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Analysis of VOCs by EPA 524.4 with Nitrogen as Purge and Carrier Gas

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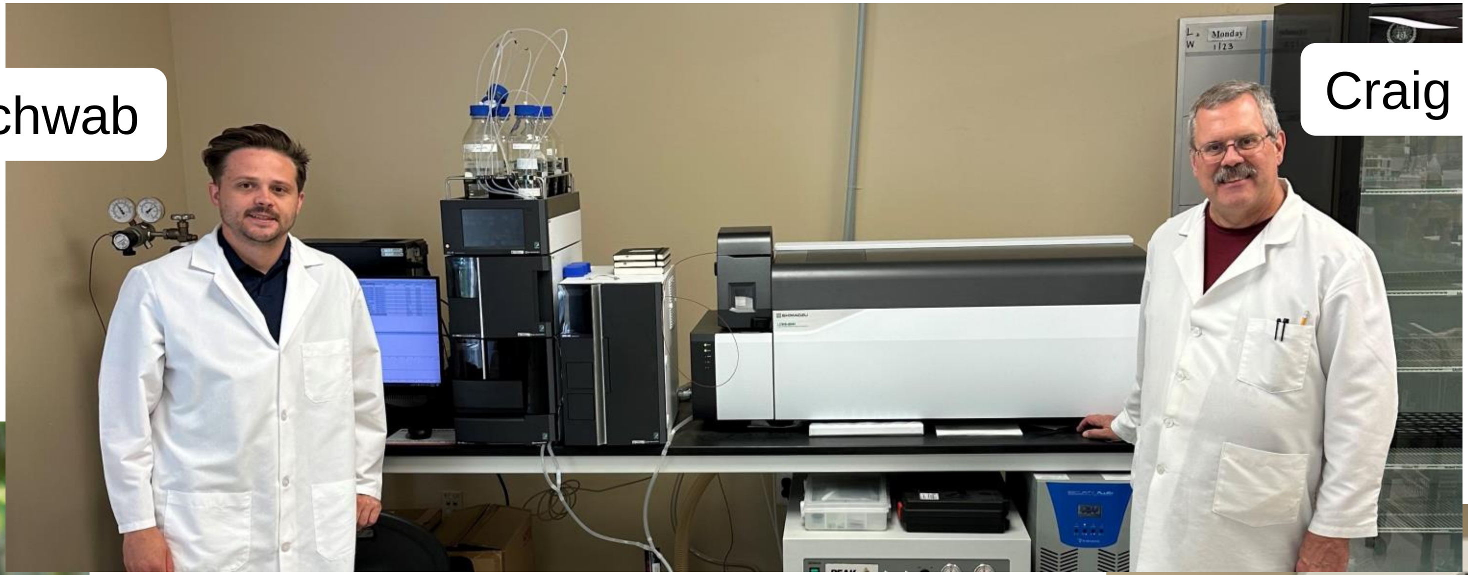
Team



Andrew Schwab

Craig Hudson

Adam Weltz, CEO

Criterion

The Lab Team

Today's presentation

1. Why VOCs with nitrogen?
2. Experimental plan
3. Results
4. Take-home messages
5. Q&A

An alternative to helium is essential!

Why would you want to run EPA 524.4 with nitrogen?

Benefits of using nitrogen
Can be used as carrier gas
Abundant
Inexpensive
Easy to obtain
Less safety concerns than hydrogen

Why would you want to run EPA 524.4 with nitrogen?

Benefits of using nitrogen	Challenges of using nitrogen
Can be used as carrier gas	Maintain proper GCMS operation
Abundant	Achieve overall desired sensitivity
Inexpensive	Minimize baseline noise
Easy to obtain	Pass BFB tune
Less safety concerns than hydrogen	Gain acceptance in community

