Innovative and Sensitive Method for the Determination of 1,4 Dioxane in Drinking Water by HS-GC/MS.

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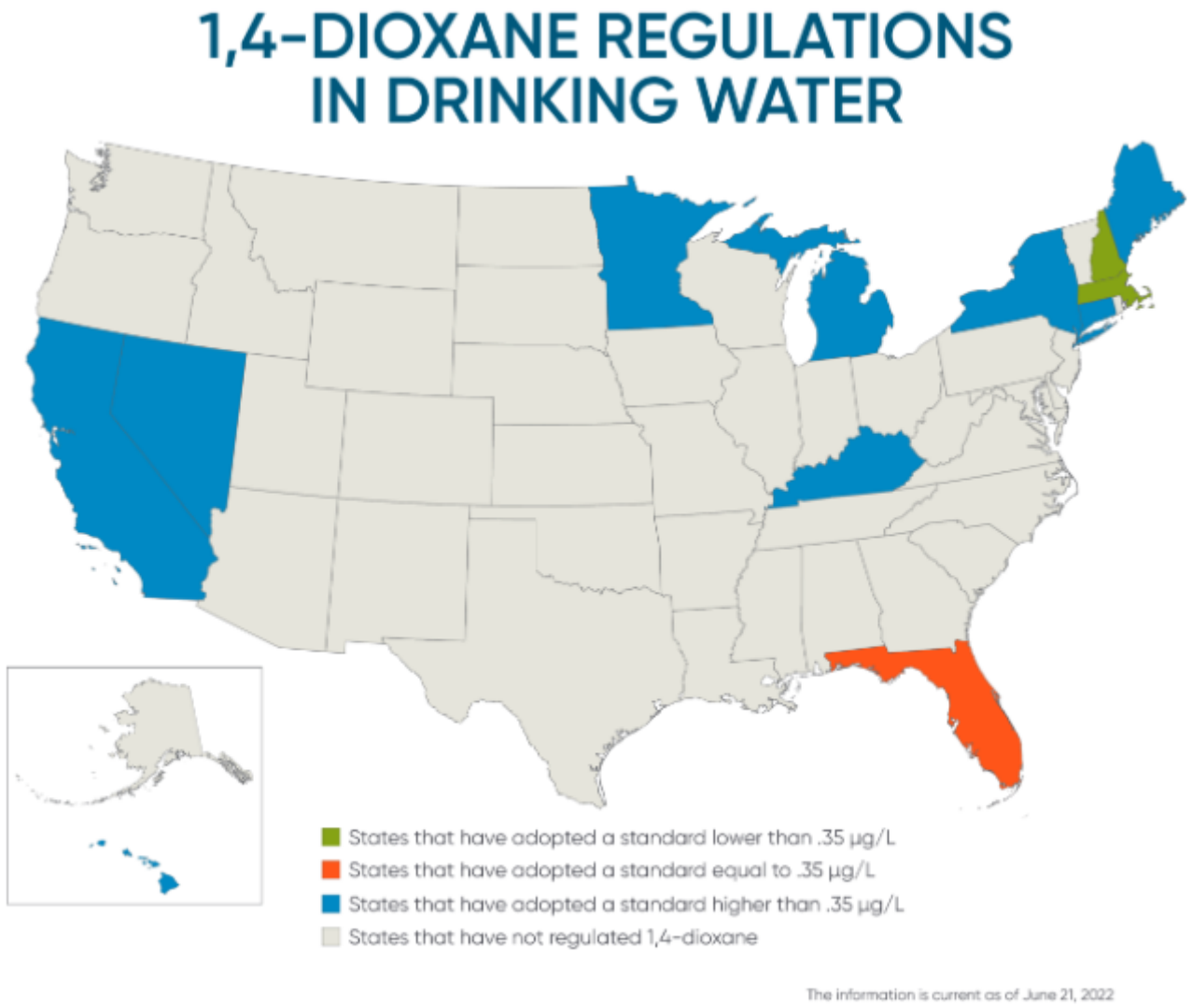
Overview

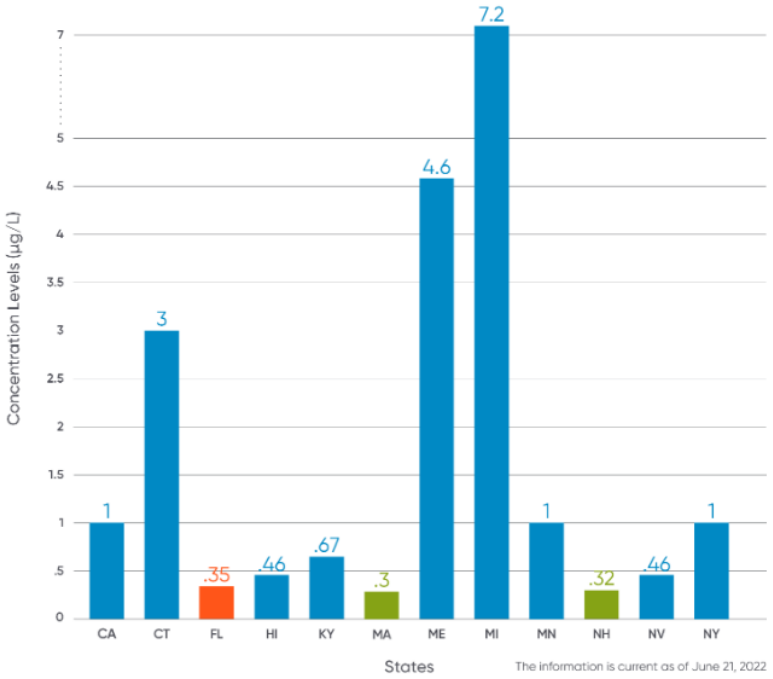
- Water quality is a global concern
- 1,4 Dioxane is highly soluble in water and thus transports though the aquifer with ease
- 1,4 Dioxane is toxic and known cancer agent
- Drinking limits are very low with some locations at 1ppb or lower

- "*1,4-Dioxane is a **likely human carcinogen** and has been found in groundwater at sites throughout the United States. The physical/chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment. It is highly mobile and does not readily biodegrade in the environment*."

