A Novel EI Source Optimized for Use with Hydrogen Carrier Gas in GC/MS and GC/MS/MS

NEMC 2022

Operational issues impacting the environmental laboratory industry

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Agilent
Trusted Answers

Helium

Helium remains the best carrier gas to use for GC/MS analysis, but…

- Supply shortages are becoming common
- Costs are rising
- Questions about sustainability are being raised

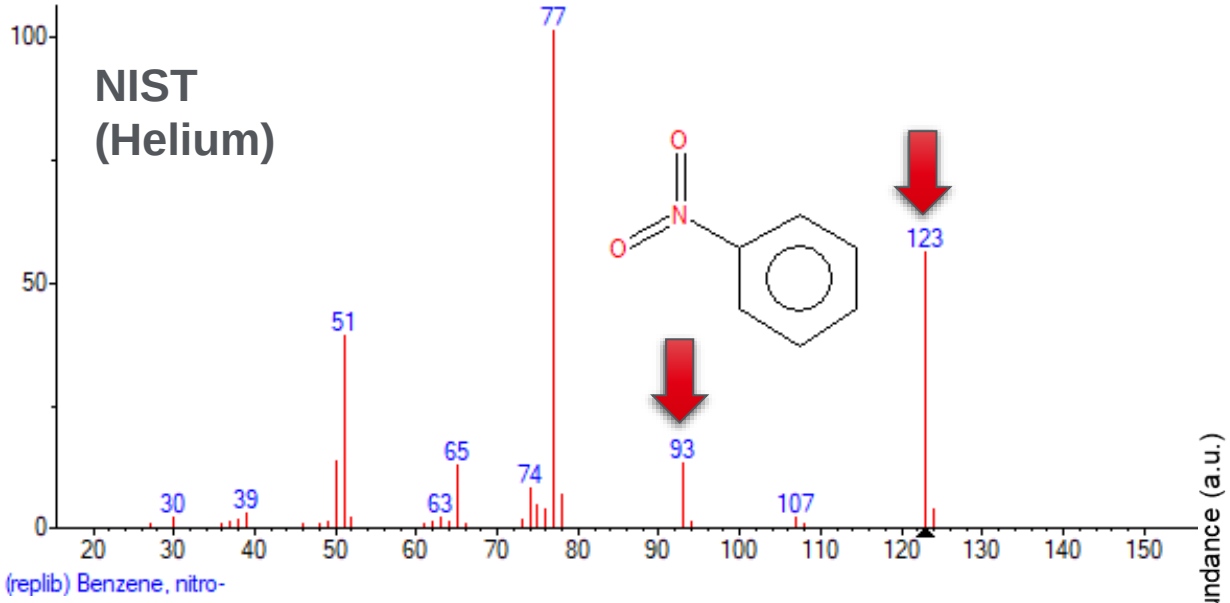
Reasons to use Hydrogen Carrier Gas

- Readily available (H_2 already used for FID and other detectors)
- Sustainable
- Lower Cost
- Cleans source during use
- Available on demand (H_2 generator) or by cylinder
- Faster analysis
- Lower temperature separation possible
- Move to “more efficient” columns
  - 30 m x 0.25 mm x 0.25 µm → 20m x 0.18 mm x 0.18 µm

But….

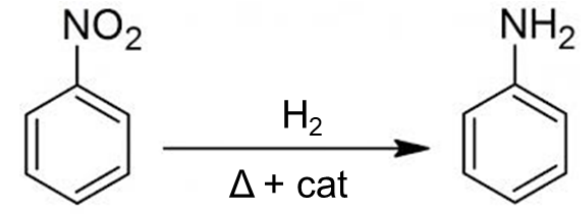
Source-Induced Problems with Hydrogen Carrier Gas: Nitrobenzene Conversion

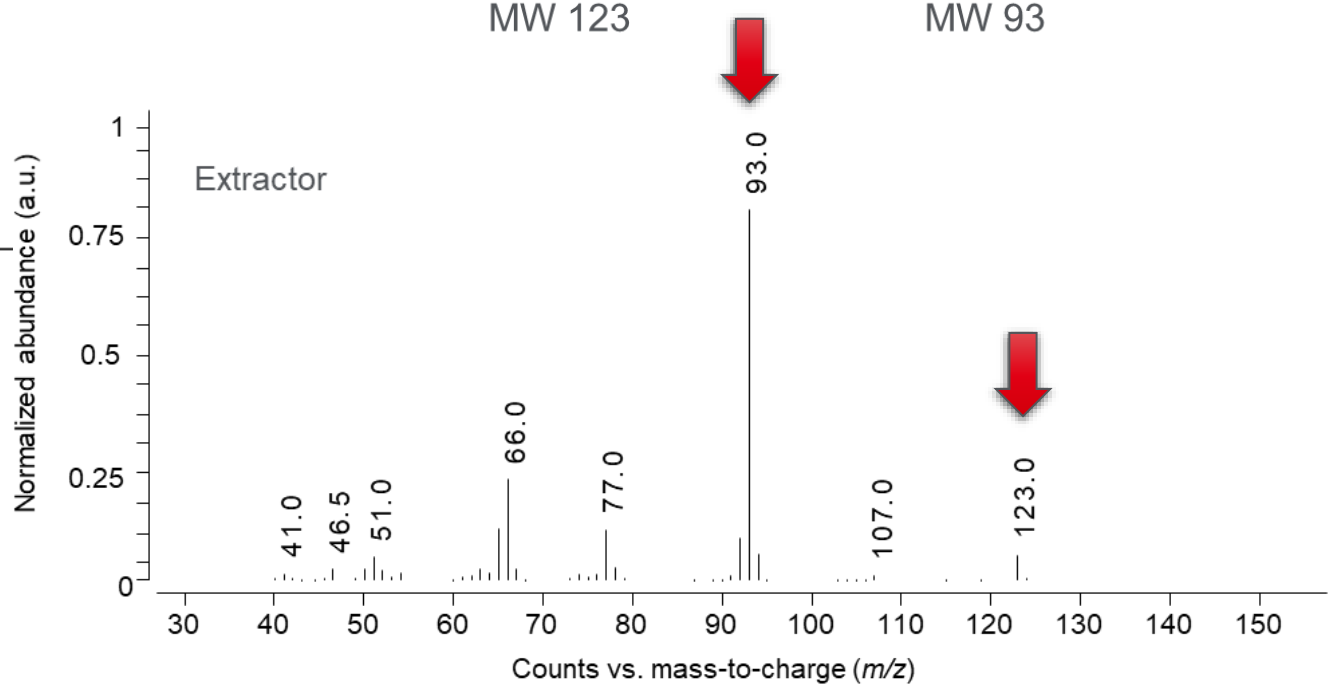
Expected mass spectrum



Conversion of nitrobenzene to aniline with H_2 carrier gas

What really happens with H_2

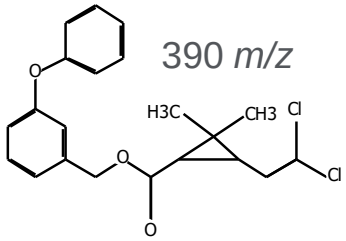




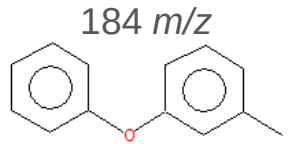
It’s Not Just Nitrobenzene…

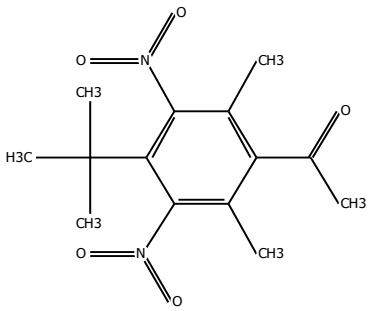
Compound Class	Example Compound(s)	H_2 Carrier Gas + Conventional GC/MS Source
Nitro compounds	Nitrobenzene, fenitrothion, ethalfluralin	Unacceptable
Heavily chlorinated compounds	DDT, endrin, heptachlor, BHC compounds, pentachlorophenol	Unacceptable
Polycyclic aromatic hydrocarbons (PAHs)	Benzo(b)fluoranthene, benzo[g,h,i]perylene,	Neutral
Alkanes >C24	Tetratriacontane, hexadecane, tetracontane	Neutral
Pesticides	Deltamethrin, fipronil, permethrin, captan	Unacceptable
Fragrance/flavor compounds	Musk ketone, musk ambrette, linalool	Unacceptable
Volatile organic compounds	1,4-dioxane, trichloromethane, bromodichloromethane	Neutral