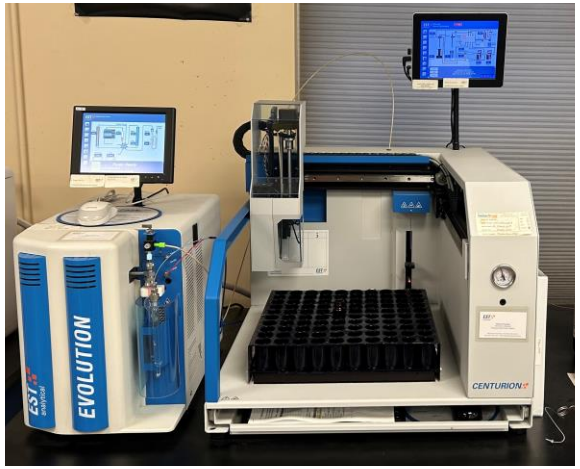
Experimental plan

GOAL: Demonstrate the method performance according to EPA Method 524.4 while using nitrogen as purge and carrier gas

Reduce

Challenges of using nitrogen
Maintain proper GCMS operation
Achieve overall desired sensitivity
Minimize baseline noise [start acquisition at m/z 45]
Pass BFB tune
Gain acceptance in community

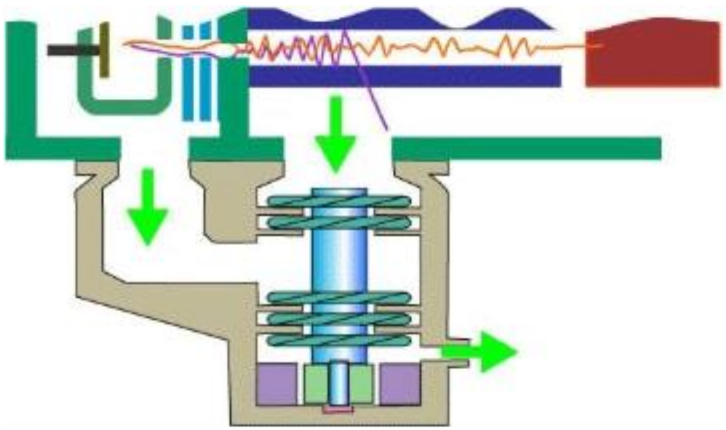
Instrumentation & optimized method



Nexis GC-2030 conditions	
Injection Temp.	200 °C
Injection Mode	Split (1:50)
Column Flow	0.8 mL/min
Flow Control Mode	Linear Velocity
Column	Restek Rtx-VMS (30m x 0.25 mm, 1.4 µm)
Oven Temp.	35 °C (4 min) → 14 °C/min to 220 °C (2 min)
Carrier Gas	Nitrogen
GCMS QP2020 NX conditions	
Solvent Cut Time	1 min
Ion Source Temp.	200 °C
Interface Temp.	220 °C
Detector Voltage	1.1 kV (Relative)
P&T EST Evolution and Centurion Autosampler	
Trap	Vocarb 3000 (K Trap)
Trap ready Temp	35 °C
Mort ready Temp	39 °C
Desorb Temp	250 °C
Trap bake Temp	260 °C
Mort bake Temp	210 °C
Purge Flow Rate	Nitrogen, 60 mL/min
Dry Purge Flow Rate	Nitrogen, 40 mL/min
Desorb Time	1 min
Bake Time	8 min
Dry Purge Time	1 min
Purge Time	11 min
Sample loop size	5 mL
Surrogate and IS Volume	5 µL

Challenge 1 – GCMS operation

CHALLENGE 1:
Maintain proper GCMS operation, with an optimized flow of nitrogen and enough vacuum for achieving the sensitivity required in the method

