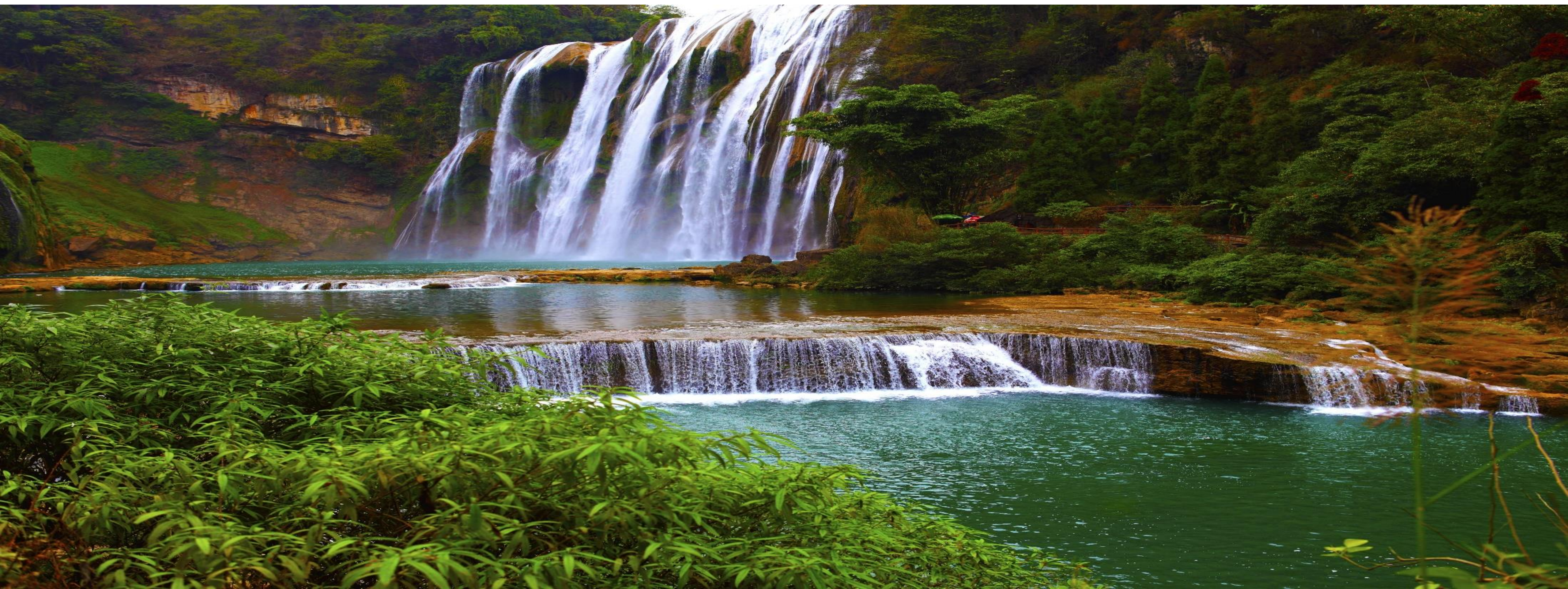


Faster, Greener and more productive: EPA Methods 8260 and 524.3



The NEMC Conference: August 1st, 2022: Arlington, VA

Lee Marotta, PerkinElmer and Jacob Rebholz, Roger Bardsley and Tom Hartlein, Teledyne Tekmar



Space

Gas	Abundance (%)
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon Dioxide	0.04
Neon	0.0018
Helium	0.00052
Methane	0.00017
Krypton	0.00011
Hydrogen	0.000055
Water	~ 1