Permethrin

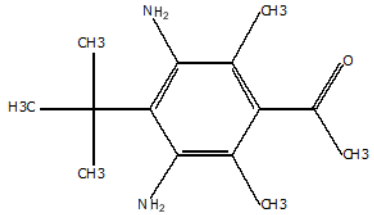


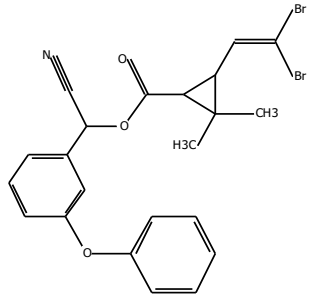
Phenoxytoluene



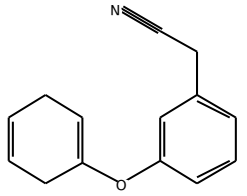


Musk ambrette



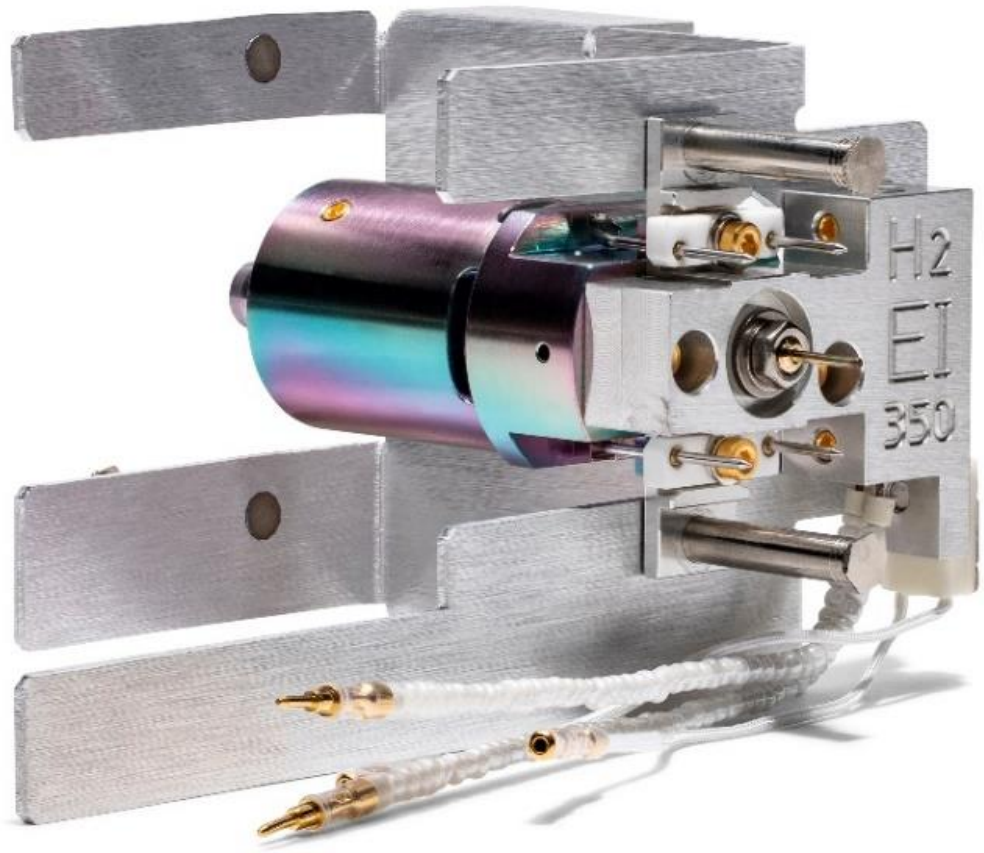


Deltamethrin



(m-phenoxyphenyl)-acetonitrile

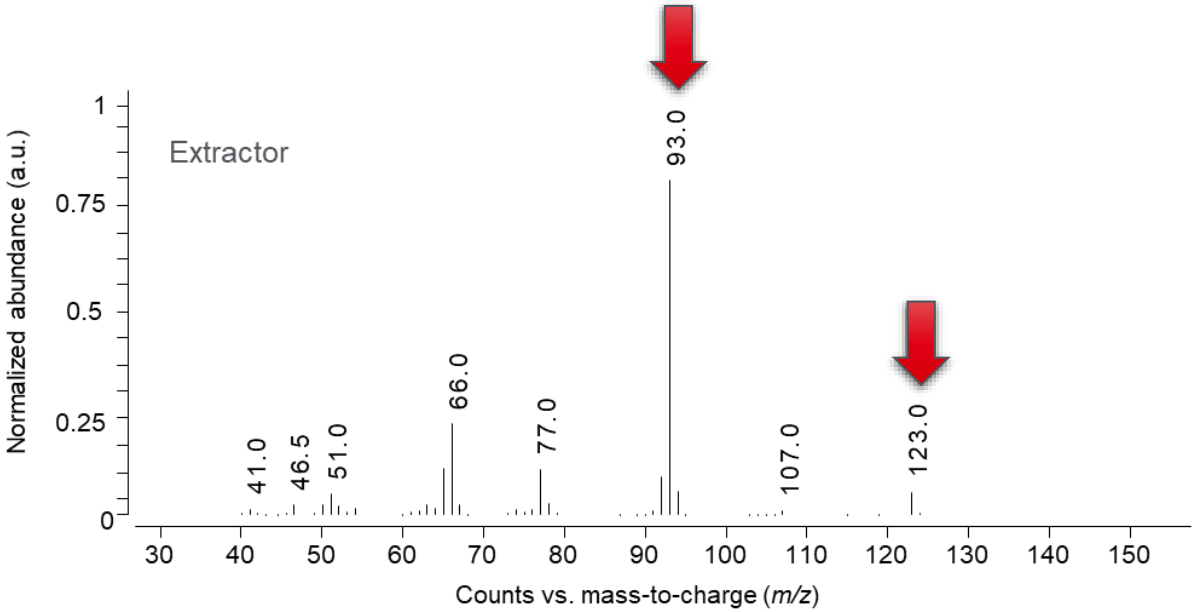
Agilent HydroInert Source for Hydrogen Carrier Gas on GC/MS



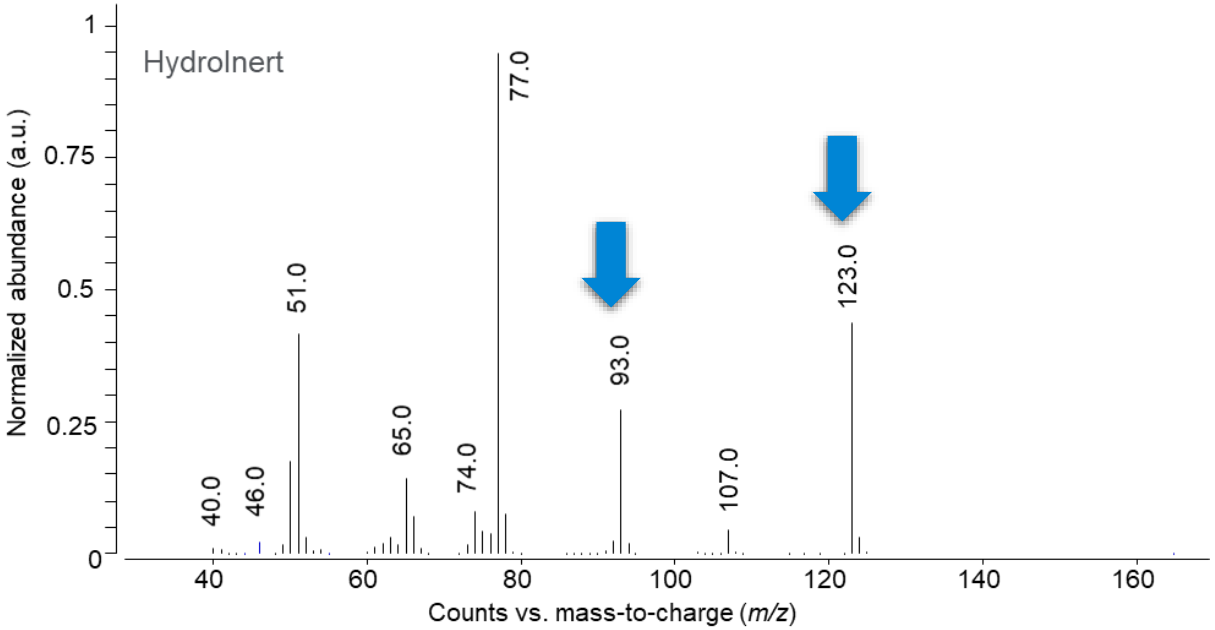
- Allows for the use of Hydrogen Carrier Gas with better supply and reduced costs
- Faster, shorter separations
- Reduces loss of sensitivity and spectral anomalies
- Reduced source cleaning and maintenance