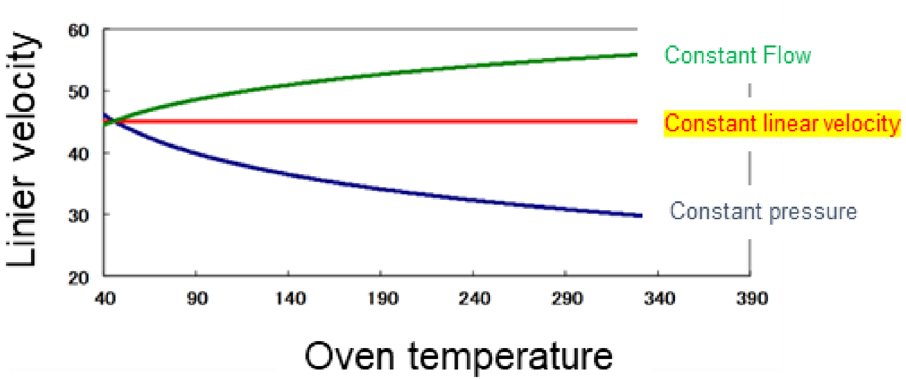


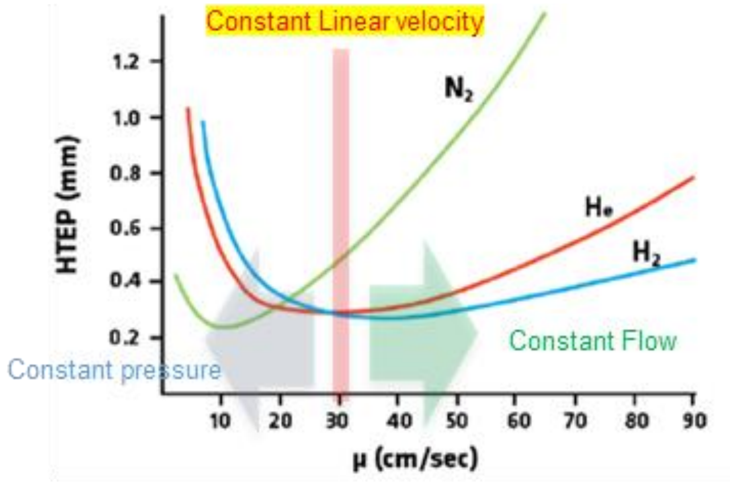
SOLUTION B:
Use a turbo molecular pump with sufficient power

Challenge 1 – GCMS operation

CHALLENGE 1:
Maintain proper GCMS operation, with an optimized flow of nitrogen and enough vacuum for achieving the sensitivity required in the method

SOLUTION B:
Use constant linear velocity gas control used to maintain good chromatography, with AART function for automatic RT updates