Earth



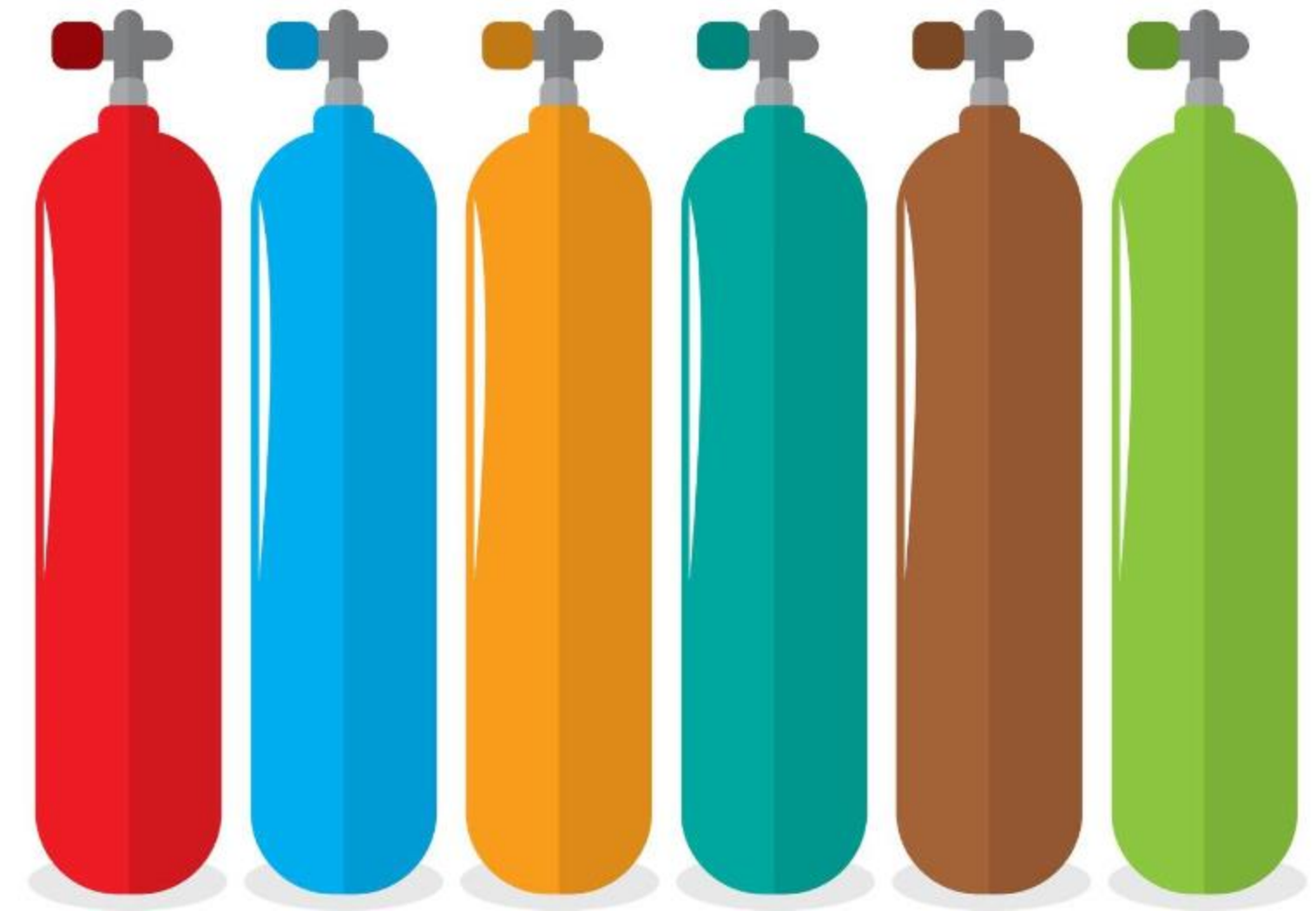
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Krypton	0.00011
Hydrogen	0.000055
Water	~ 1

Application Usage

Application	Usage (%)
Lifting	15.1
Magnetic Resonance Imaging (MRI)	15.0
Welding	14.9
Chromatography	7.6
Heat Transfer	6.4
Leak Detection	5.6
Pressurizing	5.5
Fibre Optics	4.1
Diving Mixtures	4.0
Superconductors	2.9
Inert Atmospheres	2.7
Nuclear Magnetic Resonance (NMR)	1.3
Other	14.9

Should Chromatographers Be Investigating Alternate Carrier Gases?

- Shortage appears to be more severe
- \$\$\$ is very high
- Preserve Helium for other uses

