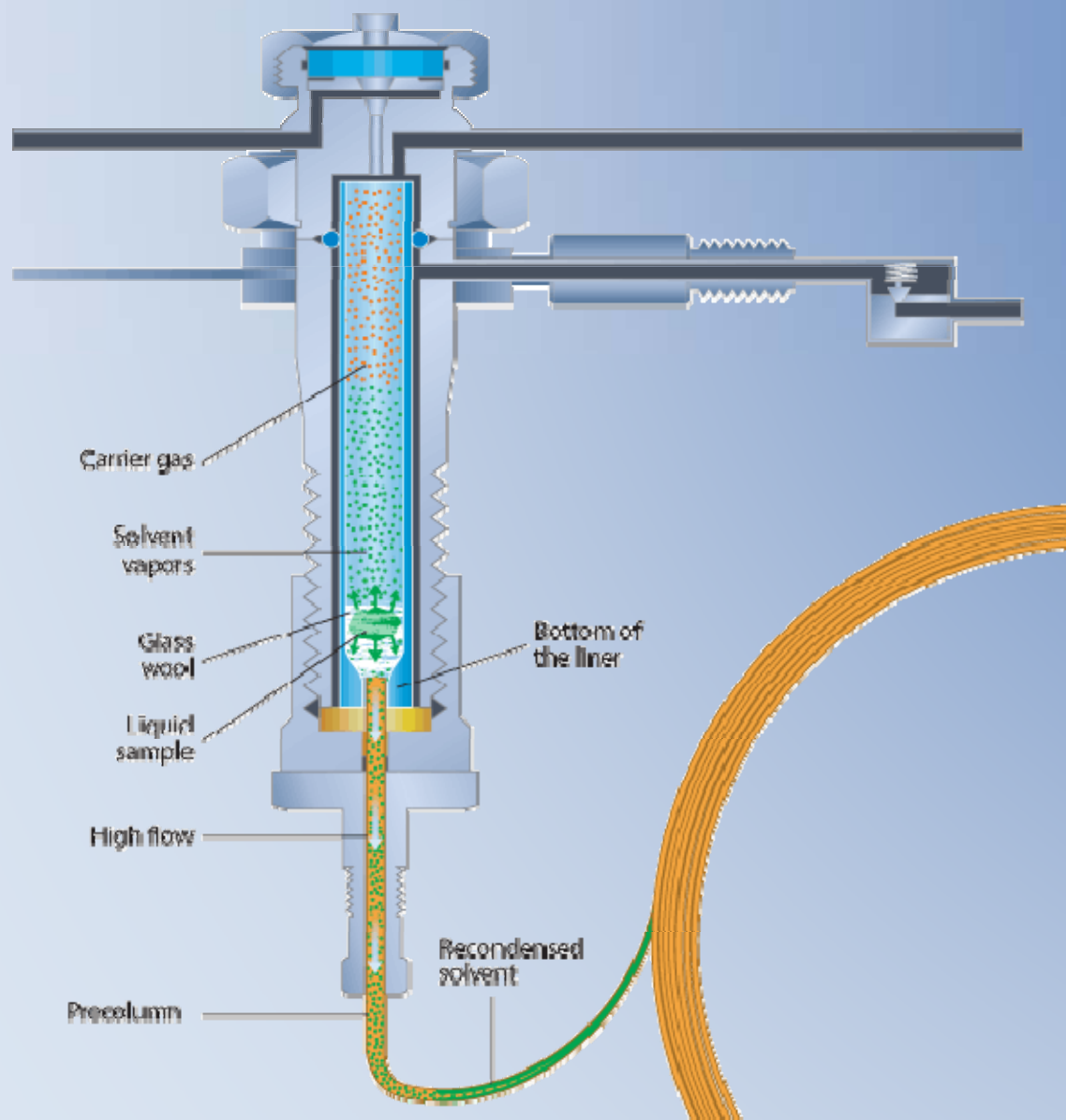


## CSR-LVSI



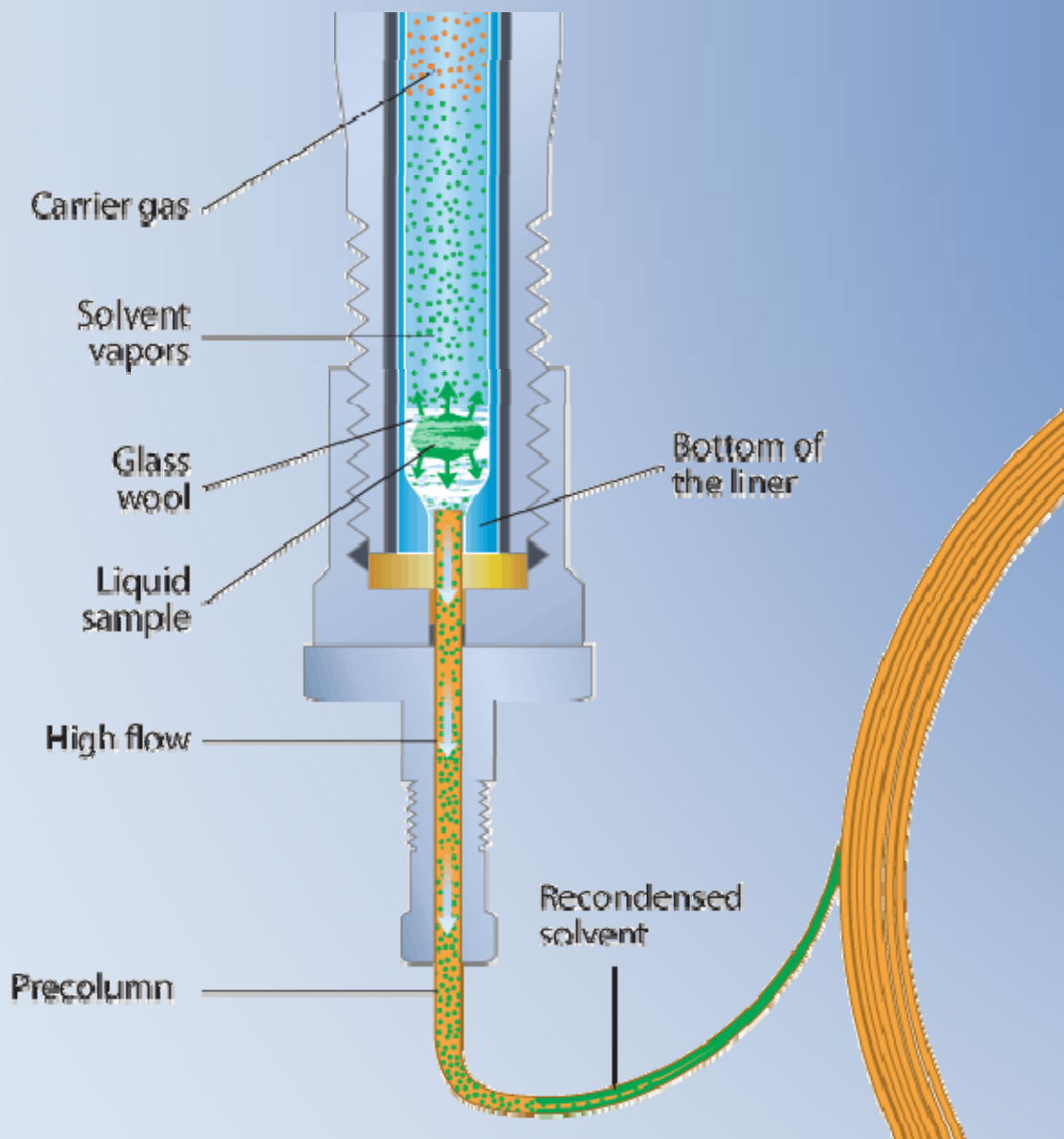
Step 1 – Fast injection forming tight liquid band near head of the column