USA 1,4-Dioxane Regulations

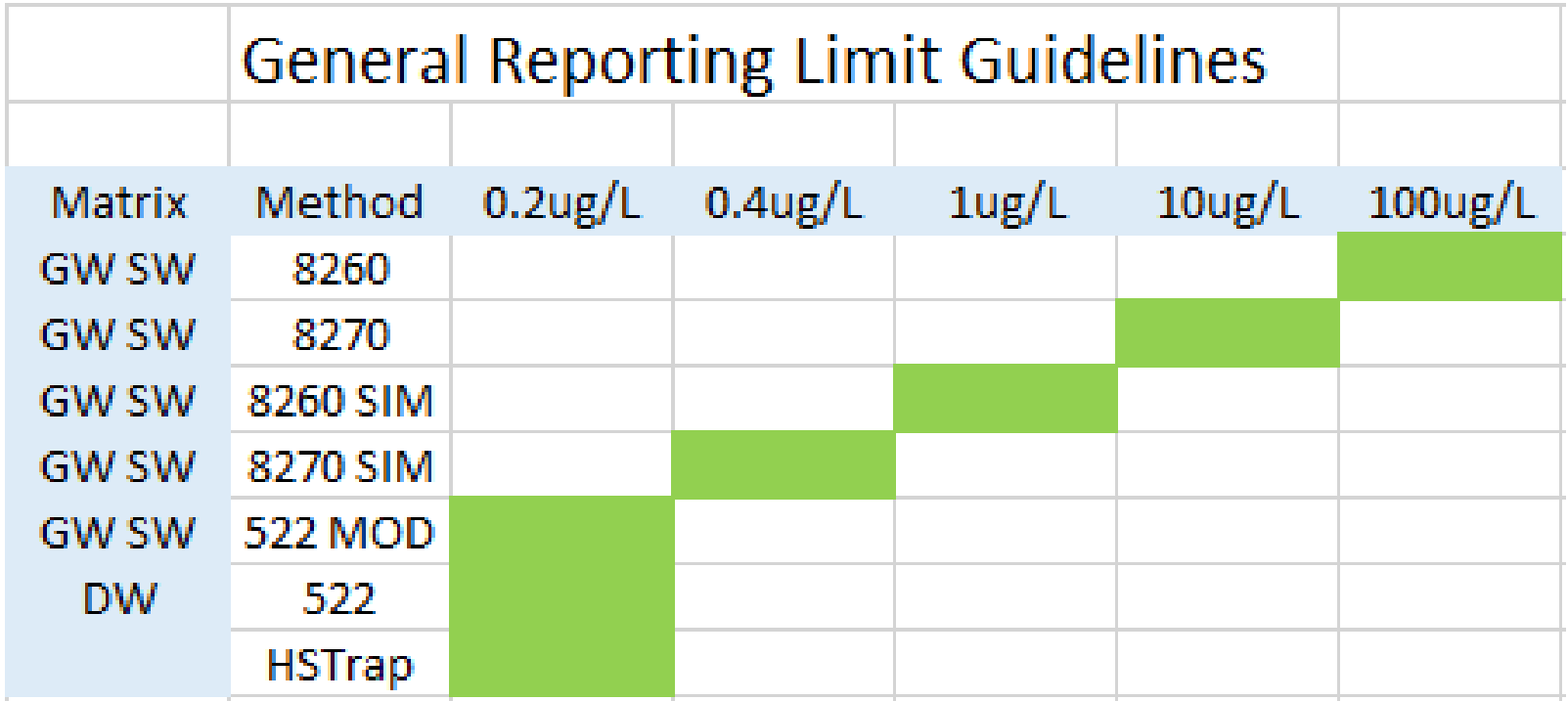


- Images from https://www.jdsupra.com/legalnews/state-by-state-regulation-of-1-4-8538403/



Contract Lab Reported DL

- All regulated states are less than 10ug/L, thus 8260 and 8270 are challenged
- It is expected the limits will likely continue to drop.



General Reporting Limit Guidelines						
Matrix	Method	0.2ug/L	0.4ug/L	1ug/L	10ug/L	100ug/L
GW SW	8260					
GW SW	8270					
GW SW	8260 SIM					
GW SW	8270 SIM					
GW SW	522 MOD					
DW	522					
	HSTrap					

Methods for the Chromatographic Analysis of 1,4 Dioxane

- USEPA 8260 Purge and Trap
- USEPA 8270 Liquid/liquid
- USEPA 522 with SPE
- Method proposed using HSTrap

USEPA8260 Purge and Trap

Utilizes Purge and Trap with excellent recoveries with most VOC. 1,4 dioxane is high water solubility with a very large partition coefficient thus the need for heated purge. The heated purge temperature significantly increases the water load on the trap/column thus lead to interferences by water.