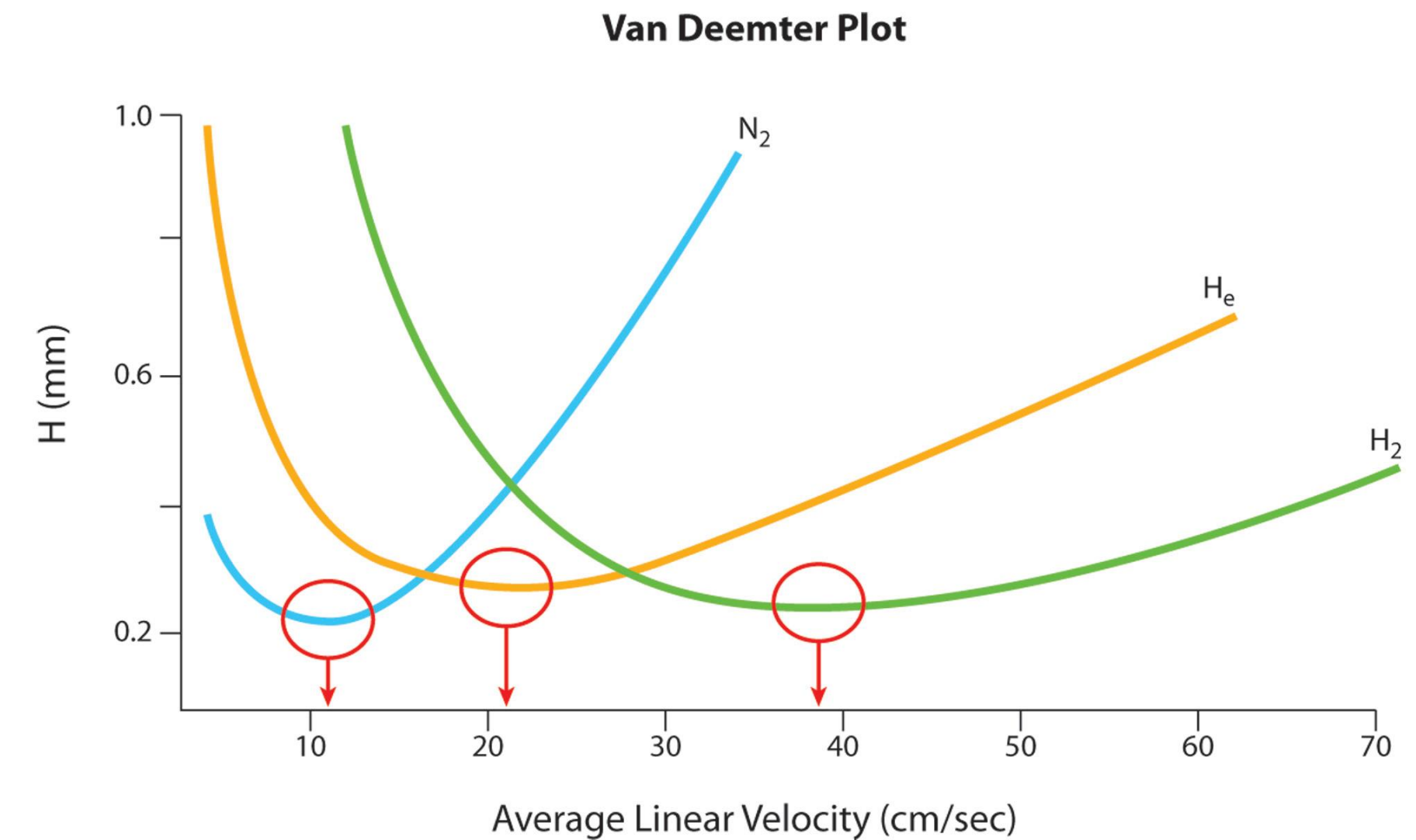




Performance

Challenges That Were Resolved

- Hydrogen:
 - Possible protonation
 - 2 to 4 times reduction in response
- Nitrogen:
 - Chromatography efficiency
 - 15 times reduction in response



Slide courtesy of Restek Corporation

Tidbits to Consider

Parameter	Helium	Hydrogen	Nitrogen
Safety	Safe	Caution	Safe
Source	Cylinder	Cylinder or Generator	Cylinder or Generator
Cost	Expensive	Cost Effective	Cost Effective
Supply	Concern	n/a	n/a
Inertness	Inert	Highly Reactive	Inert
BFB	Passes	Passes	Passes

Experiments

Comparing carrier gases

- Chromatographic Efficiency
- Meeting criteria for methods 524 and 8260
- Productivity