# CSR-LVSI



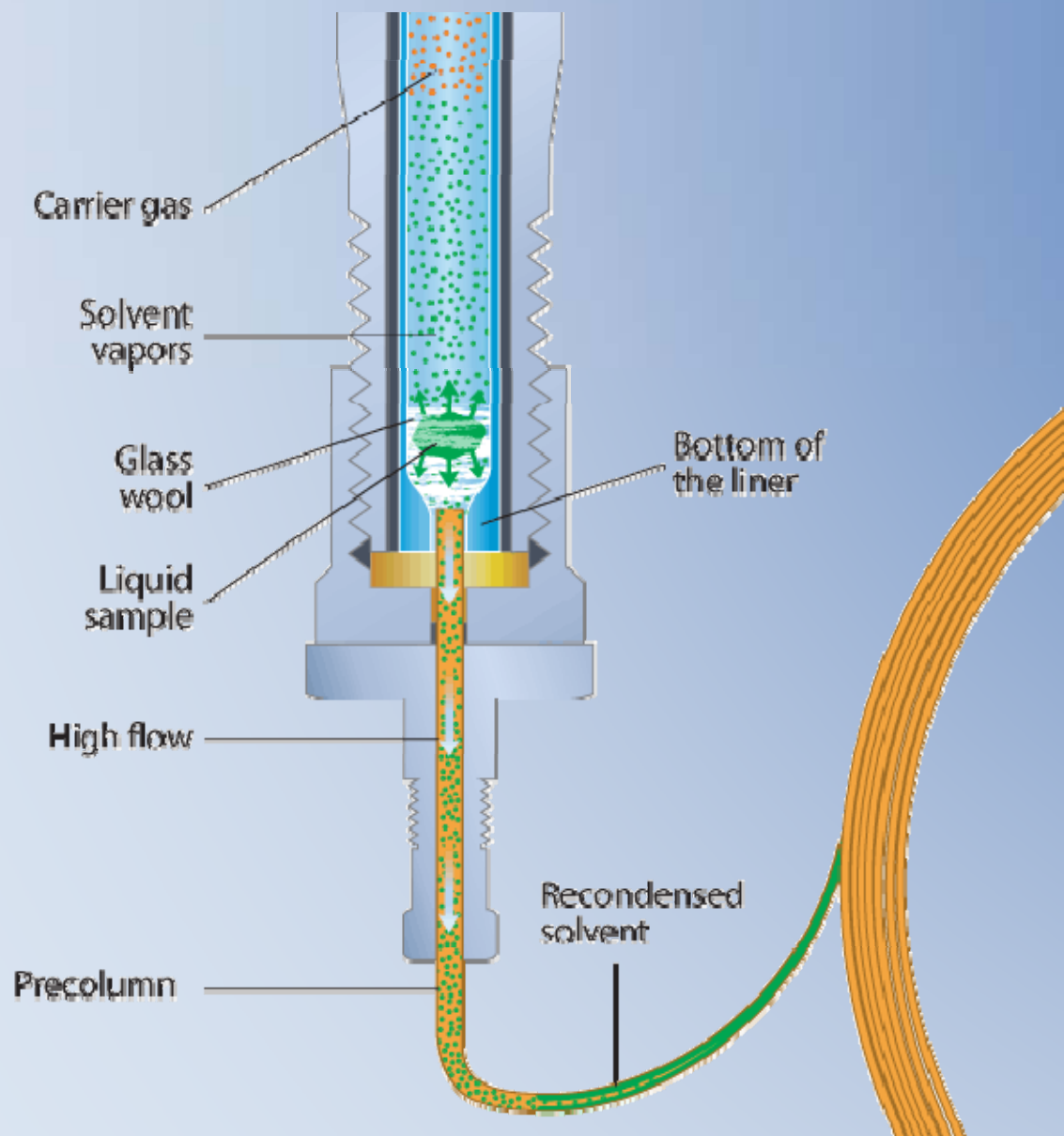
Step 2 – Auto pressure surge jump starts transfer of solvent vapor to pre-column