Advantages-- can be used on existing 8260 equipment

Liquid-Liquid with USEPA8270

- If care is taken to prevent loss of 1,4 dioxane during sample extraction, good numbers can be achieved. Recommended to use 1,4 dioxane-d8 as a surrogate to correct for sample loss from the sample prep step. This is incorrectly called Internal Standard correction.
- Advantages-- can be used on existing 8270 semi volatile systems with ease

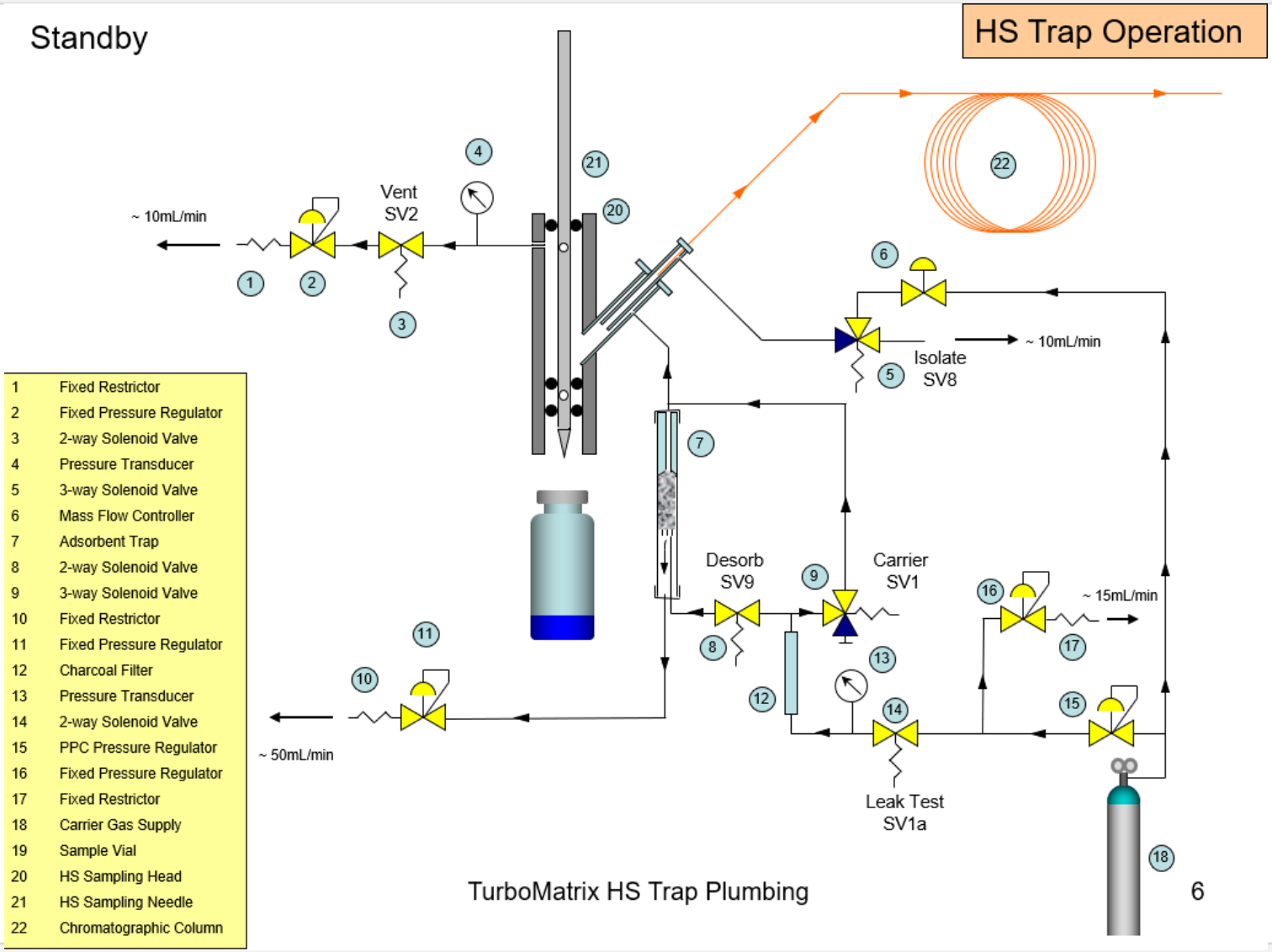
SPE with USEPA 522

- EPA 522 require the sample be passed through a SPE cartridge for sample enrichment. The SPE cartridge is washed with an elution solvent which is run with a liquid Injection on an 8270 like system
- Advantage---great enhancement in signal with reduced background
- Disadvantage---significant labour required for sample prep and use of expensive isotopically labeled standard