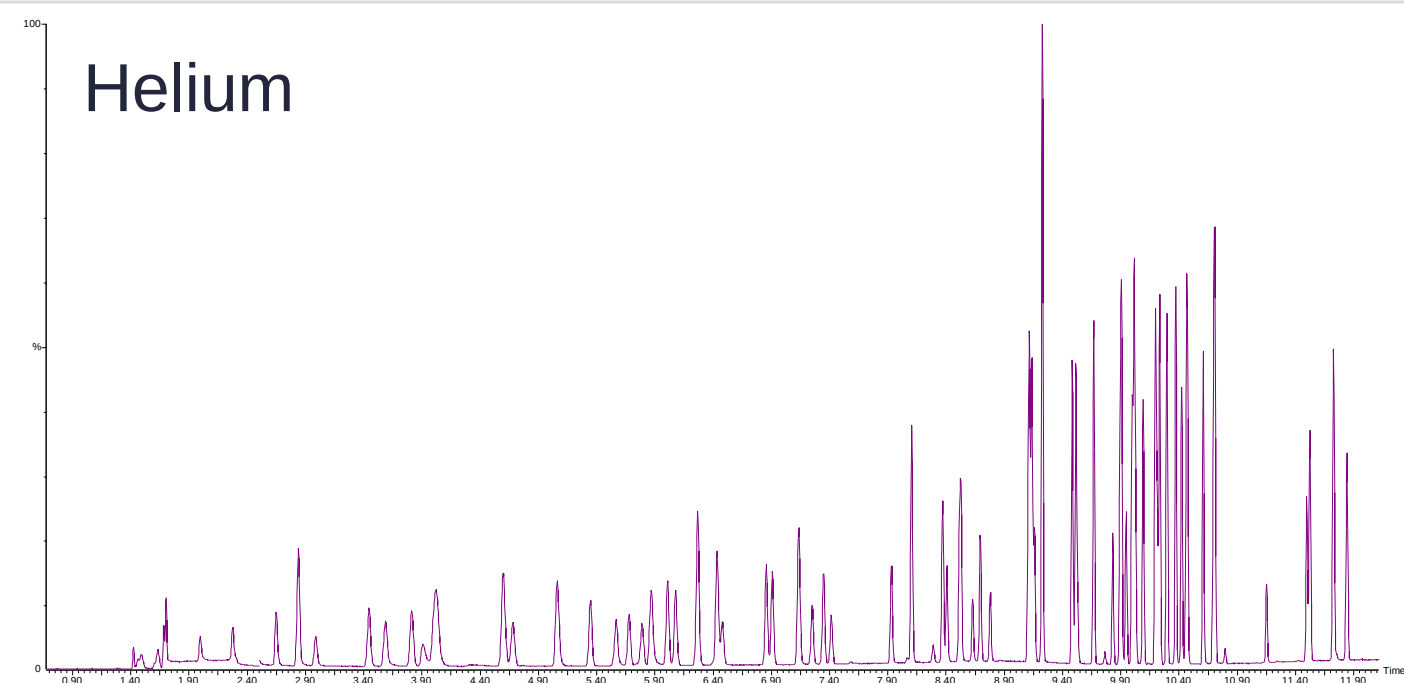


The PerkinElmer
Clarus SQ 8 GCMS

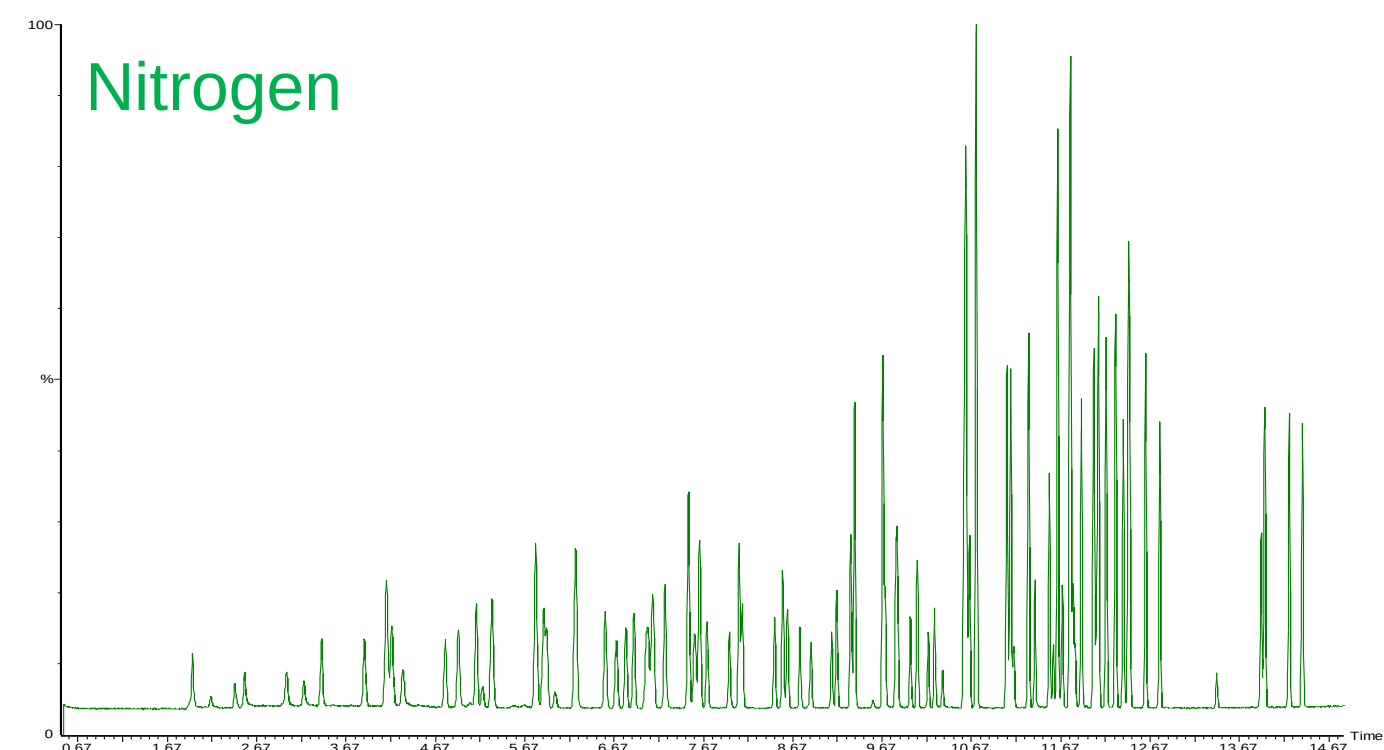
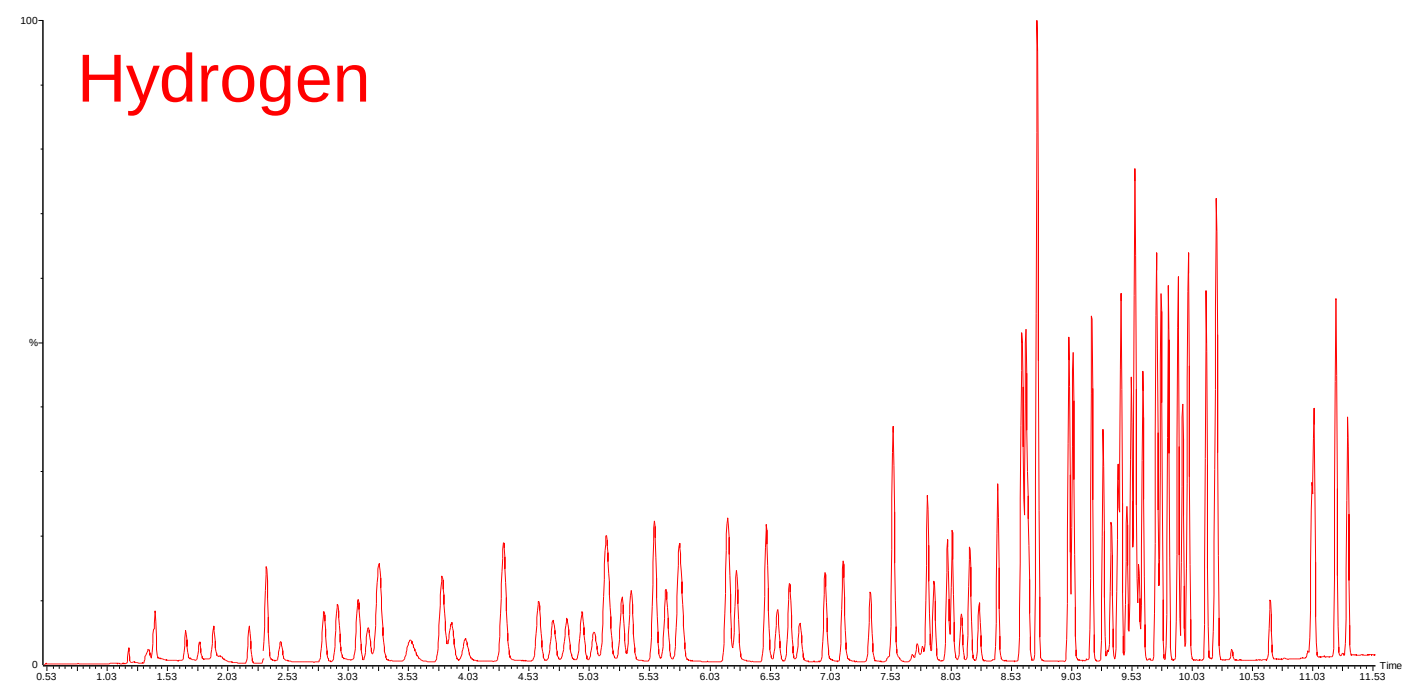


The Teledyne Tekmar
Atomx xyz Purge and Trap

US EPA Method 8260 Chromatography



Peak Resolution for Nitrogen is Excellent!





Methods 524 and 8260

US EPA 524.2 and 524.3

- Meet tune criterion
- Chromatographic efficiency
- 0.2 ppb requirements
- Signal to noise above 30 to one or better
- Ensuring quantification meets method requirements
- Linear to 0.2 ppb (reporting limit)
- Additional Initial Demonstration of Capability (IDC)
- Precision at mid-point
- MDL
- LPIR and UPIR



Meeting Tune Criterion: Bromofluorobenzene (BFB): Used 524.2

Mass	Ref Mass	Range	Relative Abundance (%)		
			Helium	Hydrogen	Nitrogen
50	BPI	Report only	16.1	15.9	17.1
75	BPI	Report only	45.6	51.7	49.2
95	BPI	100%	100.0	100.0	100.0
96	95	$\geq 5\% \text{ -- } \leq 9\%$	6.4	6.5	7.5
173	174	$< 2\%$	0.4	0.6	0.8
174	95	$>50\% \text{ -- } < 100\%$	83.9	75.8	83.2
175	174	$\geq 5\% \text{ -- } \leq 9\%$	6.6	6.2	7.3
176	174	$>95\% \text{ -- } <105\%$	99.8	101.4	97.8
177	176	$\geq 5\% \text{ -- } \leq 10\%$	6.4	5.4	6.9