# CSR-LVSI



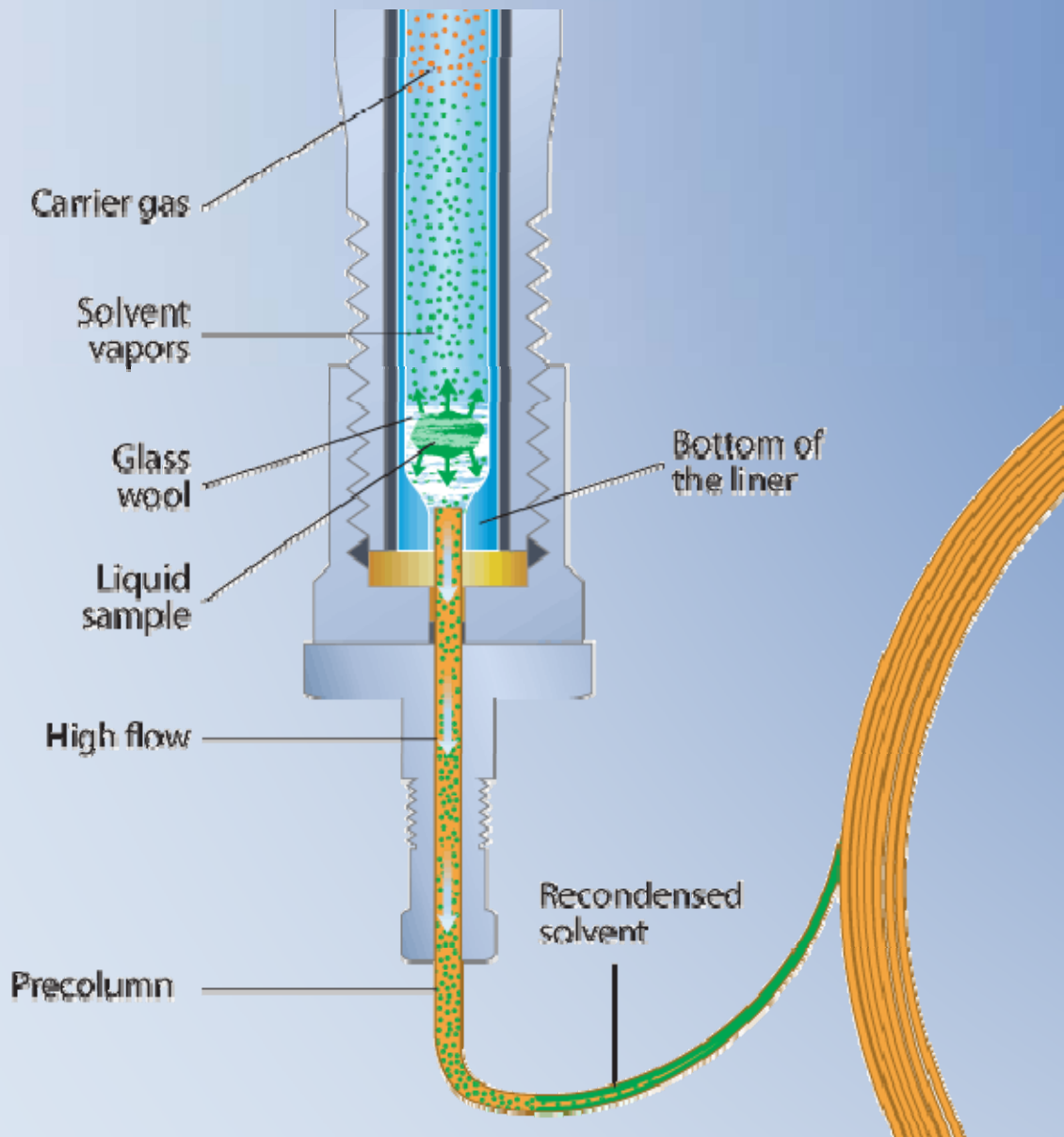
Step 3 –  
Transfer with  
concurrent  
recondensation  
of solvent vapor