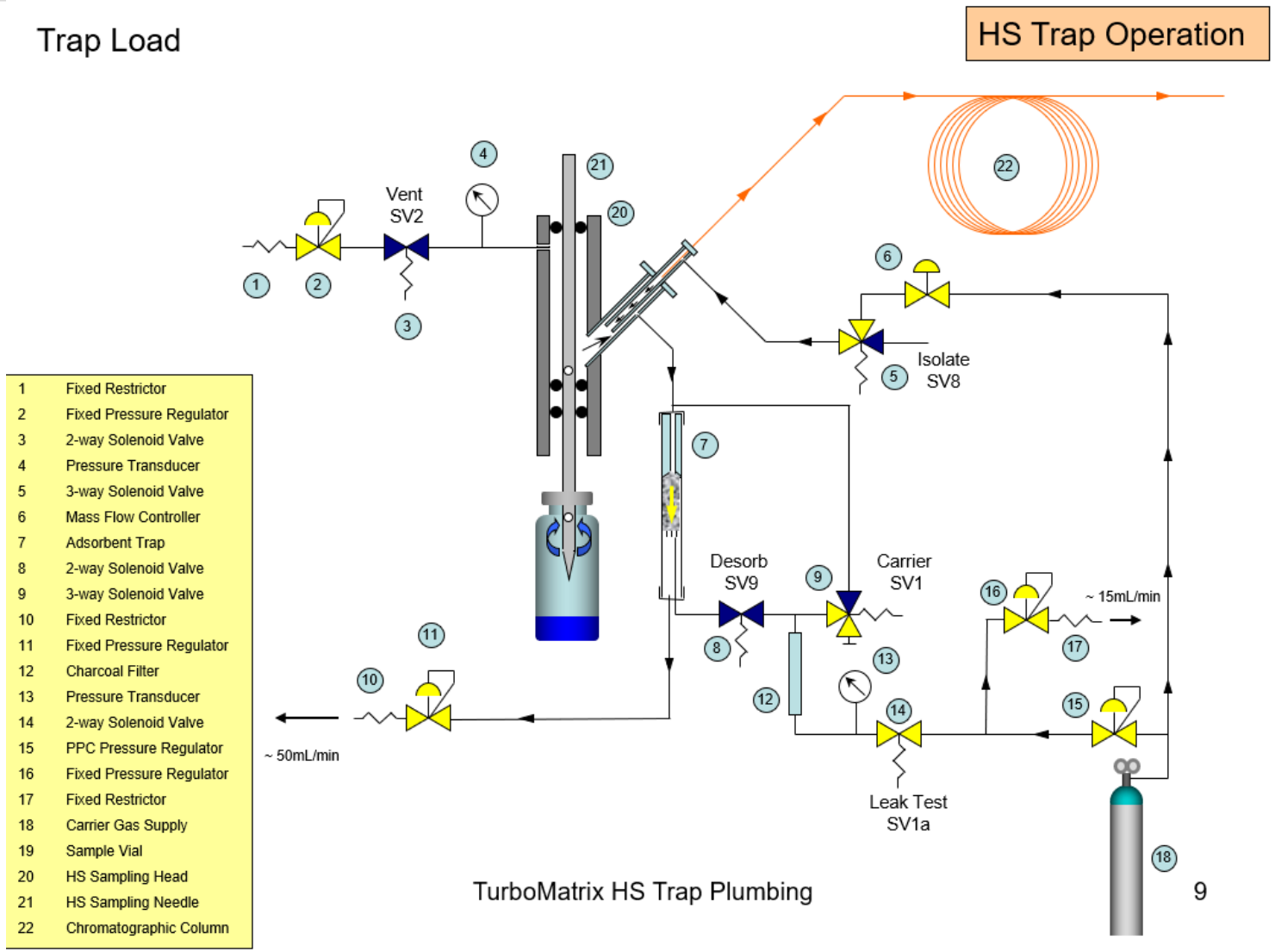
1,4 Dioxane using HSTrap as modified USEPA 8260

- Less sample prep than 8270 and 522
- Better DL than 8260 and existing modifications
- High Precision

HSTrap – How it works Standby



HSTrap – How it works Pressurization/Trap Load



TurboMatrix HS Trap Plumbing

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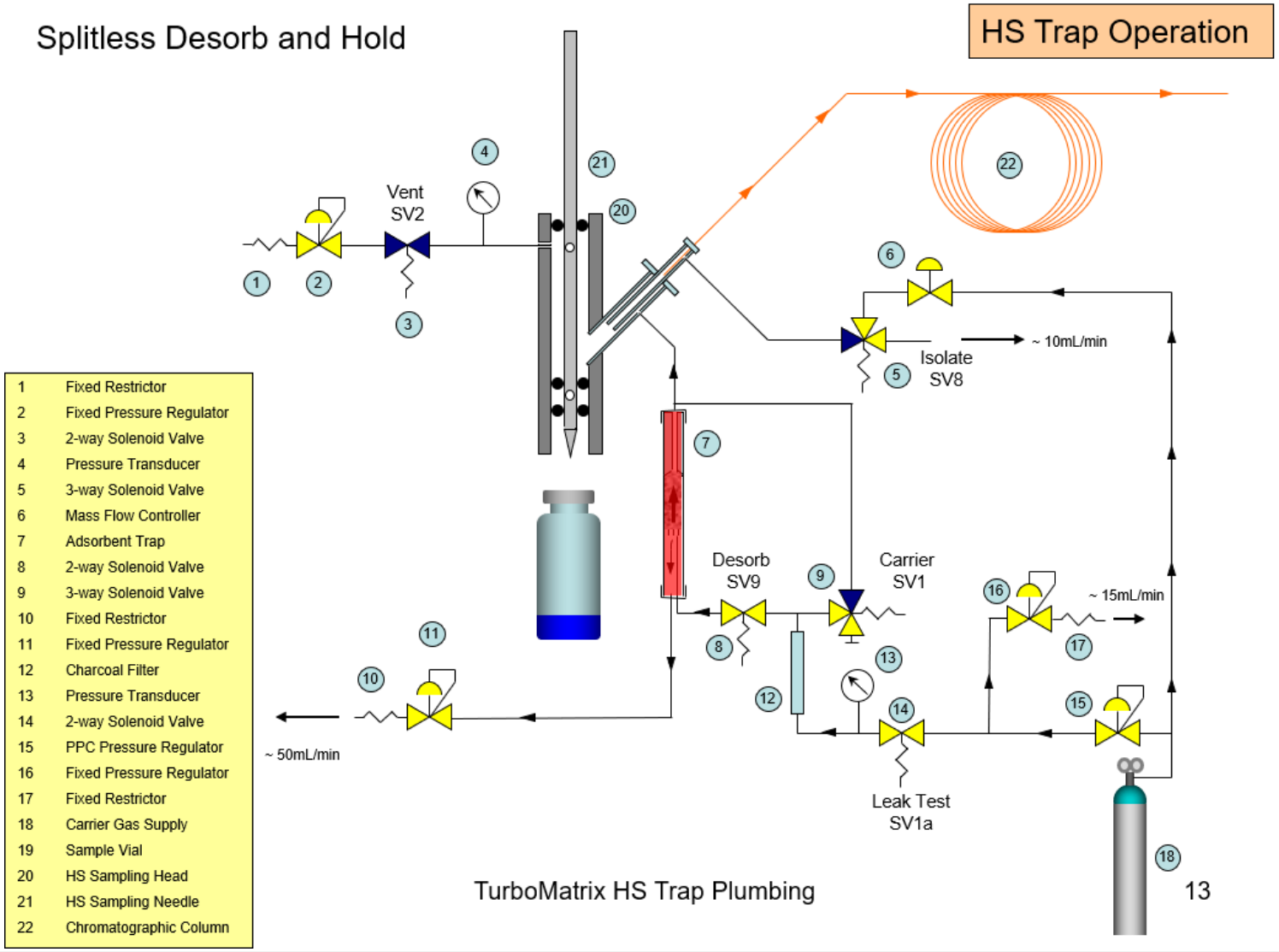
HSTrap – How it works Desorb