Linearity and Reporting Limit (readable list)

Method Linear Range: 0.2 to 50 ppb

Carrier	Helium			Hydrogen			Nitrogen		
Compound Name	Linearity	0.2ppb std	S:N @ 0.2 ppb	Linearity	0.2 ppb std	S/N @ 0.2ppb	Linearity	0.2ppb std	S/N @ 0.2ppb
Vinyl Chloride	0.9999	0.21	470:1	0.9998	0.21	175:1	0.9998	0.19	55:1
1,3-Butadiene	0.9998	0.23	360:1	0.9996	0.20	73:1	1.0000	0.20	36:1
Carbon disulfide	1.0000	0.21	250:1	0.9999	0.23	222:1	1.0000	0.20	230:1
Methylene chloride	0.9999	0.20	440:1	0.9999	0.20	93:1	1.0000	0.20	480:1
Methyl tert-Butyl Ether	0.9999	0.20	110:1	0.9994	0.21	350:1	0.9999	0.19	68:1
Chloroform	0.9999	0.19	260:1	1.0000	0.22	85:1	1.0000	0.20	308:1
Benzene	0.9998	0.20	120:1	1.0000	0.21	460:1	1.0000	0.21	134:1
Toluene	1.0000	0.20	550:1	1.0000	0.20	454:1	0.9999	0.18	208:1
Chlorobenzene	1.0000	0.22	320:1	0.9999	0.22	845:1	0.9998	0.17	257:1
1,2-Dichlorobenzene	1.0000	0.21	450:1	1.0000	0.20	484:1	0.9999	0.23	186:1
Naphthalene	1.0000	0.21	820:1	0.9996	0.24	367:1	0.9998	0.24	246:1

Precision at Midpoint (20 ppb), LPIR and UPIR

Carrier Gas	Helium			Hydrogen			Nitrogen		
Compound Name	%RSD @ midpoint	LPIR	UPIR	%RSD @ midpoint	LPIR	UPIR	%RSD @ midpoint	LPIR	UPIR
Vinyl Chloride	3.9	73	126	7.6	78	105	6.9	56	128
1,3-Butadiene	3.7	84	133	2.3	75	100	2.1	67	126
Carbon disulfide	5.1	54	92	3.2	96	115	3.4	88	130
Methylene chloride	3.0	70	112	4.7	87	100	4.6	74	123
Methyl tert-Butyl Ether	1.5	86	116	3.7	97	105	3.3	72	130
Chloroform	1.7	62	111	1.9	93	110	2.2	85	133
Benzene	2.1	77	96	2.3	78	105	2.0	73	111
Toluene	1.7	89	127	4.7	82	100	2.1	67	98
Chlorobenzene	1.5	105	145	2.0	84	133	2.2	68	79
1,2-Dichlorobenzene	1.4	87	131	1.7	82	113	1.2	90	103
Naphthalene	0.6	79	128	1.1	103	120	0.9	107	134



US EPA Method 8260 Comparing Three Carrier Gases

Performance Using Helium and Hydrogen

Compound	Helium using 125:1 split ratio				Hydrogen using 70:1 split ratio			
	Linear r^2	S:N at RL 0.2 ppb	% RSD @ 20 ppb	% Recovery	Linear r^2	S:N at RL 0.2 ppb	% RSD @ 20 ppb	% Recovery
Vinyl Chloride	0.9994	470:1	3.86	97.2	0.9997	720:1	7.57	99.7
1,3-Butadiene	0.9990	360:1	3.72	100.7	0.9992	380:1	2.26	99.1
Carbon disulfide	0.9992	250:1	5.05	89.4	0.9977	280:1	3.24	92.9
Methylene chloride	0.9991	440:1	3.01	97.1	0.9989	270:1	4.71	105.1
Methyl tert-Butyl Ether	0.9999	110:1	1.52	96.6	0.9996	540:1	3.75	99.1
Chloroform	0.9999	260:1	1.68	94.8	0.9997	150:1	1.89	95.3
Benzene	0.9997	120:1	2.08	95.8	0.9997	620:1	2.31	97.7
Toluene	0.9996	550:1	1.67	100.5	0.9996	840:1	4.65	95.4
Chlorobenzene	0.9998	320:1	1.54	99.8	0.9999	845:1	1.96	96.0
1,2-Dichlorobenzene	0.9999	450:1	1.44	105.5	0.9996	585:1	1.68	97.2
Naphthalene	0.9997	230:1	0.63	100.5	0.9994	700:1	1.06	98.9