# CSR-LVSI



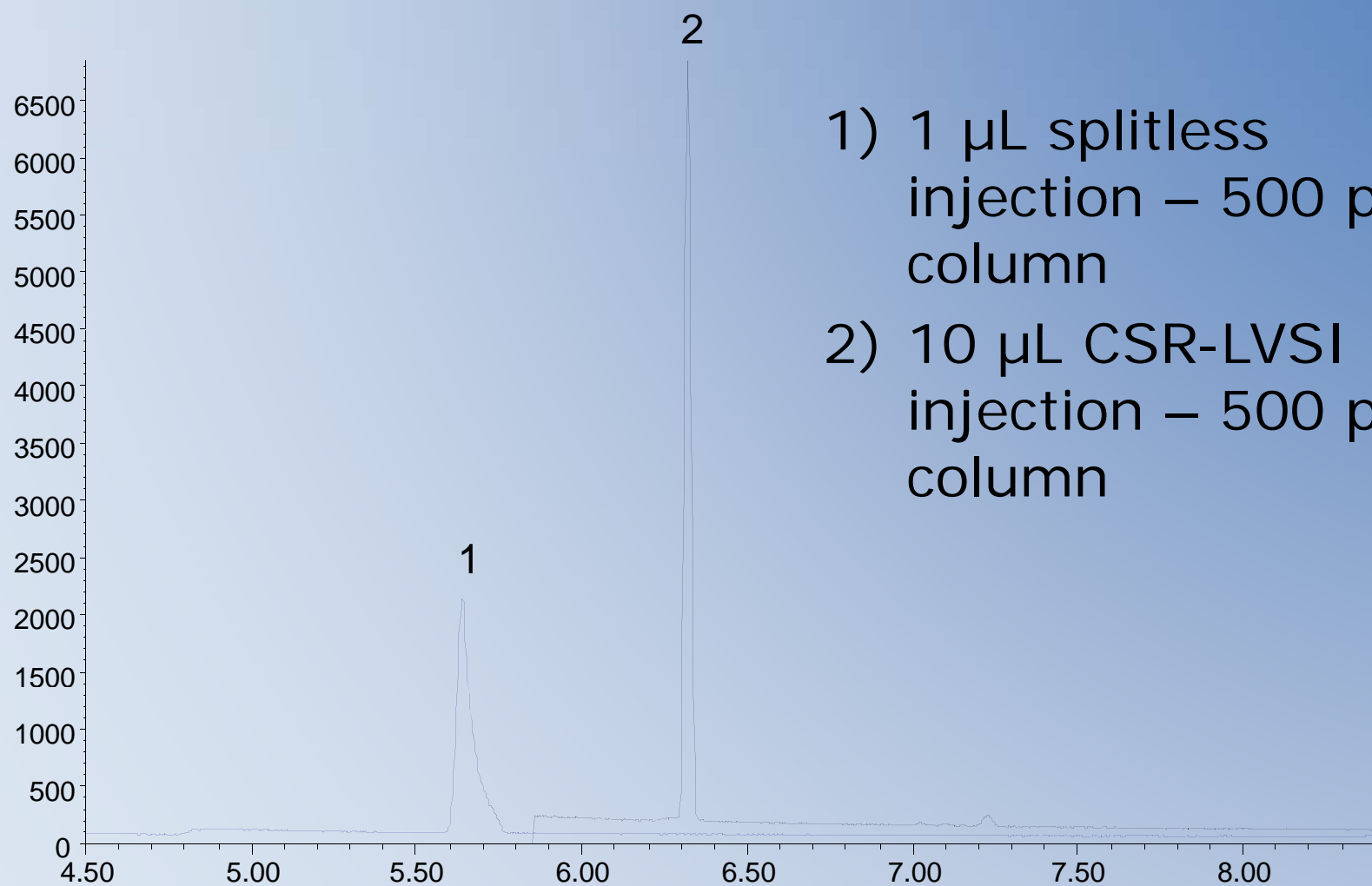
Step 4 –  
Transfer of  
solute occurs  
after solvent  
transfer

# CSR-LVSI



Step 5 –  
Evaporation of  
solvent from  
pre-column  
concentrates  
solutes into a  
narrow band

# CSR-LVSI vs. Standard Splitless Injection



- 1) 1  $\mu$ L splitless injection – 500 pg on column
- 2) 10  $\mu$ L CSR-LVSI injection – 500 pg on column

# Analytical Run Conditions

- GC-MS Instrumentation – Agilent 7890/5975C with 7683 ALS
- Autosampler – 25  $\mu\text{L}$  syringe, 10  $\mu\text{L}$  injection
- Inlet - Sky single taper 4 mm ID liner with wool, 120  $^{\circ}\text{C}$ , gas saver off, splitless, hold time = 1.0 min, 80 mL/min purge flow
- Column – Rxi<sup>®</sup>-624Sil MS, 30 m, 0.25 mm ID, 1.4  $\mu\text{m}$ , Rxi<sup>®</sup> deactivated pre-column, 5 m, 0.25 mm ID, constant flow @ 1.4 mL/min
- Oven – 35  $^{\circ}\text{C}$  (hold 1.0 min) to 120  $^{\circ}\text{C}$  @ 12  $^{\circ}\text{C}/\text{min}$  (hold 1 min) = 9.1 min
- MSD – Source 230  $^{\circ}\text{C}$ , Quad 150  $^{\circ}\text{C}$ , Solvent delay 5.0 min