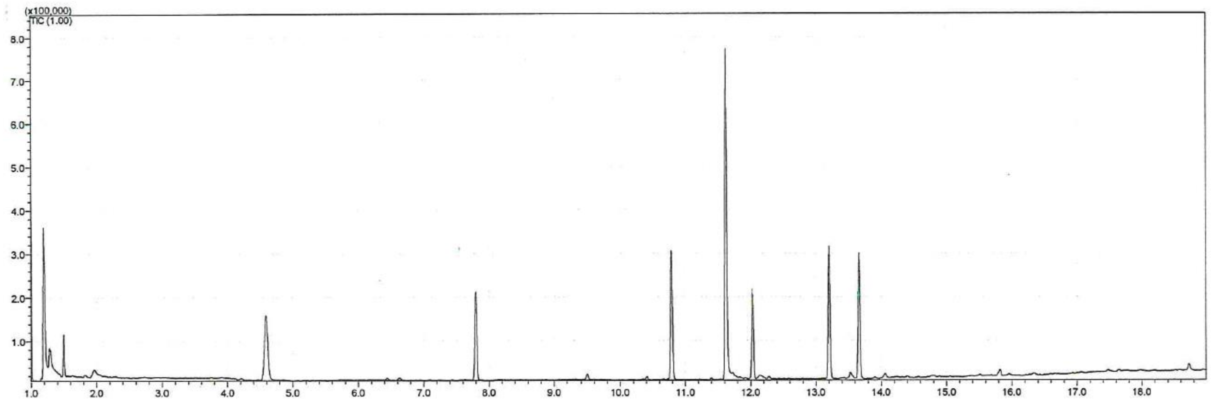


Challenge 2 – Overall desired sensitivity

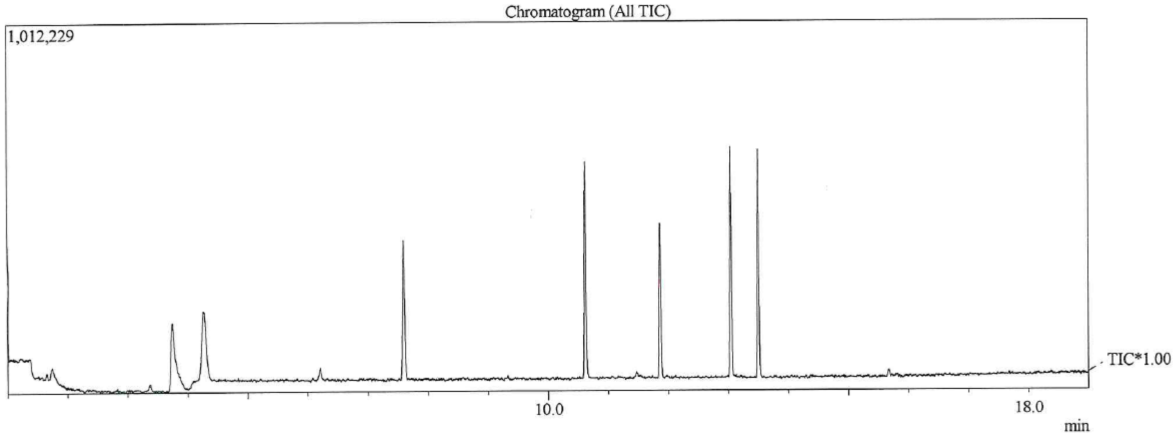
CHALLENGE 2:
Purging efficiency of nitrogen is lower than that of helium, hence, less mass of target compounds is transferred to GCMS

SOLUTION:
Increase the flow rate and purge temperature to improve the purging efficiency

Helium – optimized conditions



Nitrogen – optimized conditions



Challenge 3 – BFB Tuning

CHALLENGE 4:

BFB not passing the required criteria

TABLE 1. 4-BROMOFLUOROBENZENE (BFB) MASS INTENSITY CRITERIA

m/z	Required Intensity (relative abundance)
95	Base peak, 100% relative abundance
96	5 to 9% of *m/z* 95
173	Less than 2% of *m/z* 174
174	Greater than 50% of *m/z* 95
175	5 to 9% of *m/z* 174
176	Greater than 95% but less than 105% of *m/z* 174
177	5 to 10% of *m/z* 176

SOLUTION:

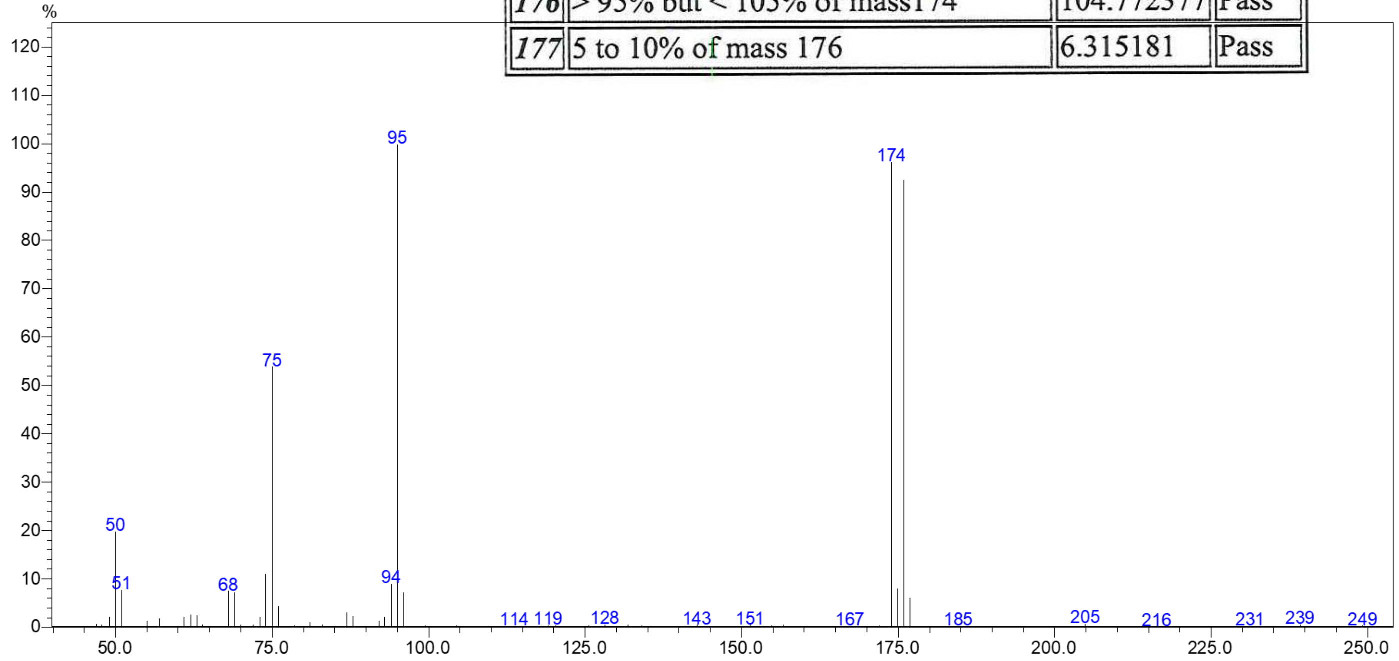
Change parameters (modified by user):