Results in Nitrogen: 8260

Mass	Ref Mass	Range	Relative Abudnace
			Nitrogen
50	95	15 to 40 %	17.1
75	95	40 to 60	47.1
95	BPI	100%	100.0
96	95	5 to 9 %	6.8
173	174	< 2%	0.9
174	95	>50%	81.0
175	174	5% to 9%	6.6
176	174	>95% -- <101%	98.6
177	176	5% to 9%	5.6

Results in Nitrogen: 8260

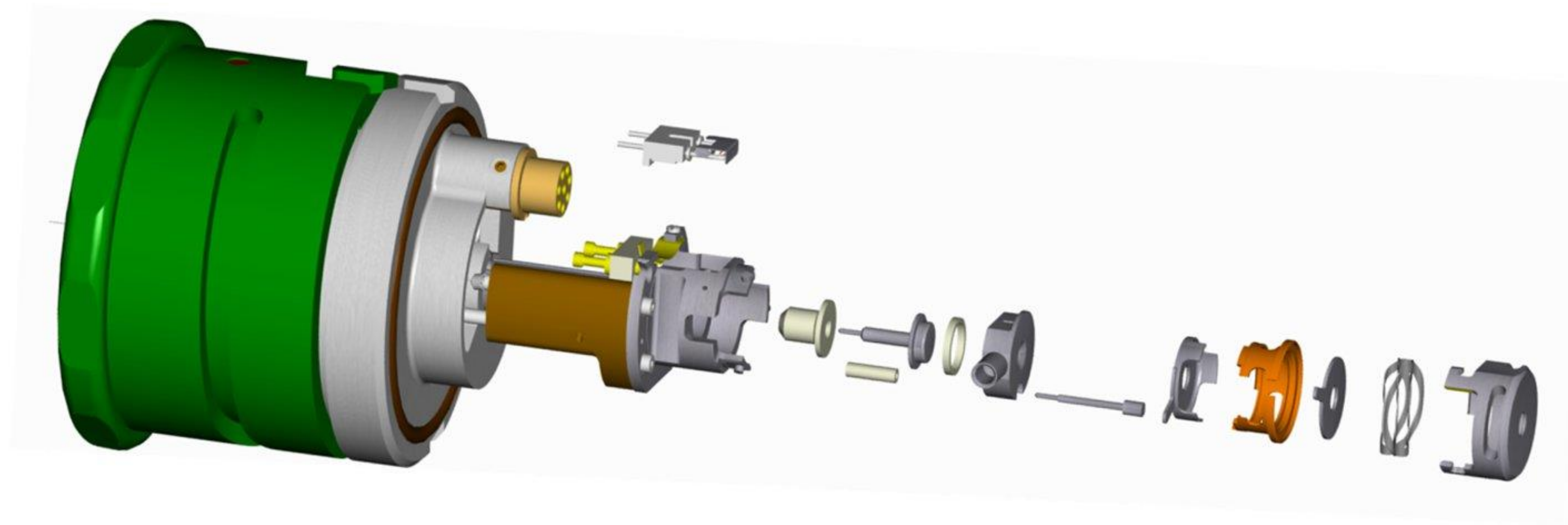
Compound Name	%RSD Calibration 0.5 to 200 ppb	Correlation Coefficient 0.5 to 200 ppb	S/N @ 0.5 ppb	%RSD @ 0.5ppb (n=7)
Vinyl Chloride	4.81	0.9999	95:1	4.70
Methylene chloride	6.50	0.9999	100:1	6.28
Methyl tert-Butyl Ether (MTBE)	3.57	0.9991	380:1	6.49
1,1-Dichloroethane	3.24	0.9997	431:1	8.69
Chloroform	3.83	0.9997	225:1	9.25
Carbon Tetrachloride	8.65	0.9995	132:1	11.36
1,1,1-Trichloroethane	3.42	0.9995	225:1	5.69
Benzene	4.36	0.9999	400:1	6.85
Toluene	3.14	0.9998	410:1	8.42
Chlorobenzene	5.16	0.9999	615:1	9.89
Ethylbenzene	8.27	0.9999	506:1	5.89
n-Butyl Benzene	3.00	0.9999	572:1	6.99
1,2-Dichlorobenzene	2.90	1.0000	605:1	5.25
1,2,4-Trichlorobenzene	2.83	0.9999	318:1	7.41
Naphthalene	6.38	0.9999	395:1	8.35