Standard Preparation

General Solution Dilution

	PPB	PPB		uL	uL	uL	PPB
Analyte	**Conc of Std**	**Desired Conc**	**Dilution factor**	**final volume**	**volume of std neede**	**actual used**	**actual final conc**
1,4 Dioxane	2,000,000	20000	100	10000	100.00	100	20000.00
	20000	200	100	10000	100	100	200.00
	20000	200	100	10000	100	10	20.00
	20000	50	400	10000	25	100	200.00
	20000	20	1000	10000	10	10	20.00
	20000	10	2000	10000	5	5	10.00
	200	2	100	10000	100	100	2.00
	200	0.5	400	10000	25	25	0.50
	200	0.1	2000	10000	5	5	0.10
			#DIV/0!		#DIV/0!		#DIV/0!
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Note: For this study, the standards are V/V so therefore ug/L values are 3% higher

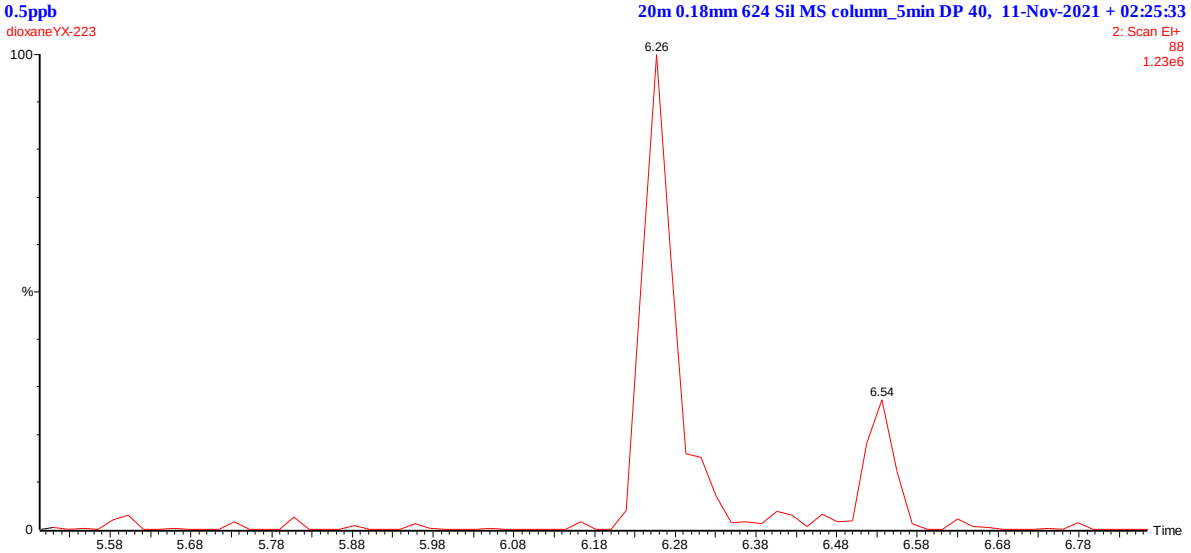
Instrument conditions

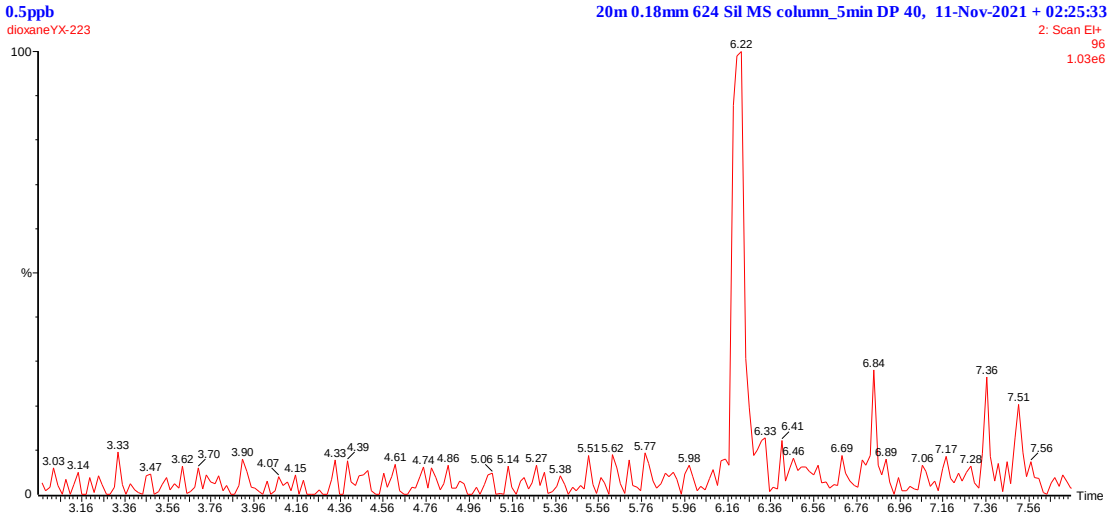
Chromatography Conditions

GC Parameters	
Instrument	PerkinElmer Clarus 690 GC
Carrier Gas	Helium
Columns	Elite-624 SIL MS 30 m 0.18 mm 1.0 u
Injector Parameters	
Carrier flow	1.8 mL/minute(1.0 min) ballastic to 0.9 mL/min
split	OFF
Type	PSS with 1mm liner
Temperature	180° C
Oven Parameters	
Oven initial temperature	40° C