Back to Nitrobenzene and H_2 Carrier Gas

Existing extractor source

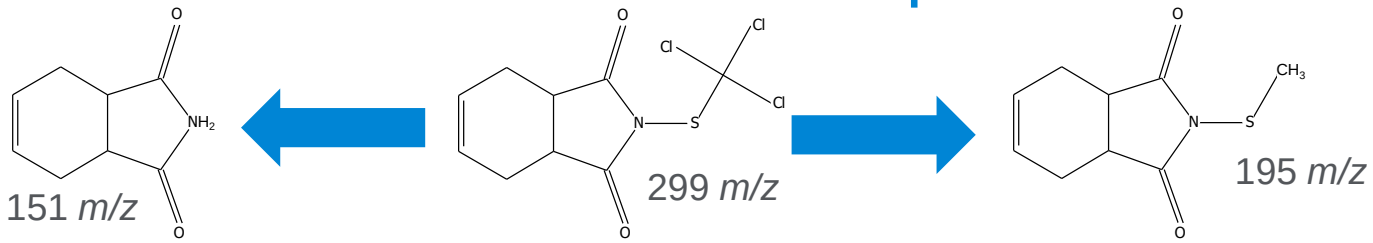


HydroInert source

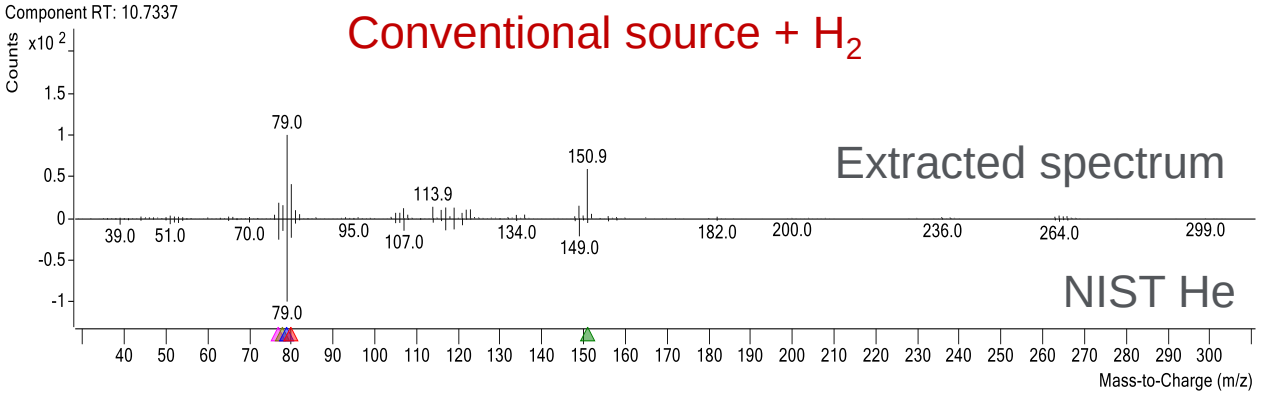


HydroInert source prevents hydrogenation

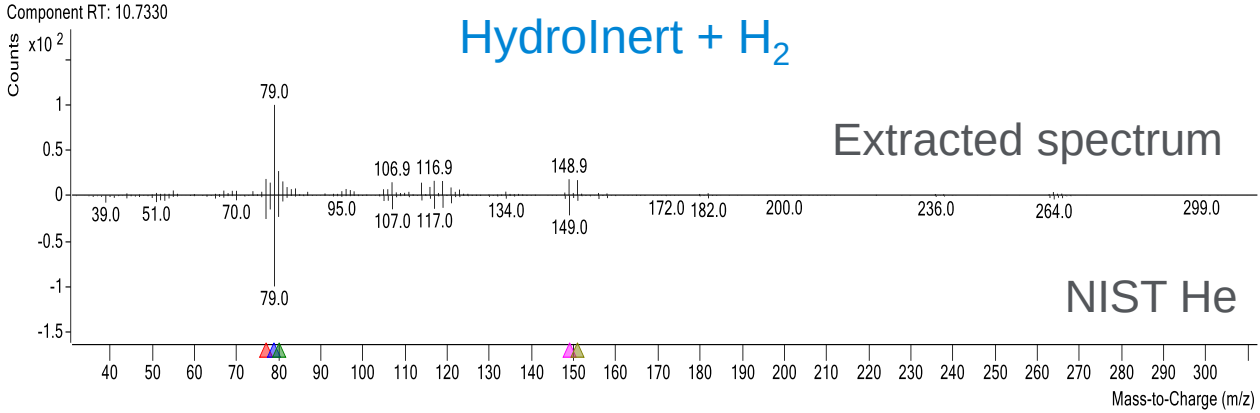
H_2 Cleavage Reactions in the Source: Captan

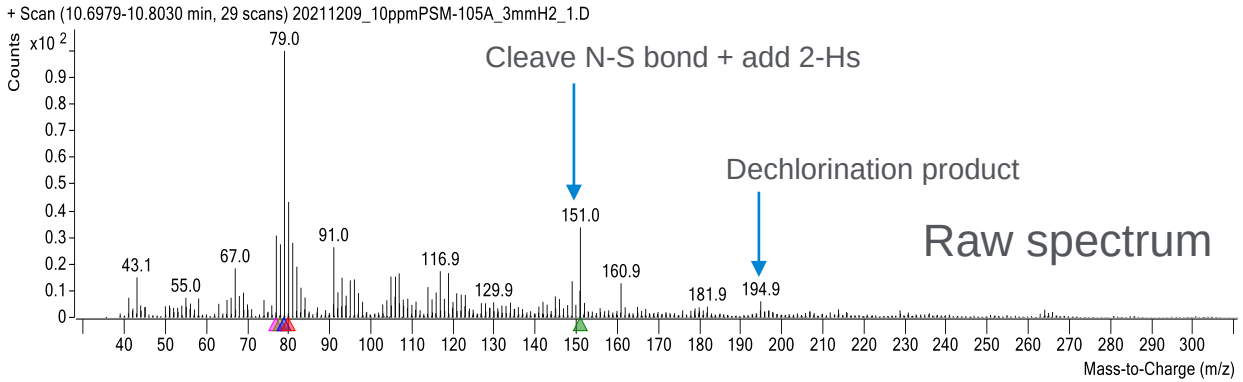


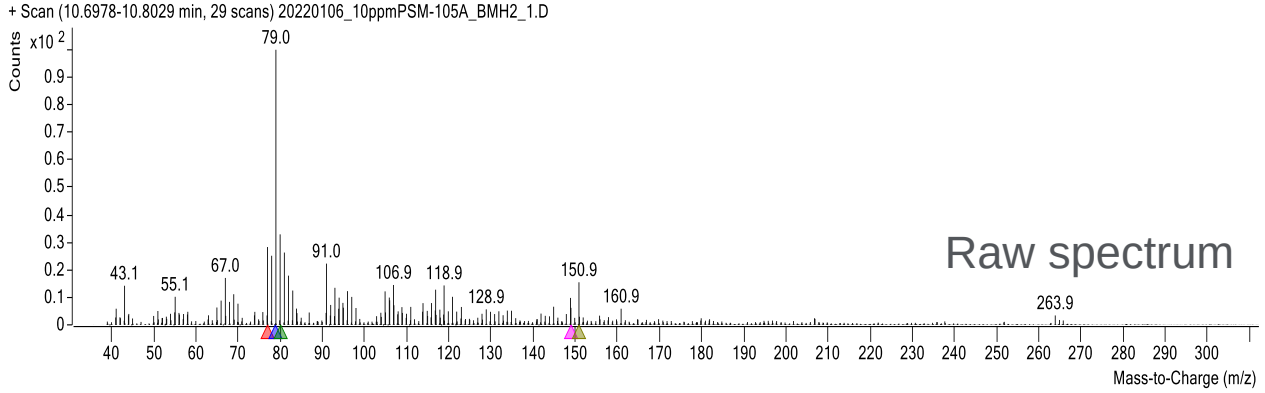
Conventional source + H_2



HydroInert + H_2

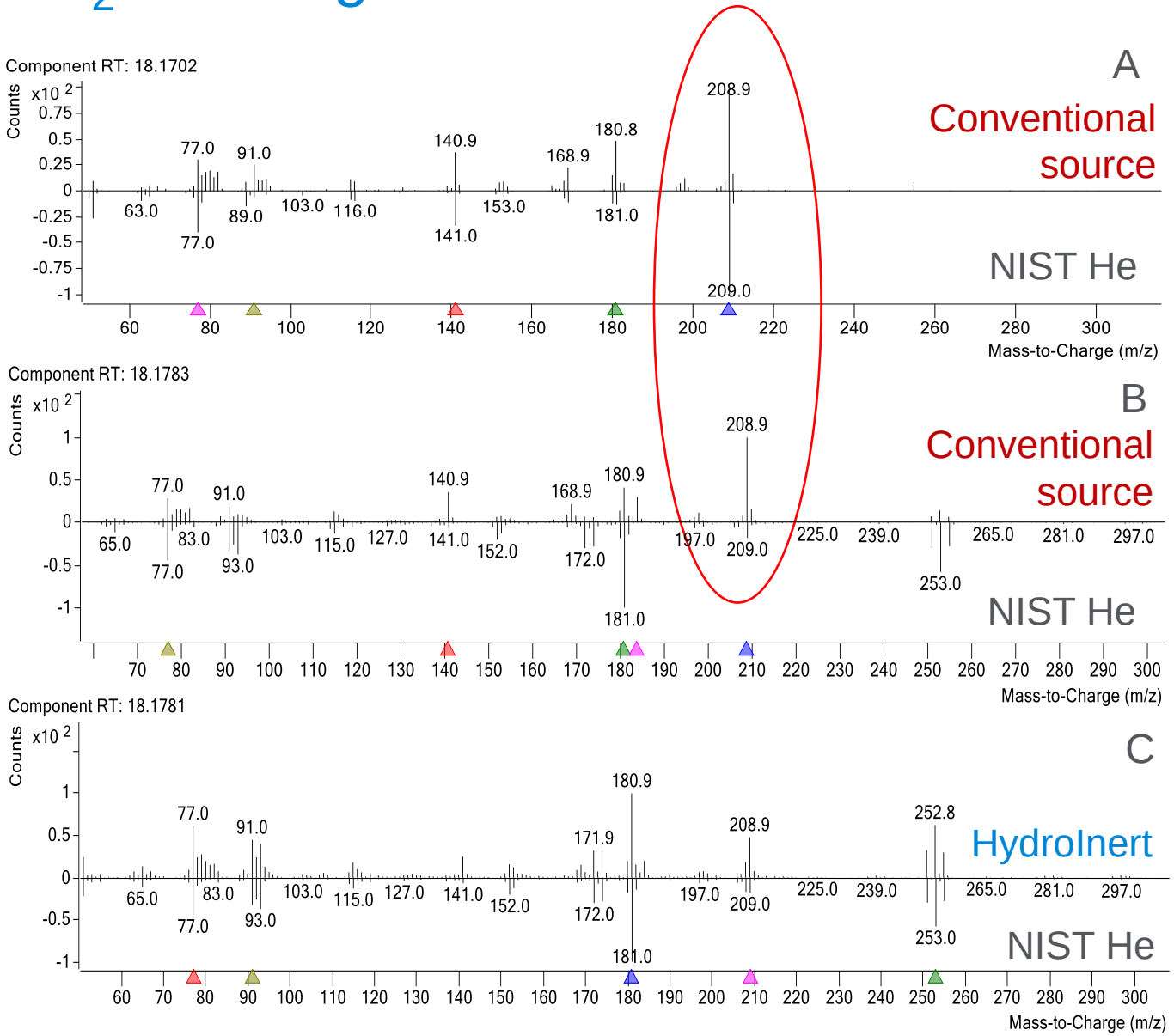




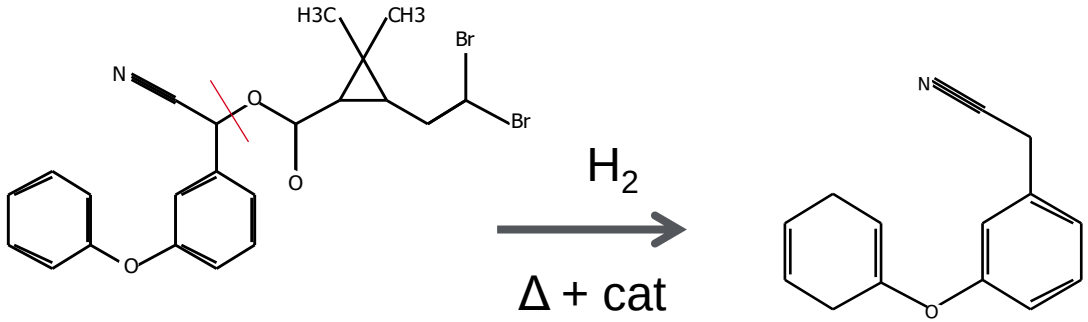


Less hydrogenation in HydroInert source and better NIST match scores

H_2 Cleavage Reactions in the Source: Deltamethrin



- (m-phenoxyphenyl)-acetonitrile identified in some runs with LMS 74.4
- Deltamethrin identified in most runs with an LMS range of 70-77



253 *m/z*

209 *m/z*

Deltamethrin identified in **all** runs with HydroInert (LMS 90+)

We Retain Our Mass Spectra, but What About Calibration Curves?