Productivity: enhancing uptime and sample throughput

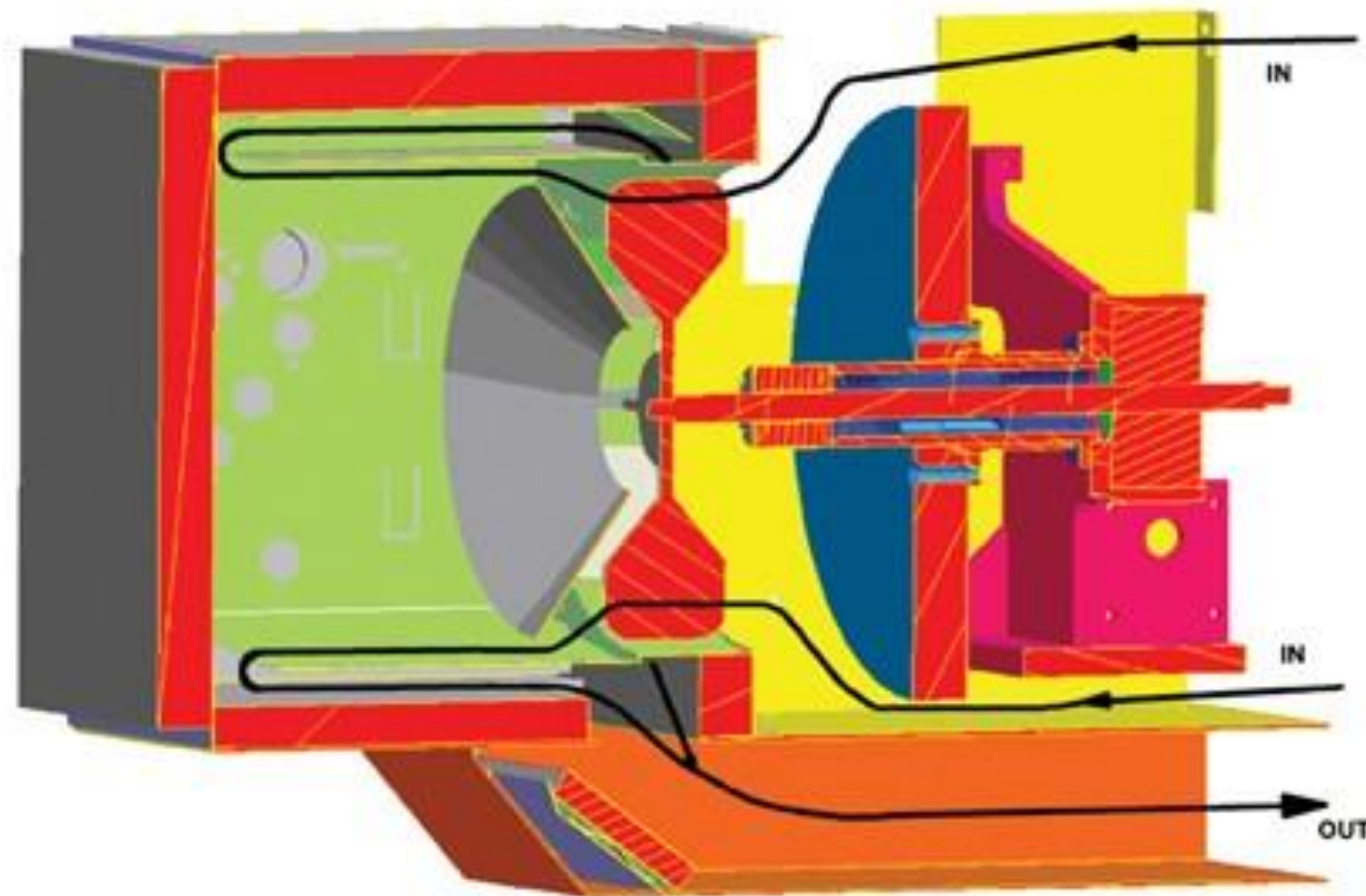
Easy to Use and Maintain: SMARTSource

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in under 5 minutes
with no tools

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Optimized Air Flow Paths allow fastest oven heat up and cool down rates

- Increase sample throughput
- Enhance column performance

- Shortest injection-to-injection time with a high-performance oven
- FASTEST available cool down rates
- Fast oven heat up rates allowing faster chromatography
- Optimal air flow paths for thermal accuracy throughout oven
- More oven program steps – 10 oven temperature program steps support the most demanding chromatography applications
- Autosampler sample pre-rinse during cooldown enhances productivity by reducing injection-to-injection time

Future Work

- Enhancing water management
- Improving detection limits
- Faster chromatography

Thank you



The PerkinElmer
Clarus SQ 8 GCMS



The Teledyne Tekmar
Atomx xyz Purge and Trap

- Questions please 😊
- Contact info:
- lee.marotta@perkinelmer.com