Oven initial hold	3 minutes
Ramp	10C/min
Final tempurature	200° C
Final time	0 minutes
Oven maximum	?
Equilibration time	?
MS Detector Parameters	
Mode	EI+
Electon Energy	70 eV
Multiplier Voltage	1700 V
Emission current	100 uA
Transfer line	200° C
Source temp	200° C
Solvent delay	2 minutes
SIFI SIR	58,64,88,96 da 0.2sec dwell 0.04 second ISD
SIFI Scan	16-100 daltons 0.1 sec/scan 0.06 sec ISD

HeadSpace Parameters	
Instrument	PerkinElmer TurboMatrix 40 HSTrap
Carrier Gas	Helium
Oven temperature	80° C
Needle temperature	110° C
Transfer line	120° C
Trap low	40° C
Trap high	325° C
cycles	1
Pressurization time	1
Decay time	2.0 minutes
Dry purge	5 minutes
Trap hold	4 minutes
Desorb time	0.5 minutes
Thermostat time	25 minutes
GC cycle time	20 minutes
Outlet split	OFF
Shaker	ON
Column pressure	33,6 psi
Vial pressure	33.6 psi
Desorb pressure	33.6 psi

0.5ppb 1,4 Dioxane and 1,4 Dioxane-d8 extracted ion from Scan in SIFI





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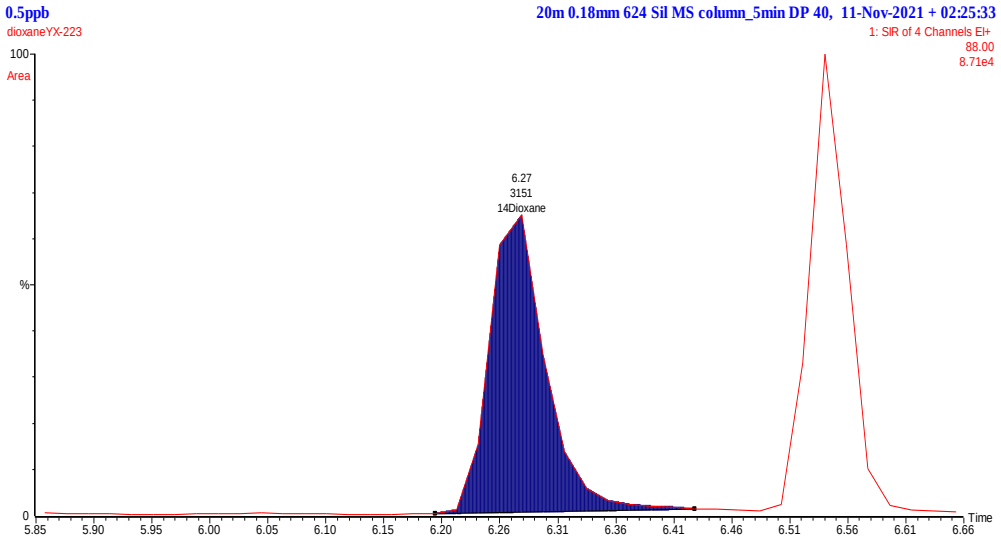
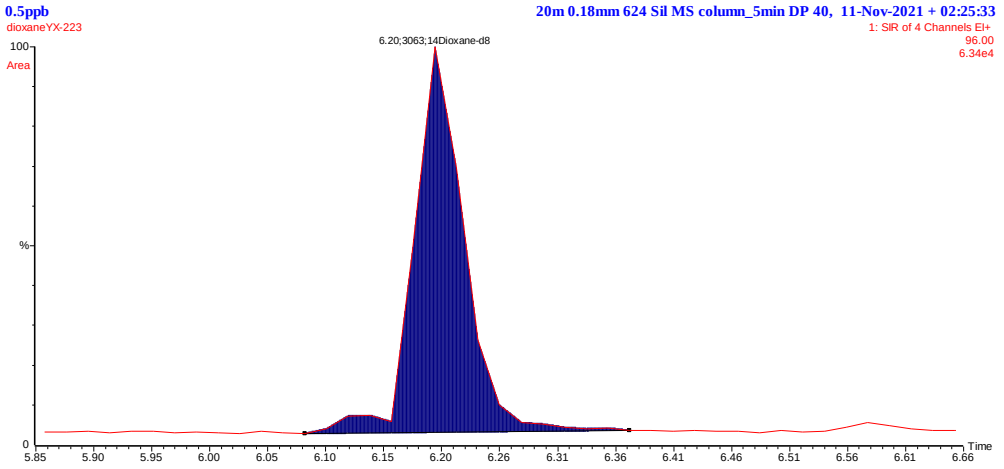
0.5ppb 1,4 Dioxane and 1,4 Dioxane-d8 SIM ions from SIFI