Can we retain our calibration range?

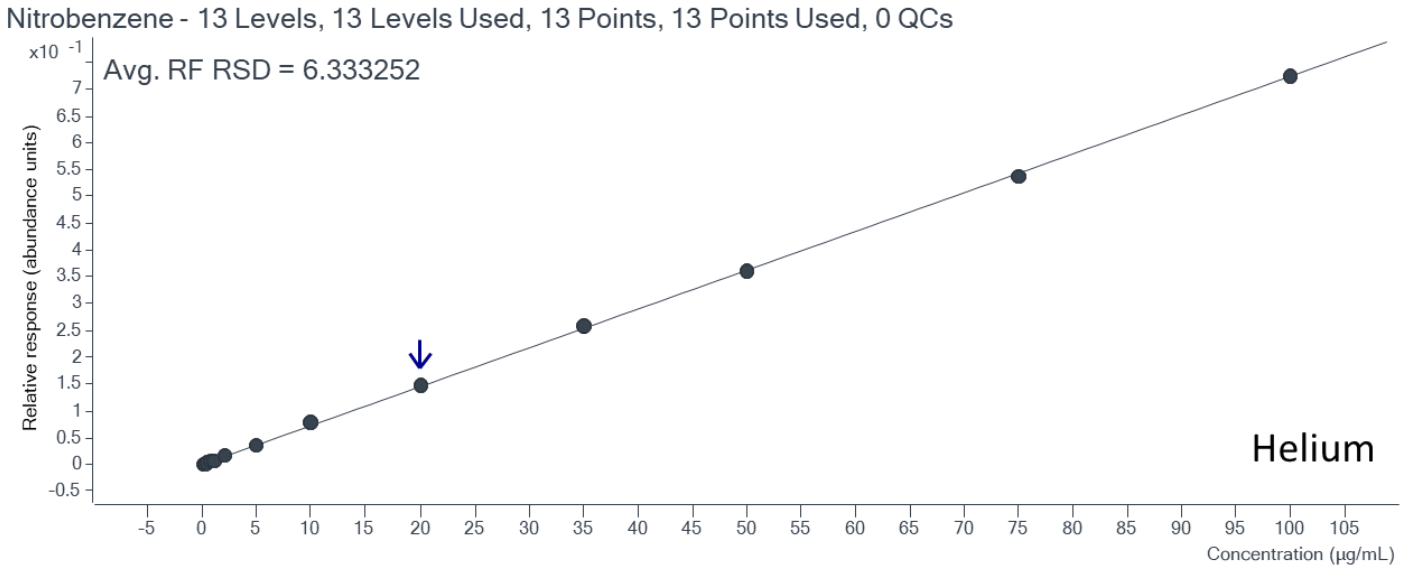
- 0.1 – 100 µg/mL

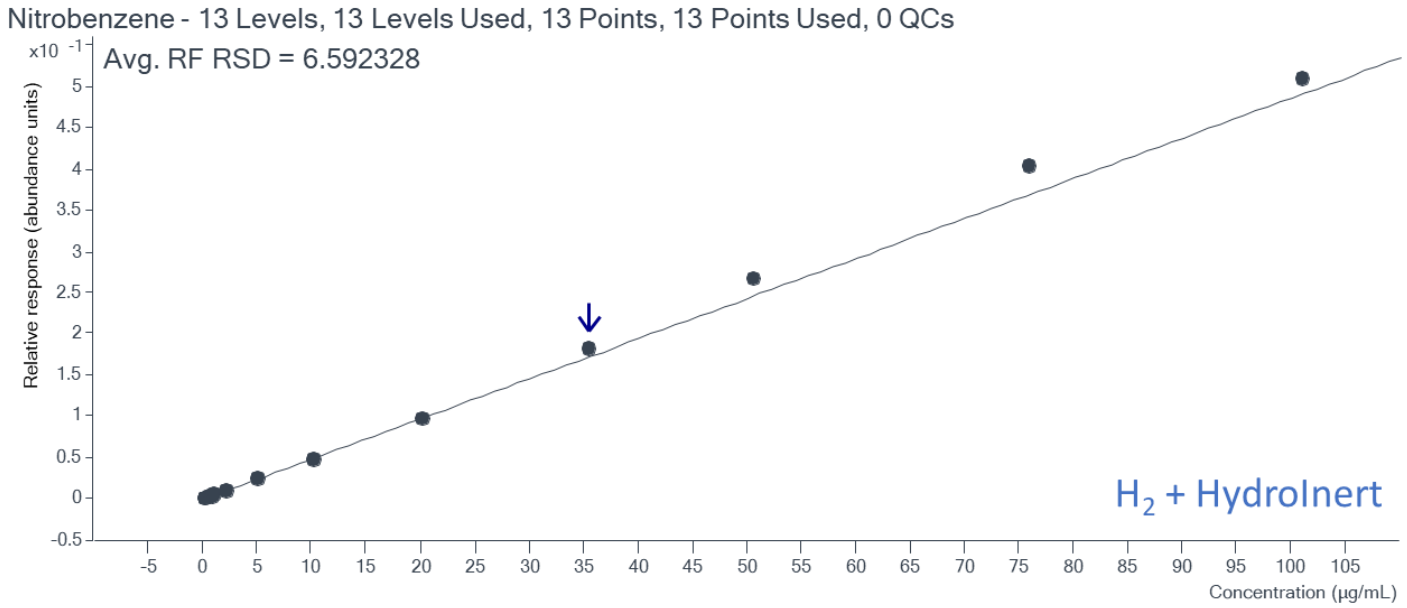
Helium + conventional source + 9 mm extraction lens
Nitrobenzene
Average RF %RSD: 6.33% RSD

H_2 + HydroInert source + 9 mm lens

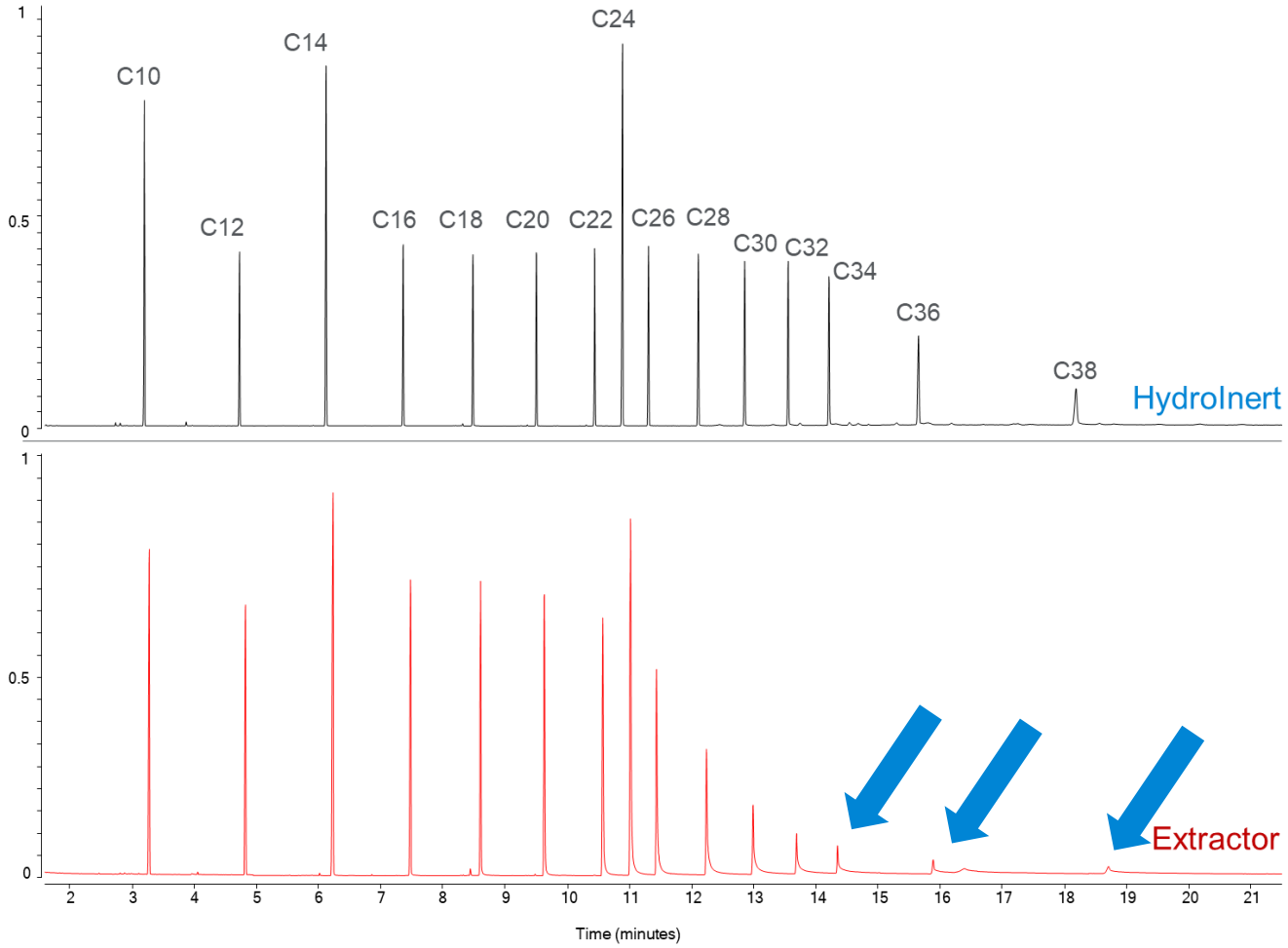
Nitrobenzene
Average RF %RSD: 6.59% RSD

Yes, we can retain calibration range, too
…with consumable and method parameter changes.