Raw section: Peak to peak, average 10

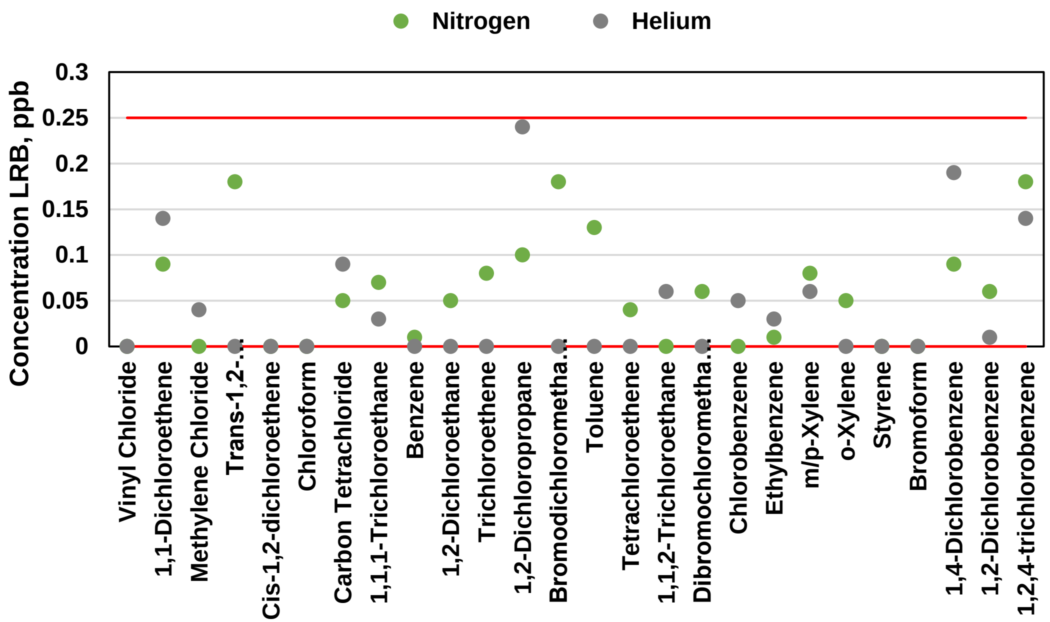
Background section:

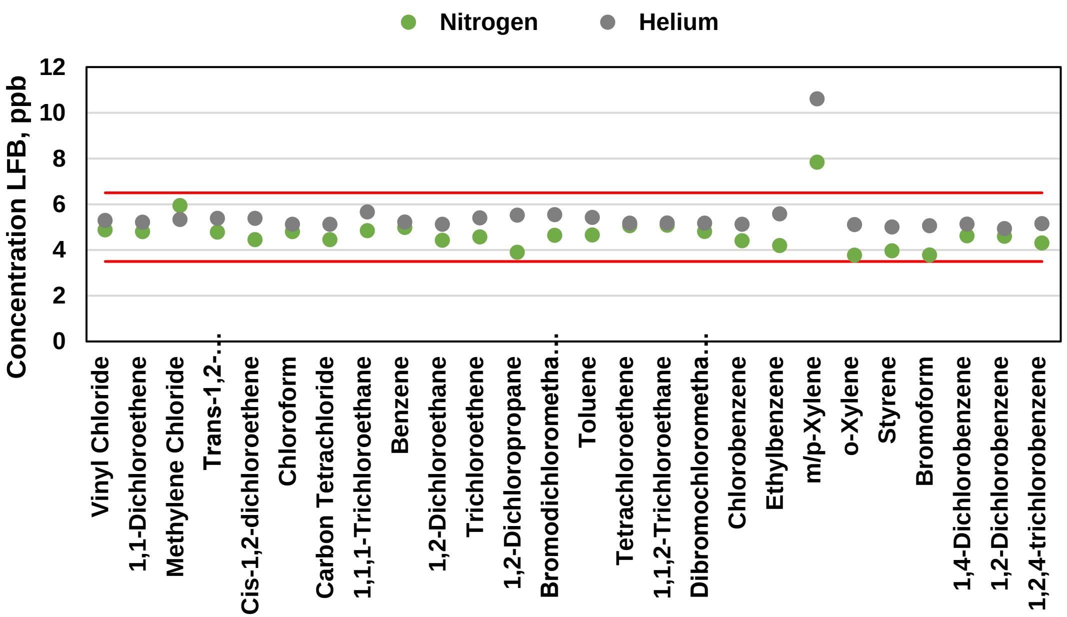
Peak Start Spectrum, average 4

m/z	*Spectrum Check Criteria*	*Result*	*Status*
95	Base Peak, 100% Relative Abundance	100.000000	Pass
96	5 to 9% of mass 95	7.840397	Pass
173	< 2% of mass 174	1.300455	Pass
174	> 50% of mass 95	89.658438	Pass
175	5 to 9% of mass 174	7.776758	Pass
176	> 95% but < 105% of mass174	104.772377	Pass
177	5 to 10% of mass 176	6.315181	Pass