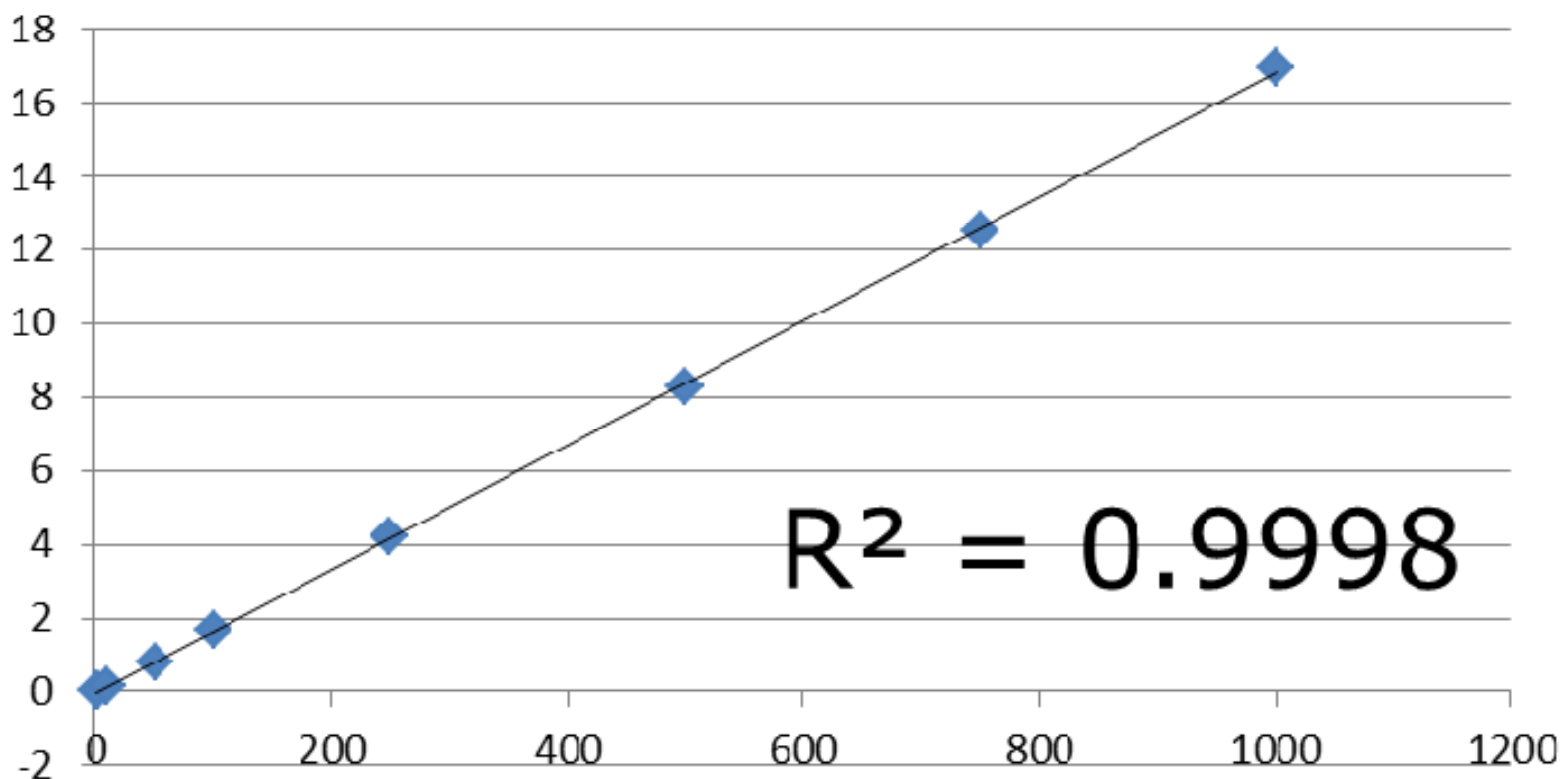


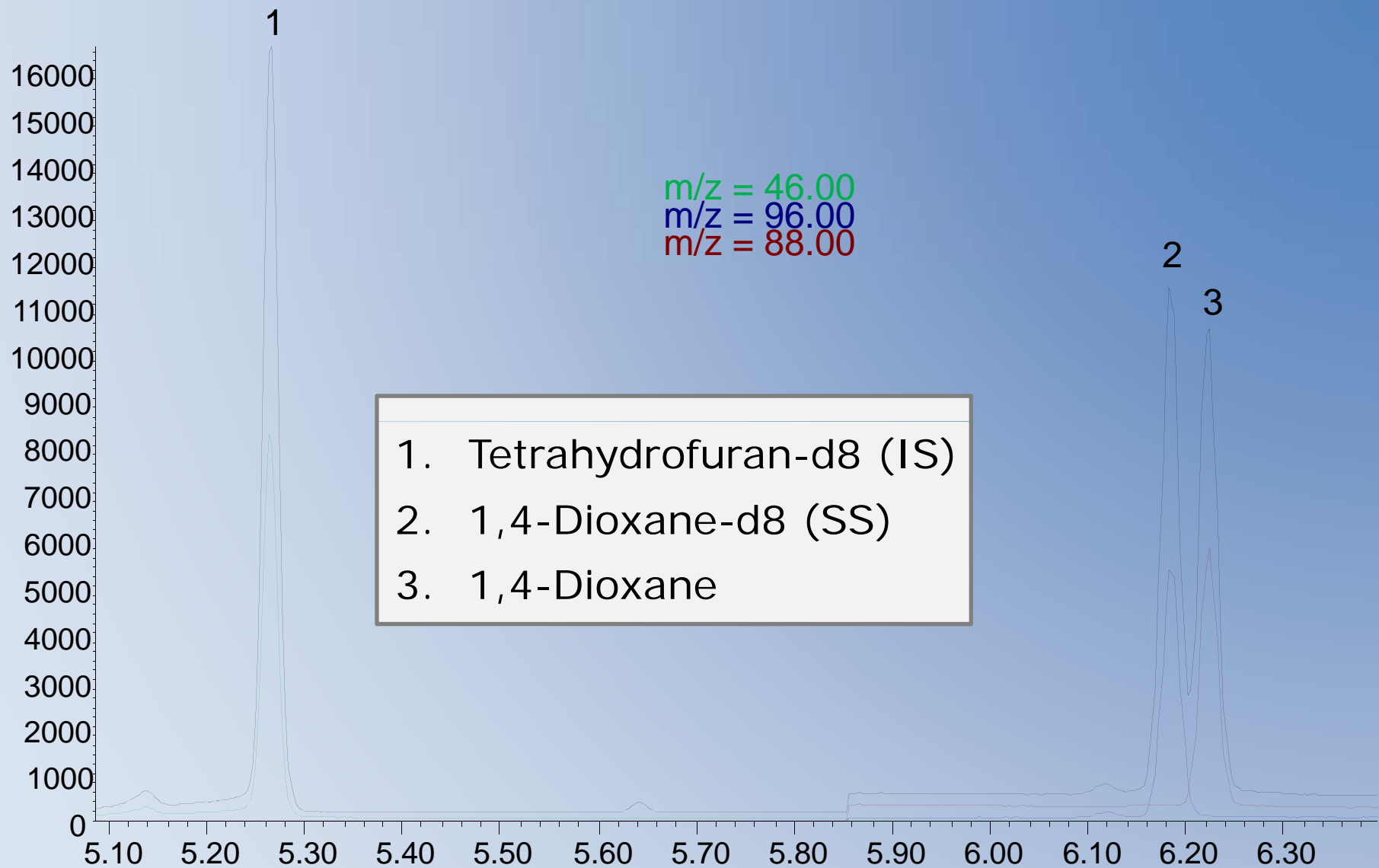
# Sample Preparation



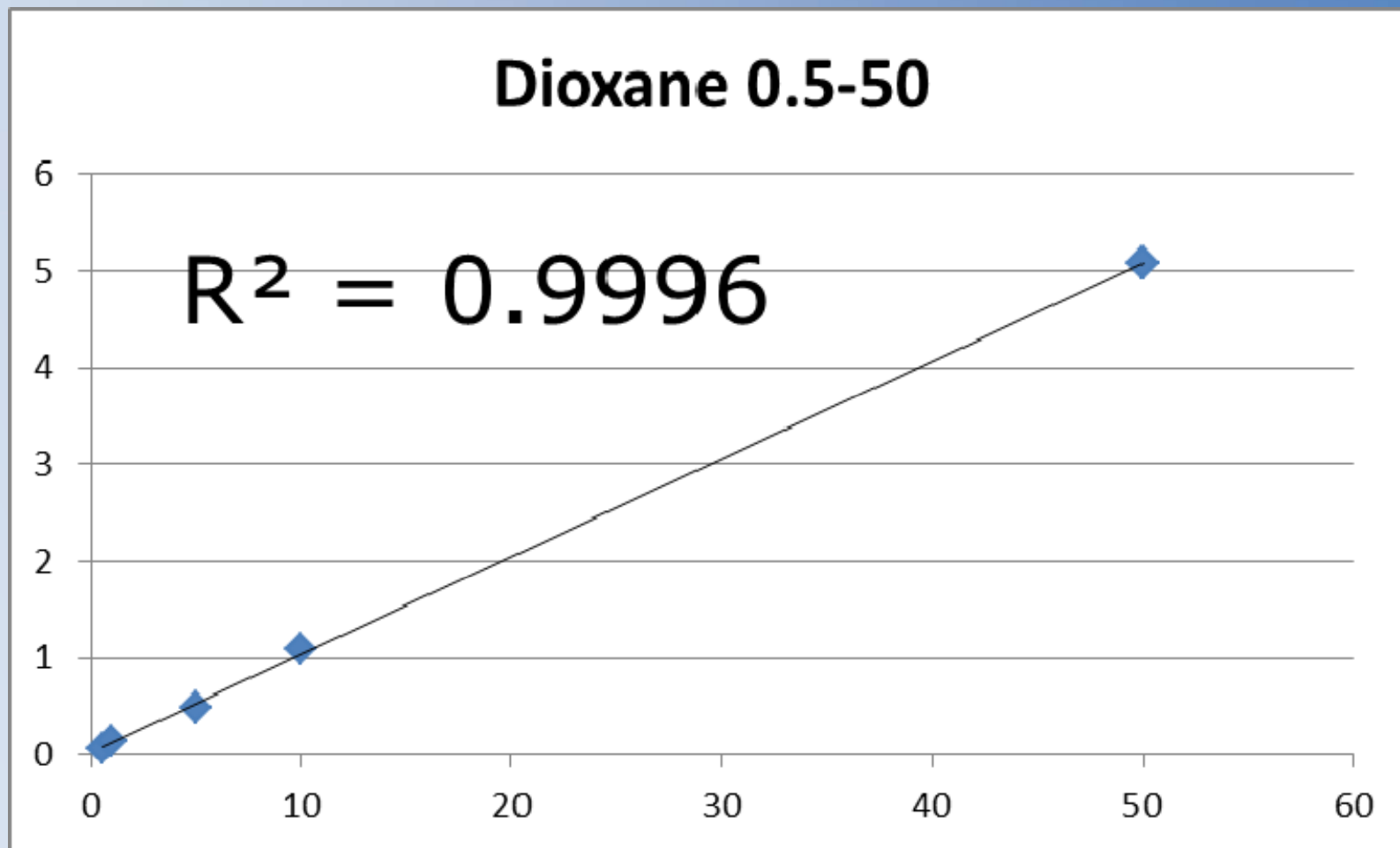
Level	Prepared Standard (pg/ $\mu$ L)	10 $\mu$ L Injection, On-Column Amount (pg)	Equivalent Concentration in 500 mL Water Sample ( $\mu$ g/L)
1	1.0	10	0.020
2	2.0	20	0.040
3	10	100	0.20
4	50	500	1.0
5	100	1,000	2.0
6	250	2,500	5.0
7	500	5,000	10
8	750	7,500	15
9	1,000	10,000	20