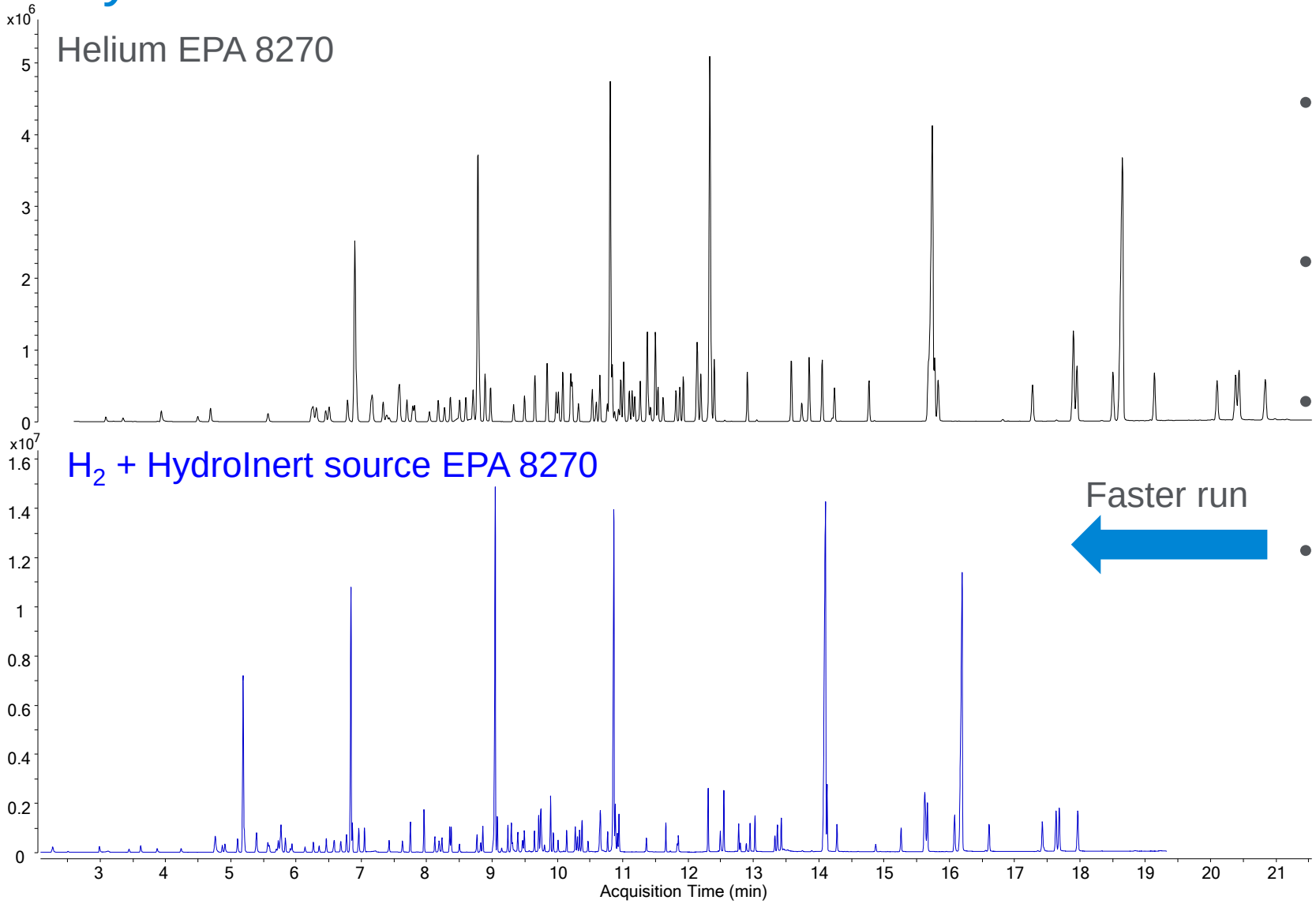
What Happens with Alkanes and H_2 Carrier Gas in GC/MS?



- Improved peak shape (reduced tailing) with HydroInert source

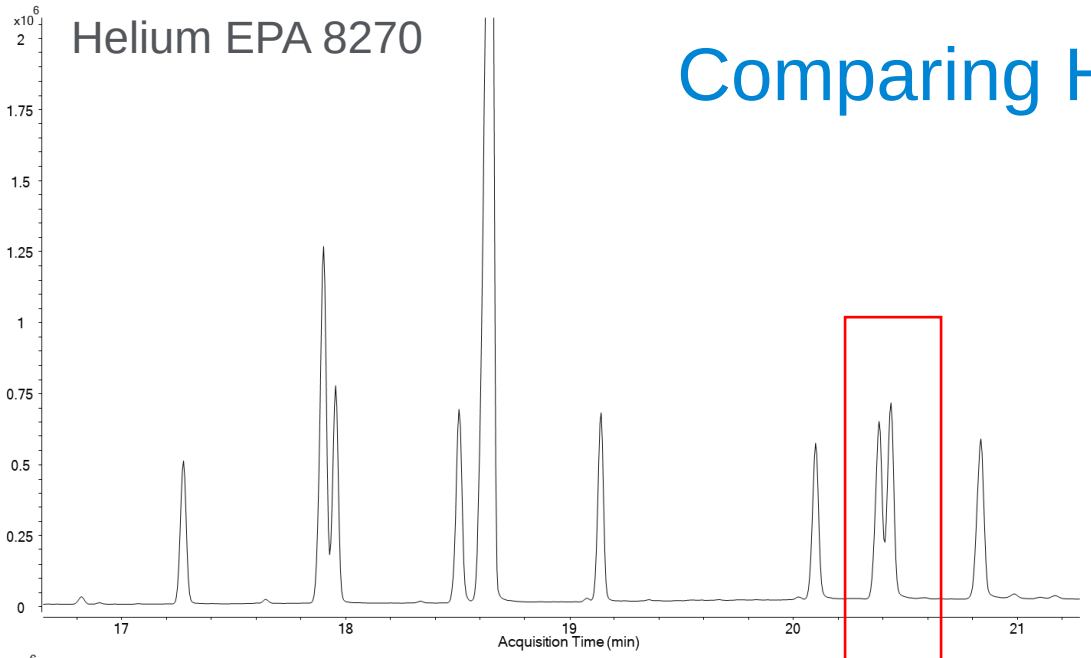
- Shorter chain alkanes do well with H_2
- Longer chain alkanes have issues with tailing

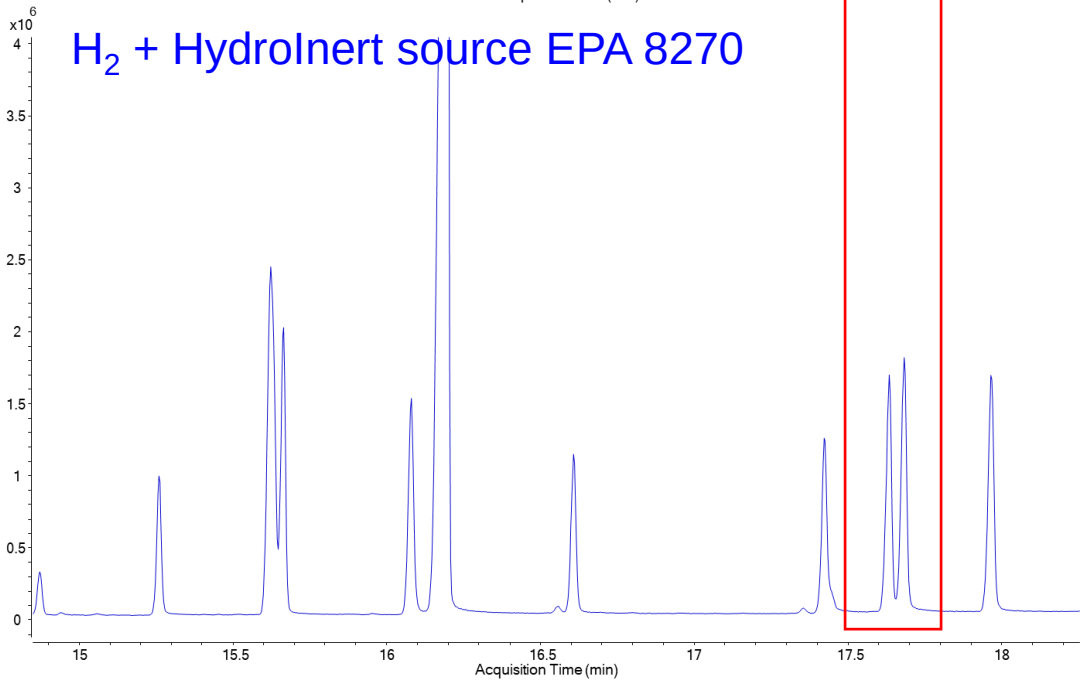
Do I Have Similar Responses Between "Normal" Helium Data and H_2 + HydroInert Source Data?



- Using the same column, injection parameters, and tune (atune.u)
- Faster constant flow rate with H_2
- Benefits of H_2
  - Narrower peaks
  - Increased resolution
- Retained sensitivity