Performance demonstration – LRB and LFB



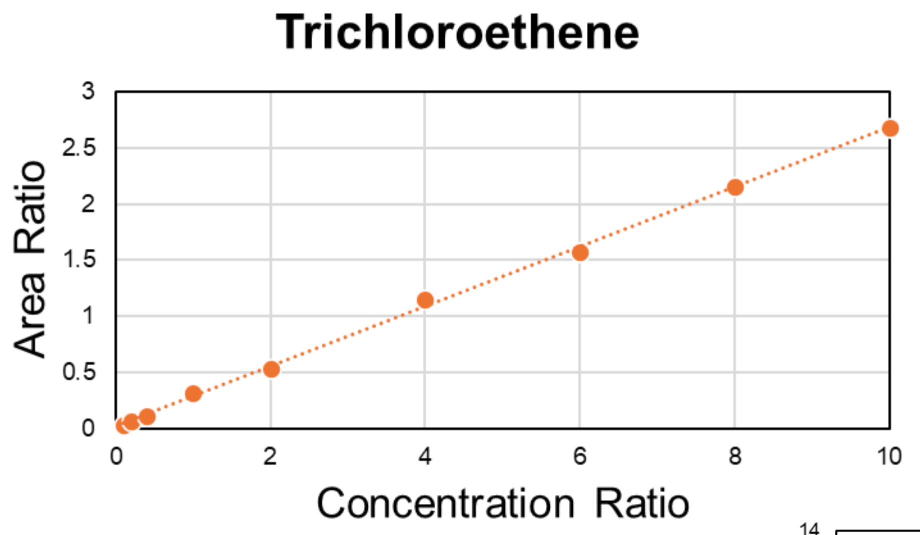


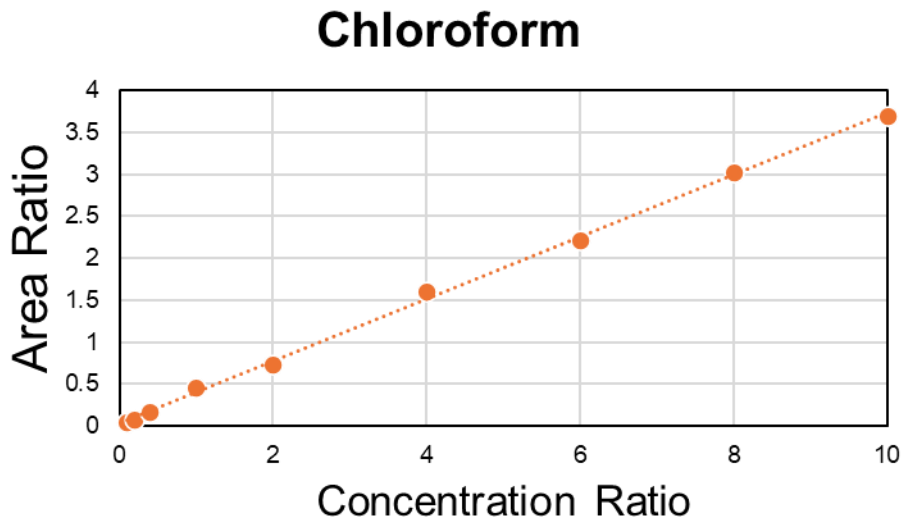
Acceptance range for LRB: non-detected to 0.25 ppb
Acceptable range LFB: 3.5 – 6.5 ppb

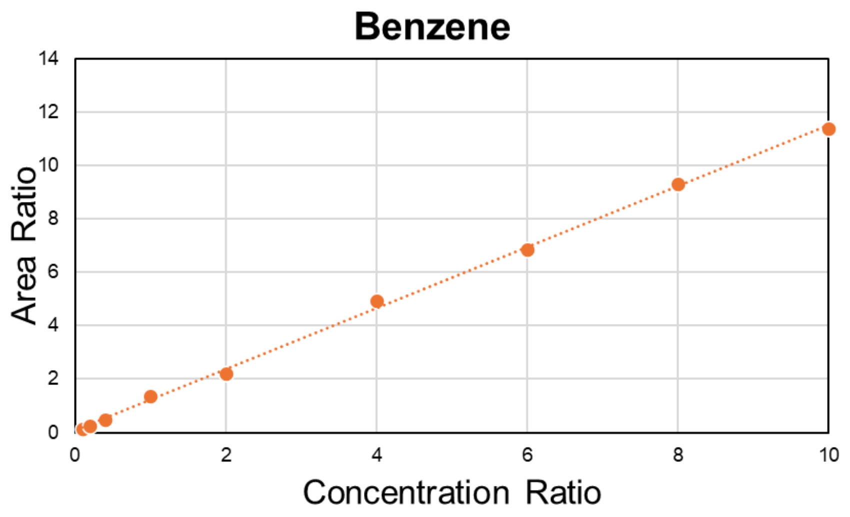
BOTH PASSED

Performance demonstration – Calibration Curves

All compounds showed acceptable calibration curves, similar results to those obtained using He