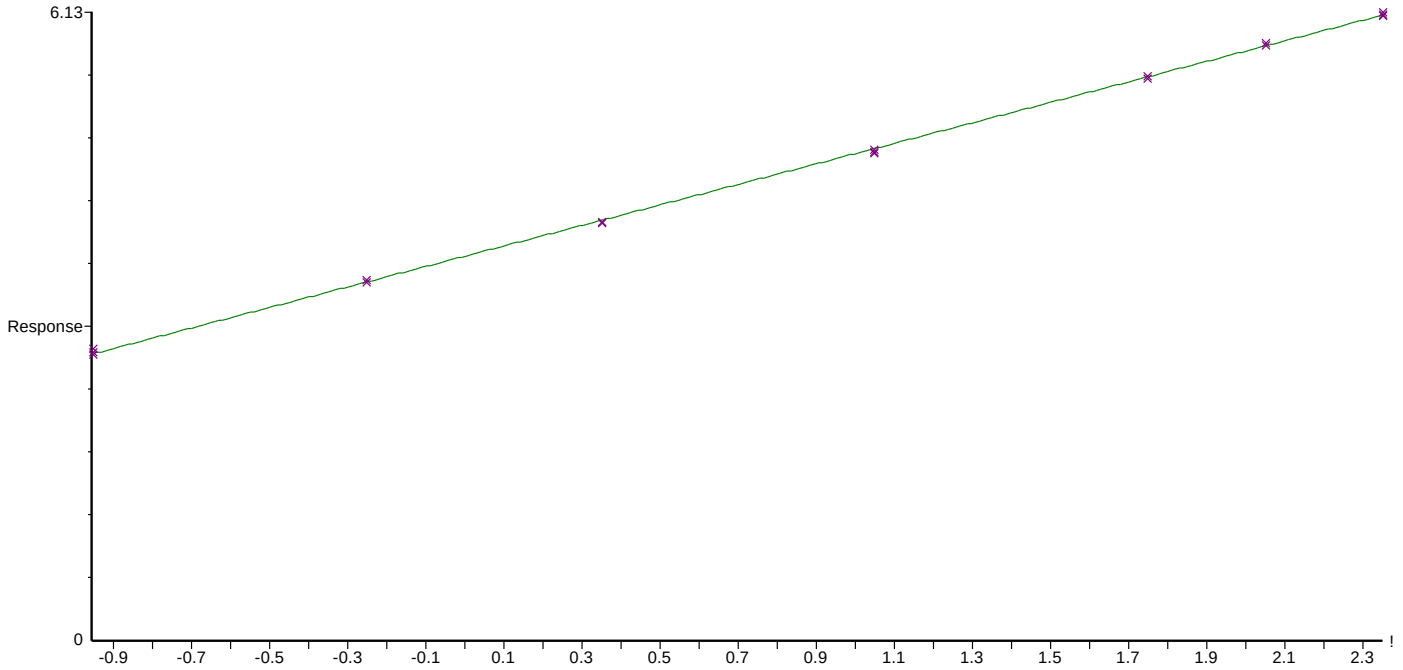




1,4 Dioxane Calibration curve LOG

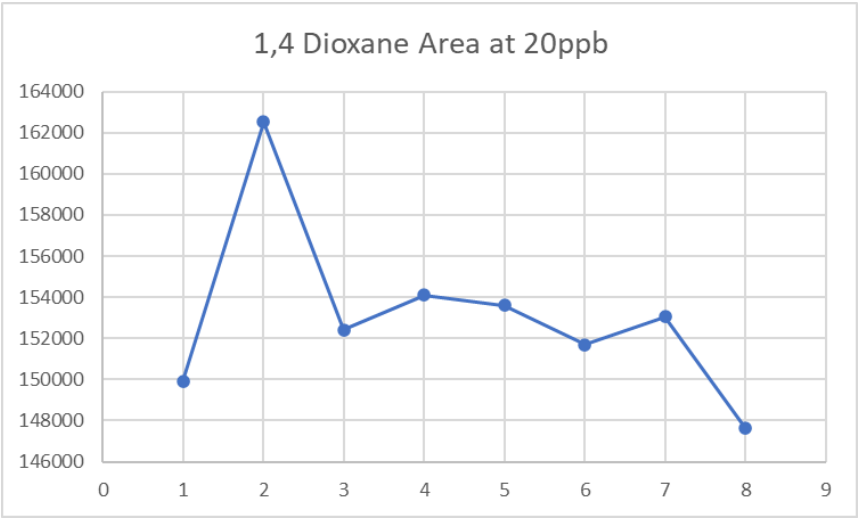
20ppb **20m 0.18mm 624 Sil MS column_5min DP 40, 05-Nov-2021 + 15:02:00**

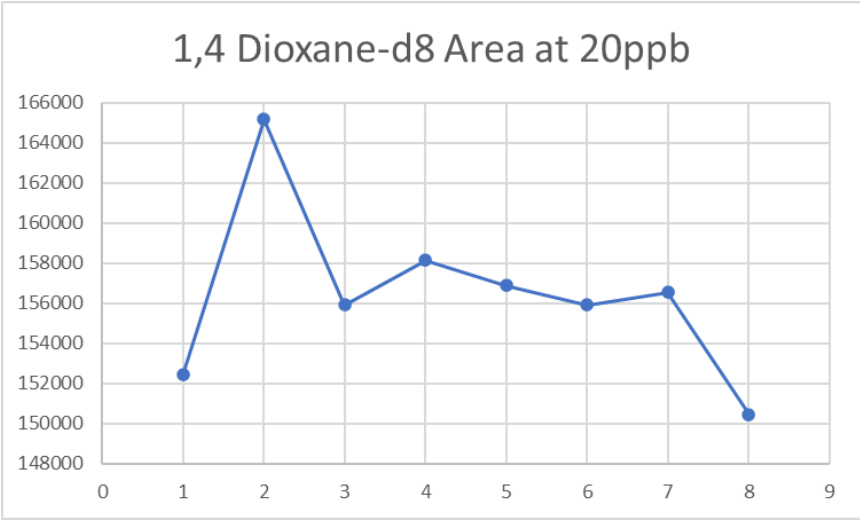
Compound 1 name: 14Dioxane
Correlation coefficient: r = 0.999806, r^2 = 0.999611
Calibration curve: 1.00269 * x + 3.80040
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: Null, Axis trans: Log