Comparing Helium and HydroInert + H_2 Results





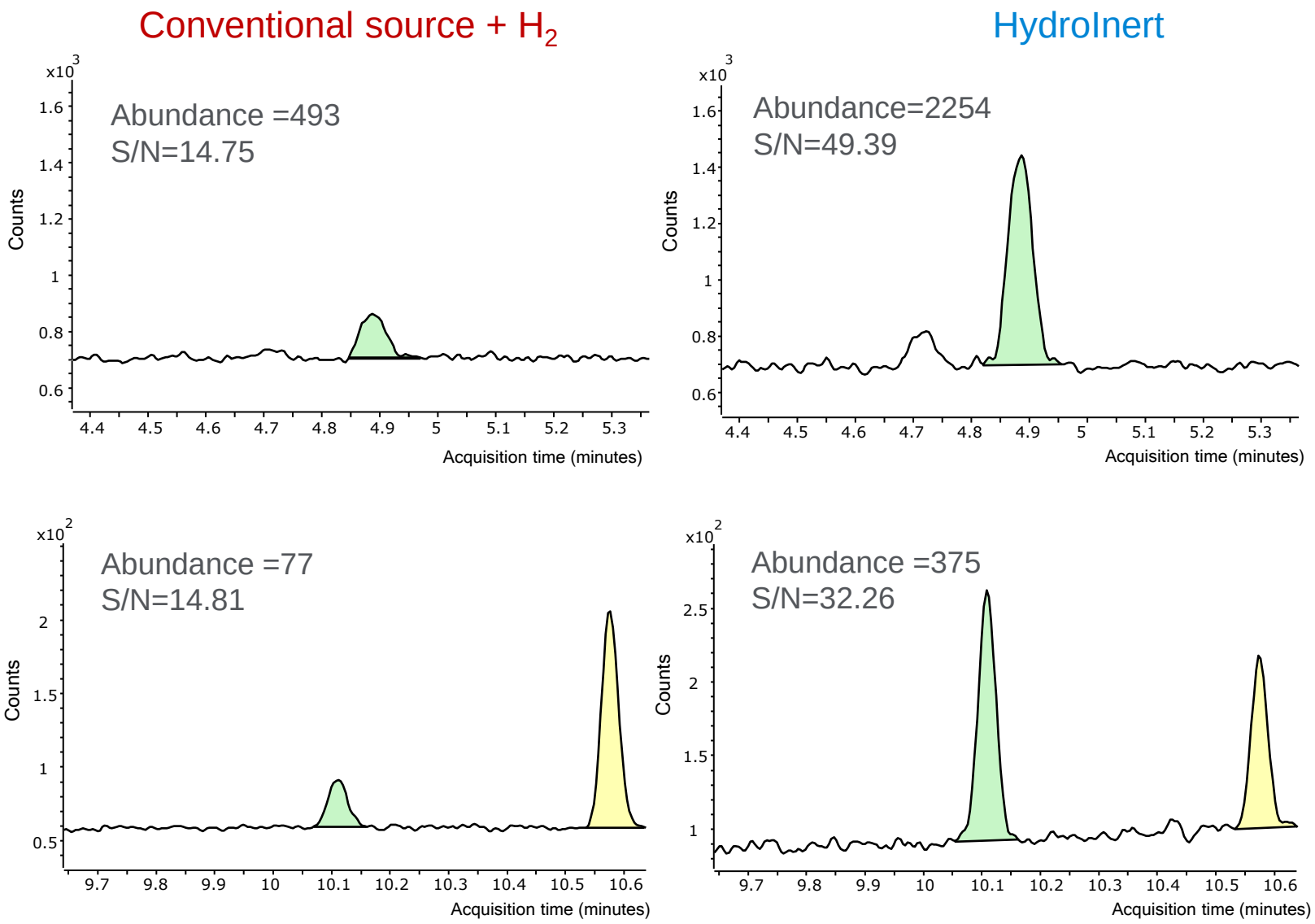
Compound	Response Factor (RF) from EPA Method 8270E	RF He GC/MS	RF H_2 HydroInert GC/MS	RF H_2 HydroInert GC/MS/MS
Acenaphthene	0.9	1.3	1.1	0.2
Acetophenone	0.01	1.2	0.4	1.0
Benzo(b)fluoranthene	0.7	1.4	1.2	1.2
Bis(2-chloroethoxy)methane	0.3	0.4	0.3	0.7
Di-n-butyl phthalate	0.01	1.3	0.8	0.8
Hexachlorocyclopentadiene	0.05	0.3	0.2	0.03
2,4-Dinitrophenol	0.01	0.2	0.1	0.02
4-Nitrophenol	0.01	0.2	0.14	0.05
2,4,6-Trichlorophenol	0.2	0.3	0.2	0.2
62 compounds		**3% low RF**	**11% low**	**19% low**

Better resolution with H_2 and the majority of RFs match to EPA 8270 RF guidelines

Sensitivity Comparison of Sources with H_2 Carrier Gas

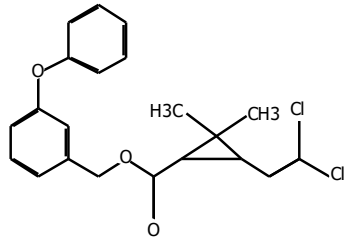
Carbon tetrachloride

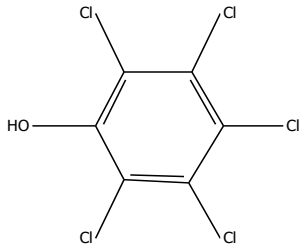
Bromoform



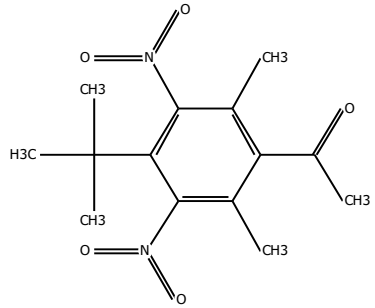
What Happens to Our Compound Classes?

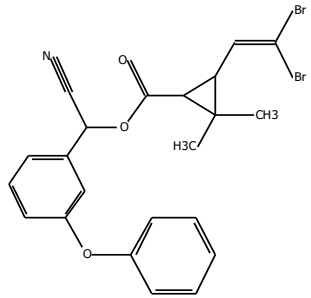
Compound Class	Example Compound(s)	H_2 Carrier Gas + Conventional GC/MS Source	H_2 Carrier Gas + HydroInert Source
Nitro compounds	Nitrobenzene, fenitrothion, ethalfluralin	Unacceptable	Differentiating
Heavily chlorinated compounds	DDT, endrin, heptachlor, BHC compounds, pentachlorophenol	Unacceptable	Differentiating
Polycyclic aromatic hydrocarbons (PAHs)	Benzo(b)fluoranthene, benzo[g,h,i]perylene,	Neutral	Neutral
Alkanes >C24	Tetratriacontane, hexadecane, tetracontane	Neutral	Neutral
Pesticides	Deltamethrin, fipronil, permethrin, captan	Unacceptable	Differentiating
Fragrance/flavor compounds	Musk ketone, musk ambrette, linalool	Unacceptable	Differentiating
Volatile organic compounds	1,4-dioxane, tichloromethane, bromodichloromethane	Neutral	Differentiating





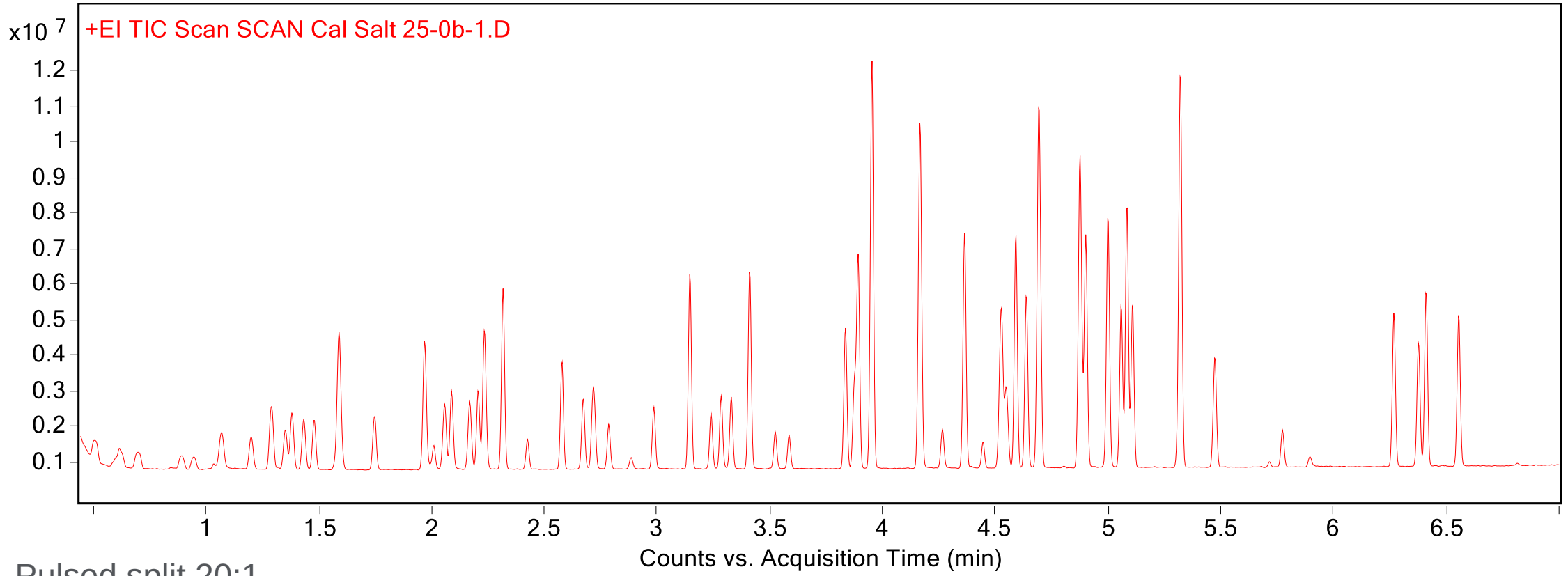
Musk ambrette





Headspace GC/MS: VOCs with H_2 Carrier and HydroInert

8697 HS/8890/5977C VOCs with H_2 Carrier and HydroInert



Pulsed split 20:1
Agilent J&W DB-624 UI 20 m x 0.18 mm x 1.0 µm
0.95 mL/min
5 g Na_2SO_4 added to each vial