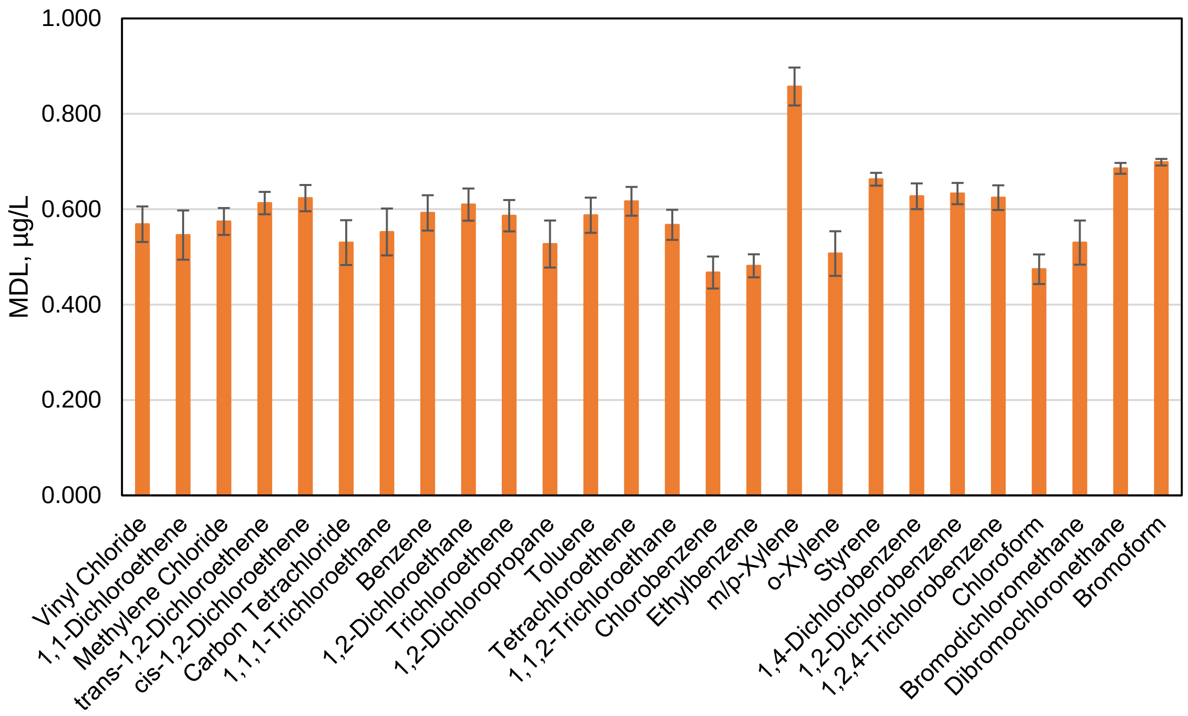




Performance demonstration – MDL

Compound Name	Calculated MDL, µg/L
Vinyl Chloride	0.117
1,1-Dichloroethene	0.162
Methylene Chloride	0.089
trans-1,2-Dichloroethene	0.074
cis-1,2-Dichloroethene	0.086
Carbon Tetrachloride	0.147
1,1,1-Trichloroethane	0.154
Benzene	0.117
1,2-Dichloroethane	0.106
Trichloroethene	0.104
1,2-Dichloropropane	0.155
Toluene	0.116
Tetrachloroethene	0.095
1,1,2-Trichloroethane	0.099
Chlorobenzene	0.105
Ethylbenzene	0.076
m/p-Xylene	0.125
o-Xylene	0.147
Styrene	0.042
1,4-Dichlorobenzene	0.085
1,2-Dichlorobenzene	0.070
1,2,4-Trichlorobenzene	0.081
Chloroform	0.10
Bromodichloromethane	0.15
Dibromochloronethane	0.04
Bromoform	0.02

All calculated MDLs passed criteria (≤0.5 µg/L) and were all <0.165 µg/L
Excellent precision and accuracy observed (n=7): %RSD <10%, 85-140%

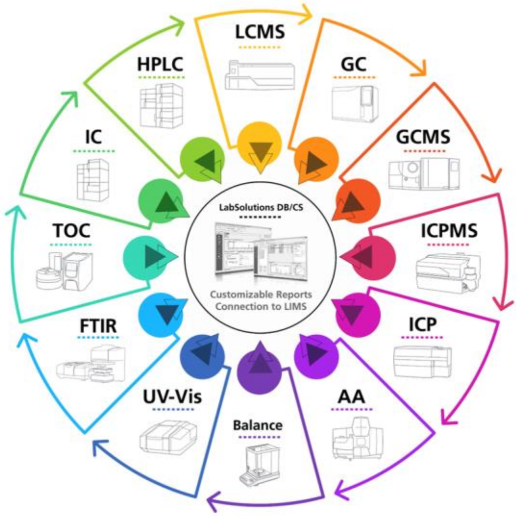


Take-Home Messages

- Challenges when using nitrogen as purge and carrier gas for method EPA 524.4 were successfully addressed.
- Performance of the method was demonstrated:
  - BFB tune
  - LRB and LFB
  - Calibration curves
  - MDLs

Passed acceptance criteria for accredited testing (detailed results not shown here), and two proficiency tests from the PA DEP, demonstrating early regulatory support

- Routine application of this method will enable environmental laboratories to continue supporting regulatory testing of VOCs, while minimizing the reliance on helium and reducing operating expenses (cost of nitrogen ~5 lower than cost of helium).



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