%RSD with External Standard

Compound 1: 14Dioxane											
#	Name	ID	Type	Std Conc	RT	Response	!				
108	dioxaneCA	new salt 2	Analyte		6.255	149933.7	19.57				
109	dioxaneCA	new salt 2	Analyte		6.255	162534.3	21.21		all 10		
110	dioxaneCA	new salt 2	Standard	20	6.255	152417.2	19.89		average	153123	
111	dioxaneCA	new salt 2	Standard	20	6.255	154108.6	20.11		stdev	4073.909	
112	dioxaneCA	new salt 2	Analyte		6.255	153615.6	20.05		%RSD	2.660547	
113	dioxaneCA	new salt 2	Analyte		6.255	151696.1	19.8				
114	dioxaneCA	new salt 2	Analyte		6.274	153057.8	19.97				
115	dioxaneCA	new salt 2	Analyte		6.274	147620.5	19.26				
Compound 2: 14Dioxane-d8											
#	Name	ID	Type	Std Conc	RT	Response	!				
108	dioxaneCA	new salt 2	Analyte		6.199	152423.8	19.41				
109	dioxaneCA	new salt 2	Analyte		6.199	165174.1	21.04		all 10		
110	dioxaneCA	new salt 2	Standard	20	6.199	155916.1	19.86		average	156431.1	
111	dioxaneCA	new salt 2	Standard	20	6.199	158152.2	20.14		stdev	4061.379	
112	dioxaneCA	new salt 2	Analyte		6.199	156876.9	19.98		%RSD	2.596273	
113	dioxaneCA	new salt 2	Analyte		6.199	155899.9	19.86				
114	dioxaneCA	new salt 2	Analyte		6.199	156552.8	19.94				
115	dioxaneCA	new salt 2	Analyte		6.199	150453.1	19.16				





Excellent repeatability

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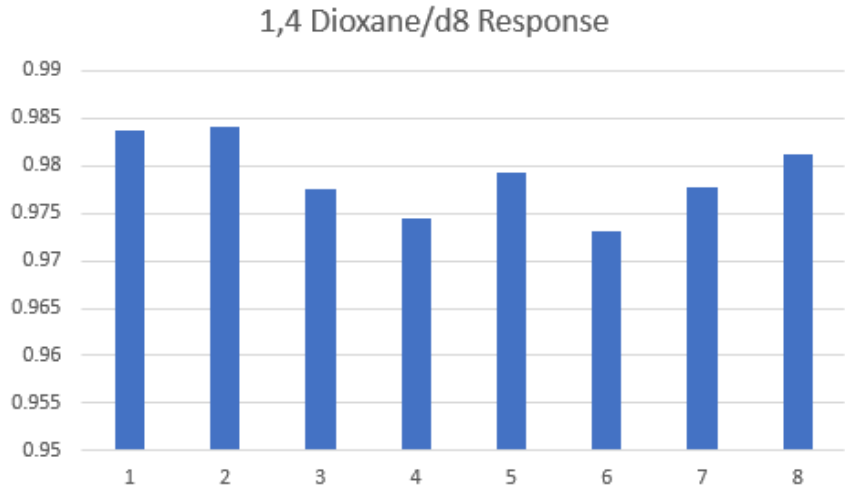
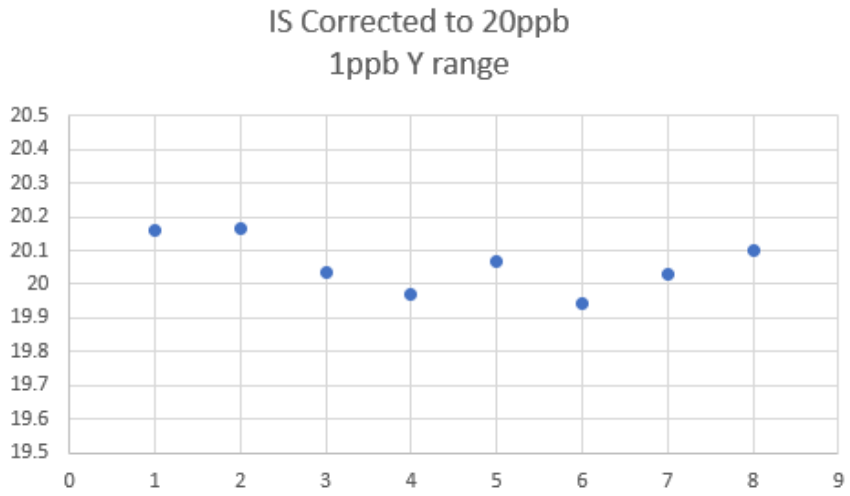
Recalculate using d-8 as Internal Standard

- As expected, the use of internal standard greatly improves the % RSD to less than 0.4%.

1,4 Dioxane	d8	
149933.656	152423.8	0.983663
162534.266	165174.1	0.984018
152417.156	155916.1	0.977559
154108.594	158152.2	0.974432
153615.609	156876.9	0.979211
151696.063	155899.9	0.973035
153057.797	156552.8	0.977676
147620.516	150453.1	0.981173
	average	0.978846
	stdev	0.003738
	%RSD	0.381864





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Conclusions

- Sample run times are faster than most traditional methods
- Less sample prep vs 8270/522
- External standard provides excellent results without extra cost associated with the use of an expensive d8 IS.
- The HSTrap method provides excellent detection limits as compared to the current environmental methods