Cal from 0.25 ppb to 25 ppb Scan mode
Cal from 0.05 ppb to 25 ppb SIM mode

VOCs: Library Match Scores vs NIST20

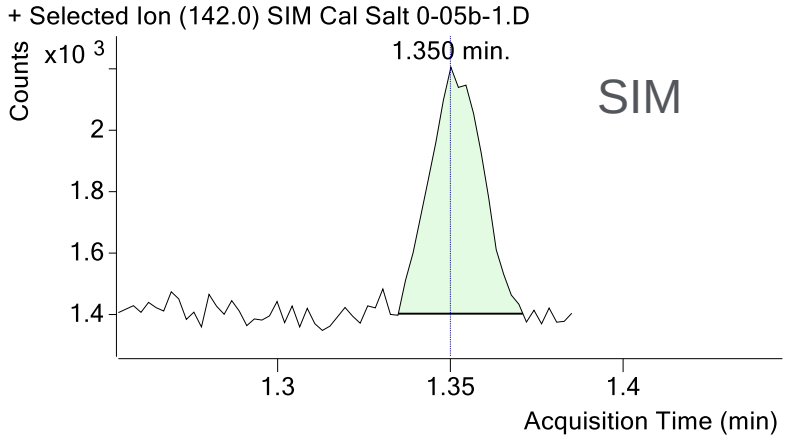
	RT (min)	LMS NIST20	
Dichlorodifluoromethane	0.507	92	
Chloromethane	0.616	97	
Ethene, chloro-	0.698	91	
Methane, bromo-	0.891	96	
Ethyl Chloride	0.945	92	
Trichloromonofluoromethane	1.068	96	
Ethyl ether	1.199	97	
Ethene, 1,1-dichloro-	1.289	98	
Acetone	1.316	87	*
Methane, iodo-	1.351	99	
Carbon disulfide	1.380	95	
Allyl chloride	1.433	97	
Methylene chloride	1.479	97	
2-Propenenitrile	1.574	90	
Ethylene, 1,2-dichloro-, (E)-	1.587	99	
Propane, 2-methoxy-2-methyl-	1.592	98	
Ethane, 1,1-dichloro-	1.747	97	
Ethylene, 1,2-dichloro-, (Z)-	1.968	95	
Propane, 2,2-dichloro-	1.970	80	**
2-Butanone	1.975	72	*
Propanenitrile	1.994	67	*
2-Propenoic acid, methyl ester	2.010	97	
Methylacrylonitrile	2.053	95	
Methane, bromochloro-	2.060	97	
Trichloromethane	2.088	98	
Tetrahydrofuran	2.091	96	
Ethane, 1,1,1-trichloro-	2.169	98	
Butane, 1-chloro-	2.206	97	
1-Propene, 1,1-dichloro-	2.233	96	
Carbon Tetrachloride	2.237	96	
Benzene	2.317	94	
Benzene, fluoro-	2.425	98	
Trichloroethylene	2.578	99	
Propane, 1,2-dichloro-	2.673	98	
Methyl methacrylate	2.714	98	
Methane, dibromo-	2.723	98	
Methane, bromodichloro-	2.786	98	
Propane, 2-nitro-	2.884	93	
Chloromethyl cyanide	2.888	63	*
1-Propene, 1,3-dichloro-, (Z)-	2.986	98	
Toluene	3.146	99	
1-Propene, 1,3-dichloro-, (E)-	3.240	98	
Methacrylic acid, ethyl ester	3.284	98	
Ethane, 1,1,2-trichloro-	3.329	98	
Tetrachloroethylene	3.411	91	
Propane, 1,3-dichloro-	3.412	90	
Methane, dibromochloro-	3.524	98	
Ethane, 1,2-dibromo-	3.586	99	
Benzene, chloro-	3.836	99	
Ethane, 1,1,1,2-tetrachloro-	3.876	96	
Ethylbenzene	3.892	98	
Benzene, 1,3-dimethyl-	3.953	99	
o-Xylene	4.165	89	
Styrene	4.169	96	
Methane, tribromo-	4.266	99	
Benzene, (1-methylethyl)-	4.364	98	
p-Bromofluorobenzene	4.446	97	
Ethane, 1,1,2,2-tetrachloro-	4.521	97	
Benzene, bromo-	4.529	97	
Propane, 1,2,3-trichloro-	4.547	84	
2-Butene, 1,4-dichloro-, (E)-	4.554	65	**
Benzene, propyl-	4.592	98	
Benzene, 1-chloro-2-methyl-	4.638	98	
Mesitylene	4.691	91	
Benzene, 1-chloro-4-methyl-	4.698	95	
Benzene, tert-butyl-	4.875	97	
Ethane, pentachloro-	4.881	86	
Benzene, 1,2,4-trimethyl-	4.902	98	
Benzene, (1-methylpropyl)-	5.001	98	
Benzene, 1,3-dichloro-	5.059	99	
p-Cymene	5.085	97	
Benzene, 1,4-dichloro-	5.110	99	
1,2-Dichlorobenzene-D4	5.314	78	**
Benzene, n-butyl-	5.321	96	
Benzene, 1,2-dichloro-	5.324	92	
Ethane, hexachloro-	5.475	97	
Propane, 1,2-dibromo-3-chloro-	5.775	98	
Benzene, nitro-	5.896	94	
Benzene, 1,2,4-trichloro-	6.269	99	
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	6.379	91	
Naphthalene	6.412	99	
Benzene, 1,2,3-trichloro-	6.557	99	

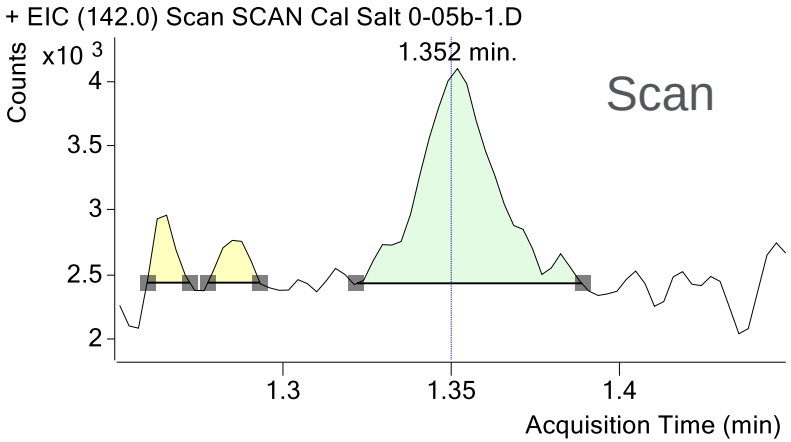
Average LMS = 94

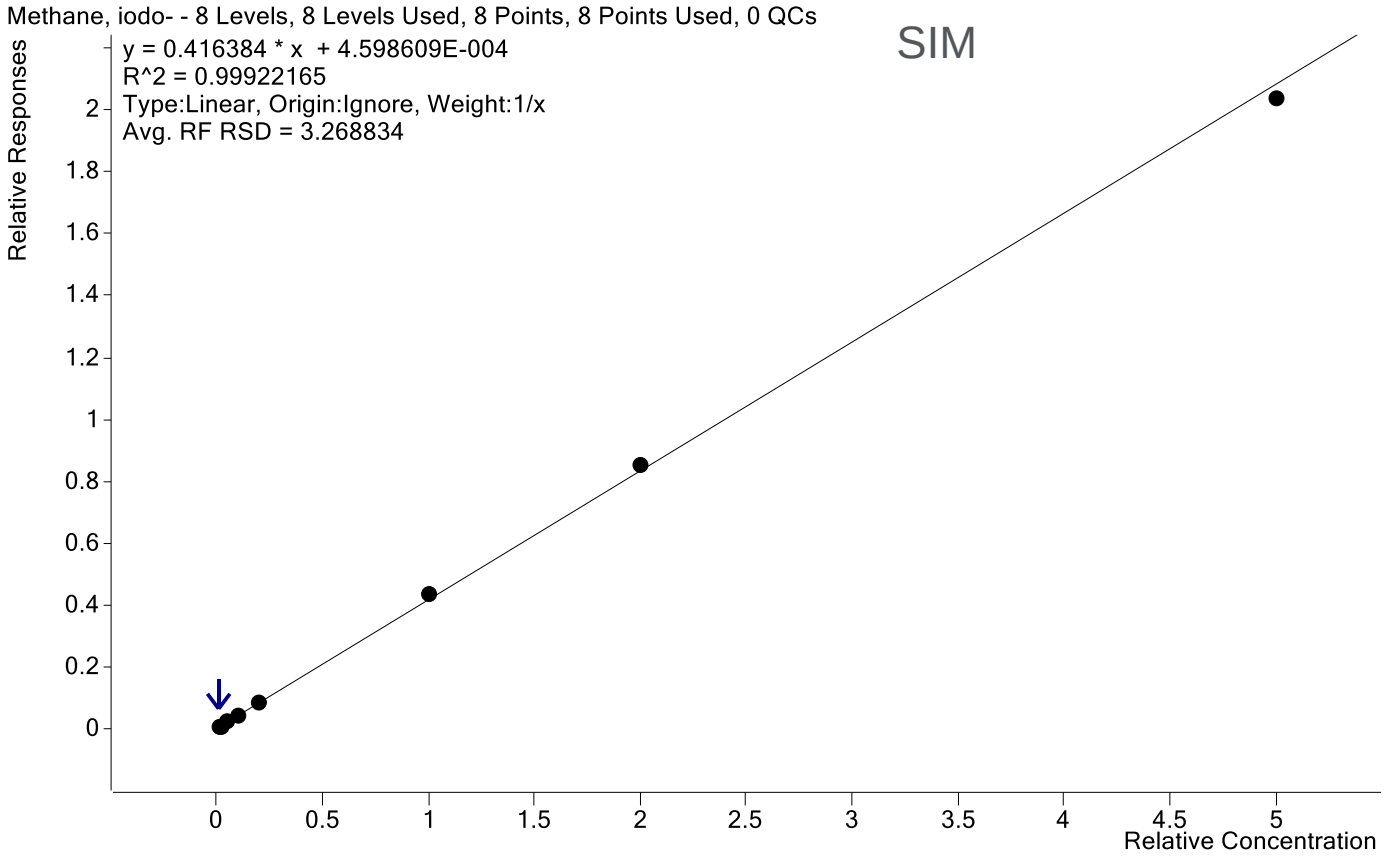
* Low-responding compound

** Spectral interference from overlapping peaks

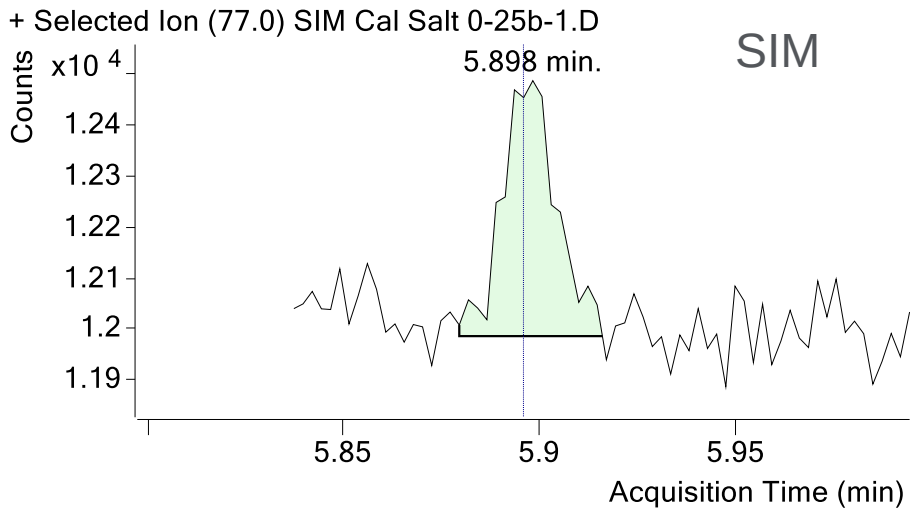
Iodomethane: Good Linearity from 0.05 ppb – 25 ppb