## Dioxane 1-1000



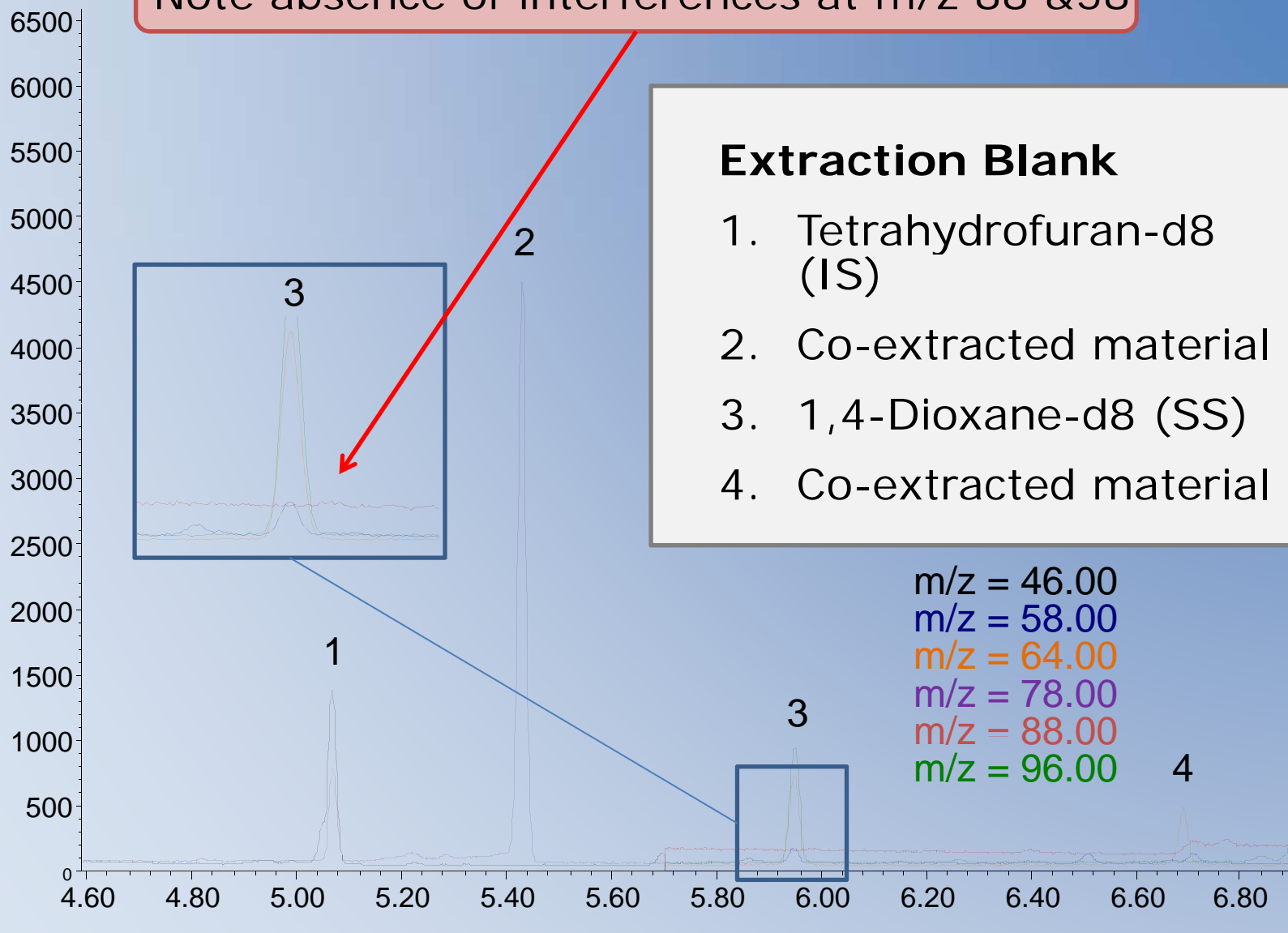


## Dioxane 0.5-50

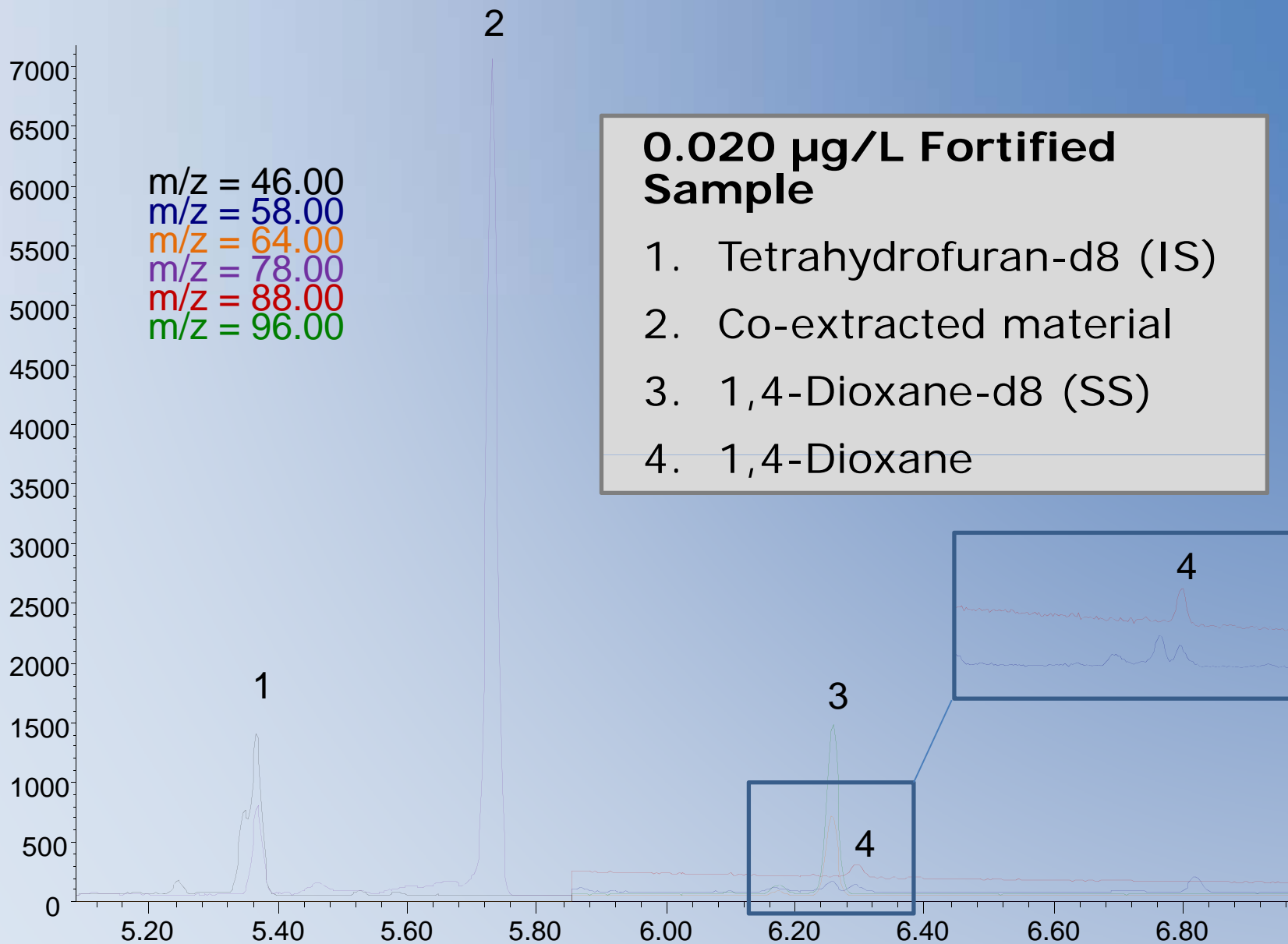


Abundance

Note absence of interferences at m/z 88 & 58

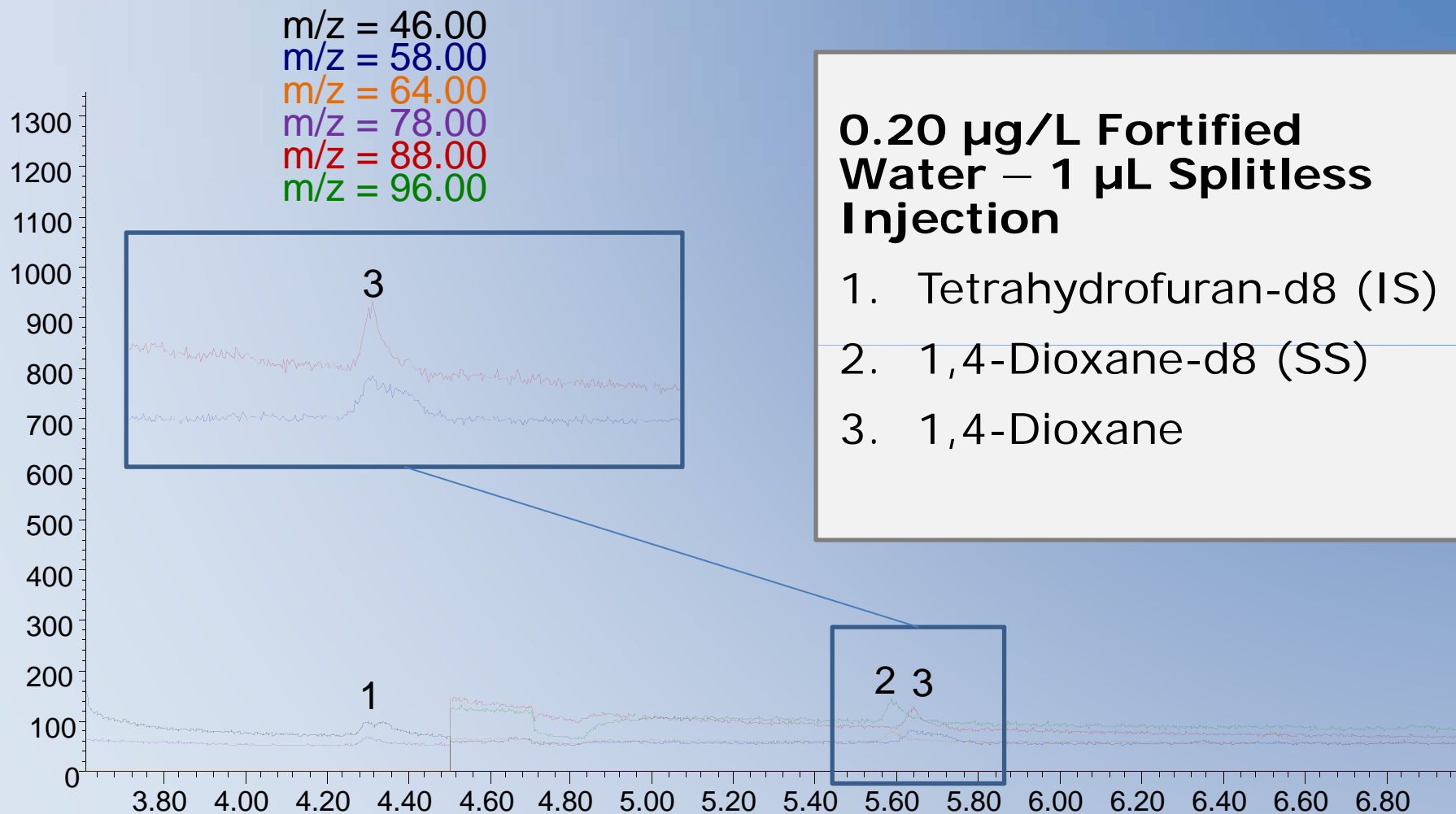


Time-->



## 0.20 µg/L Fortified Water – 1 µL Splitless Injection

1. Tetrahydrofuran-d8 (IS)
2. 1,4-Dioxane-d8 (SS)
3. 1,4-Dioxane





# Summary of Results

Matrix	Fortified Sample Conc. ( $\mu\text{g/L}$ )	Volume of Sample Extracted (L)	Theoretical Extract Conc. ( $\text{pg}/\mu\text{L}$ )	Recovery ( $\text{pg}/\mu\text{L}$ )	1,4-Dioxane % Recovery	Surrogate % Recovery
Bottled drinking water	0.0050	1.0	0.5	0.40	80	125
Bottled drinking water	0.20	0.50	10	9.2	92	102
Bottled drinking water	0.20	1.0	20	18	87	96
Reagent water	0.020	0.50	1.0	1.0	100	88
Reagent water	0.20	0.50	10	8.4	84	92
Reagent water	0.0	0.50	0.0	-	-	86

# Conclusion

- CSR-LVSI using an unmodified Agilent split/splitless GC inlet has been shown to be a technically viable approach.
- Solvent recondensation refocuses the solutes into a tight band on the column, improving the chromatography.
- Using CSR-LVSI with a standard inlet provides a cost-effective way to meet ever decreasing detection and quantitation limits.

# Questions?

## References

- [1] P. Grimmett, J. Munch, Method Development for the Analysis of 1,4-Dioxane in Drinking Water Using Solid-Phase Extraction and Gas Chromatography-Mass Spectrometry, J. of Chromatographic Science 47 (2009) 31.
- [2] U.S. EPA, Unregulated Contaminant Monitoring Rule 3.  
<http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/index.cfm> (accessed March 2, 2012).
- [3] P. Magni, T. Porzano, Concurrent Solvent Recondensation Large Sample Volume Splitless Injection, J. Sep. Sci. 26 (2003) 1491.
- [4] Patent No: US 6,955,709 B2.