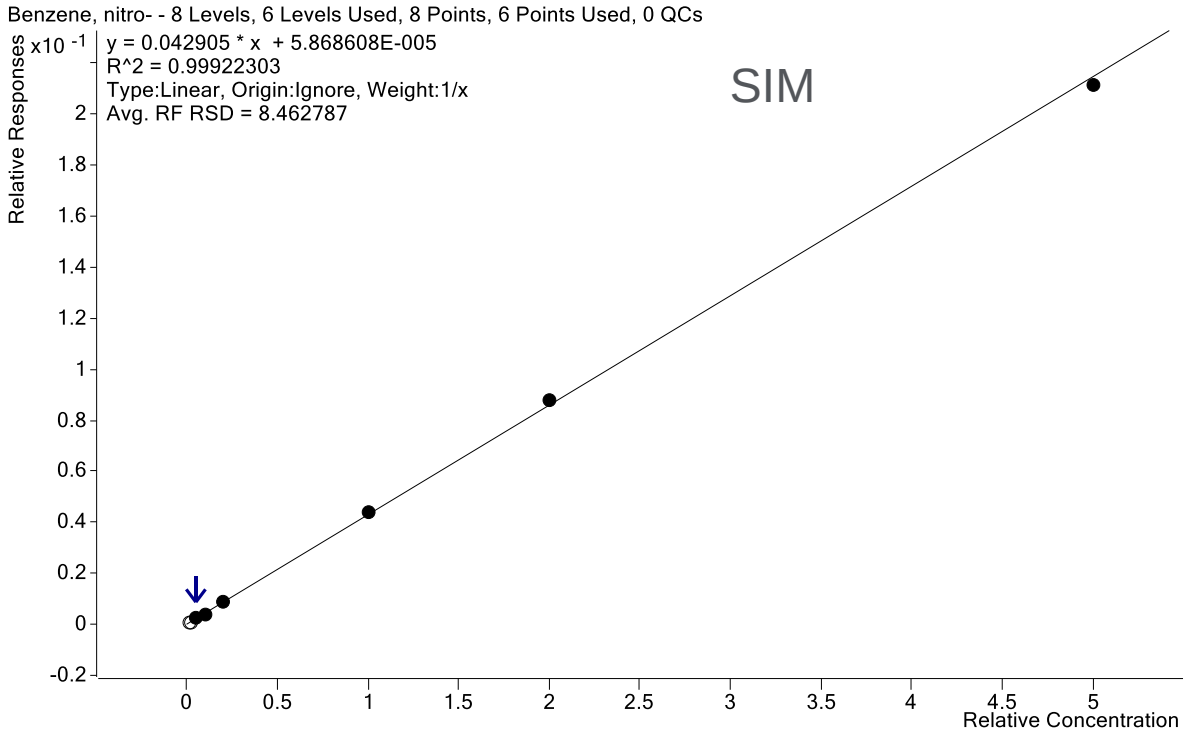






Nitrobenzene: Linearity from 0.25 ppb – 25 ppb





Being a polar analyte, nitrobenzene is a low responder in static headspace analysis.

It does, however, exhibit good linearity.

MDLs: SIM HS/GC/MSD VOAs with H_2 Carrier and HydroInert

Name	RT Min min	Conc for MDL	MDL µg/L
Dichlorodifluoromethane	0.508	0.10	0.011
Chloromethane	0.615	0.10	0.022
Ethene, chloro-	0.698	0.05	0.008
Methane, bromo-	0.891	0.10	0.029
Ethyl Chloride	0.945	0.05	0.010
Trichloromonofluoromethane	1.067	0.05	0.008
Ethyl ether	1.198	0.05	0.017
Ethene, 1,1-dichloro-	1.288	0.05	0.006
Acetone	1.317	[cont]	
Methane, iodo-	1.350	0.05	0.006
Carbon disulfide	1.379	0.05	0.003
Allyl chloride	1.432	0.05	0.014
Methylene chloride	1.478	0.05	0.007
Acrylonitrile	1.572	[0.25]	
Ethylene, 1,2-dichloro-, trans-	1.586	0.05	0.007
Methyl tert-butyl ether	1.592	0.05	0.003
Ethane, 1,1-dichloro-	1.745	0.05	0.003
Ethylene, 1,2-dichloro-, cis-	1.966	0.05	0.007
Propane, 2,2-dichloro-	1.969	0.10	0.017
Propanenitrile	1.993	[0.25]	
2-Propenoic acid, methyl ester	2.008	0.10	0.029
Methylacrylonitrile	2.052	0.10	0.032
Methane, bromochloro-	2.059	0.10	0.019
Trichloromethane	2.086	0.05	0.011
Tetrahydrofuran	2.090	0.05	0.030
Ethane, 1,1,1-trichloro-	2.168	0.05	0.007
Butane, 1-chloro-	2.205	0.05	0.007
1-Propene, 1,1-dichloro-	2.231	0.05	0.007
Carbon Tetrachloride	2.235	0.05	0.015
Benzene	2.315	0.05	0.004
Ethane, 1,2-dichloro-	2.316	0.05	0.005
Trichloroethylene	2.577	0.05	0.006
Propane, 1,2-dichloro-	2.671	0.05	0.011
Methyl methacrylate	2.713	0.05	0.033
Methane, dibromo-	2.722	0.05	0.009
Methane, bromodichloro-	2.785	0.05	0.011
Propane, 2-nitro-	2.883	0.10	0.041
Chloromethyl cyanide	2.887	[0.25]	
1-Propene, 1,3-dichloro-, cis-	2.985	0.05	0.003
Toluene	3.145	0.05	0.003
1-Propene, 1,3-dichloro-, trans-	3.239	0.05	0.005
Methacrylic acid, ethyl ester	3.283	0.05	0.008
Ethane, 1,1,2-trichloro-	3.328	0.05	0.034
Tetrachloroethylene	3.410	0.05	0.005
Propane, 1,3-dichloro-	3.412	0.05	0.007
Methane, dibromochloro-	3.524	0.05	0.008
Ethane, 1,2-dibromo-	3.585	0.05	0.005
Benzene, chloro-	3.835	0.05	0.002
Ethane, 1,1,1,2-tetrachloro-	3.875	0.05	0.007
Ethylbenzene	3.892	0.05	0.005
m-Xylene	3.953	0.05	0.001
o-Xylene	4.164	0.05	0.004
Styrene	4.169	0.05	0.005
Methane, tribromo-	4.266	0.05	0.003
Benzene, (1-methylethyl)-	4.364	0.05	0.004
p-Bromofluorobenzene	4.446	ISTD	
Ethane, 1,1,2,2-tetrachloro-	4.521	0.05	0.006
Benzene, bromo-	4.530	0.05	0.003
Propane, 1,2,3-trichloro-	4.548	0.05	0.024
2-Butene, 1,4-dichloro-, trans-	4.555	[0.25]	
Benzene, propyl-	4.592	0.05	0.008
Benzene, 1-chloro-2-methyl-	4.638	0.05	0.006
Mesitylene	4.692	0.05	0.008
Benzene, tert-butyl-	4.876	0.05	0.004
Ethane, pentachloro-	4.881	0.05	0.009
Benzene, 1,2,4-trimethyl-	4.903	0.05	0.007
Benzene, (1-methylpropyl)-	5.001	0.05	0.004
Benzene, 1,3-dichloro-	5.060	0.05	0.003
p-Cymene	5.086	0.05	0.009
Benzene, 1,4-dichloro-	5.110	0.05	0.004
1,2-Dichlorobenzene-D4	5.313	Surr	
Benzene, n-butyl-	5.322	0.05	0.012
Benzene, 1,2-dichloro-	5.325	0.05	0.003
Ethane, hexachloro-	5.476	0.05	0.008
Propane, 1,2-dibromo-3-chloro-	5.775	0.05	0.017
Benzene, nitro-	5.896	[0.25]	
Benzene, 1,2,4-trichloro-	6.270	0.05	0.007
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	6.380	0.05	0.006
Naphthalene	6.413	0.05	0.003
Benzene, 1,2,3-trichloro-	6.558	0.05	0.006

Most MDLs are in the ppt range

Summary

Developed a source for H_2 carrier gas with:

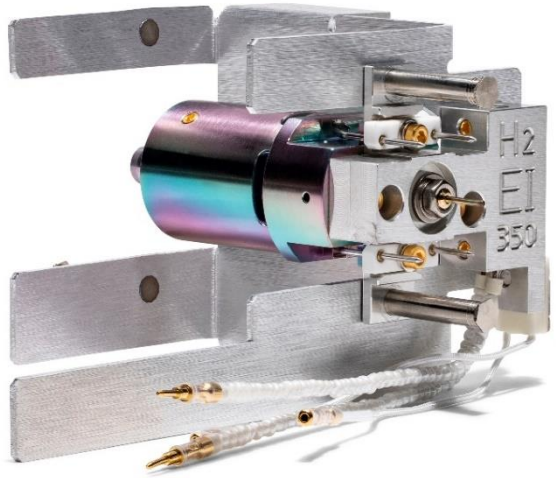
- Decreased in-source reactions with H_2
- Improved S/N
- Improved sensitivity

Gained:

- The ability to retain existing quantitative methods, libraries, and MRM transitions or SIM ions.

Still must consider:

- Time for method development
- What are the best column dimensions for H_2 and the analysis?
- Adjust inlet/injection parameters to avoid overload



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Thank you!

Any Questions?