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Migrating From He to H_2 Carrier Gas in GC-MS Analysis of Volatile and Semi-Volatile Organic Compounds in Water

Jessie Butler
Alexander N. Semyonov

The world leader in serving science

Helium and Profitability of Drinking Water Testing Labs

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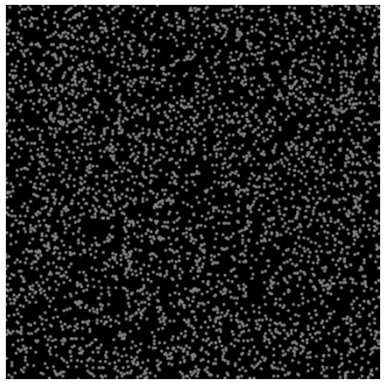
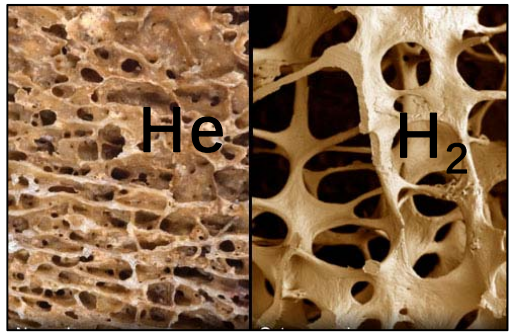
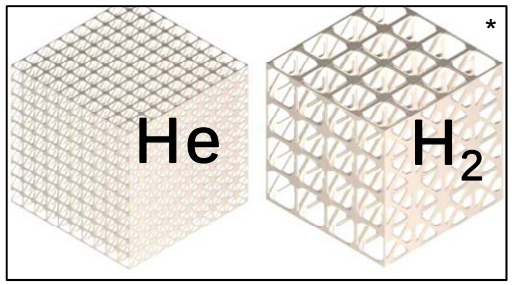
Carrier Gases: Physical Properties

Property	He	H_2	N_2	Ar
Molecular Mass, Da	4	2	28	40
Density, kg/m^3	0.18	0.09	1.25	1.78
Diffusion Coefficient, cm^2/s	0.55	0.60	0.15	0.20
Viscosity, Pa•s × 10^6	23.2	10.3	20.9	27.0
u_{opt}, cm/s	20	40	12	<10







Carrier Gas **Density**: Less is Better

Diffusion Coefficient: More is Better**

Dynamic **Viscosity** : Less is Better

* Crystal Lattice *Density Analogy* only, O.Fryazinov; A.Pasko; V.Adzhiev Computer-Aided Design 2011, 43(3) 265-277

** On the RHS of the van Demmter curve, that is.

Thermo Scientific Position on Hydrogen with GC-MS

- **Hydrogen Kit**
  - Required to Run with H_2
  - Required for H_2 Specifications
  - Includes Hydrogen Sensor
  - Requires 300 L/s Turbo Pump

- **Thermo Scientific™ Hydrogen Systems**
  - ISQ™ Single Quadrupole GC-MS
  - TRACE™ 1300 Series GC
  - TSQ™ 8000 GC-MS/MS
  - Explosion Tested & Safety Certified

- **Upgrades in the Field**
  - All existing ISQ GC-MS Systems are either already H_2 capable or are upgradeable with 300 L/s Turbo and H_2 Kit
  - IF you decide to use your existing Thermo Scientific™ DSQ™, DSQ II & ITQ GC-MS with H_2, you do so at your own risk.

ISQ GC-MS Hydrogen Carrier Installation Specs

- **ISQ Single Quadrupole GC-MS**
  - Guaranteed installation specifications with hydrogen carrier gas
  - Choice of either He or H_2 on installation spec sign-off
  - PCI/NCI same S/N!

Standard Installation Specifications*

Mode / Concentration	He	H_2
In **EI** mode, 1 µL of 1 pg/µL octafluoronaphthalene (OFN) will produce the following minimum signal to noise for m/z 272 when scanning from 50 – 300 u:	1,500:1	100:1
In **PCI** mode, 1 µL of 100 pg/µL benzophenone will produce the following minimum signal to noise for m/z 183 when scanning from 80 – 230 u using methane reagent gas:	300:1	300:1
In **NCI** mode, 2 µL of 100 fg/µL of OFN will produce the following minimum signal to noise for m/z 272 when scanning from 50 – 300 u using methane reagent gas:	600:1	600:1

* Requires Hydrogen Kit for H_2.

Hydrogen Purity Specifications

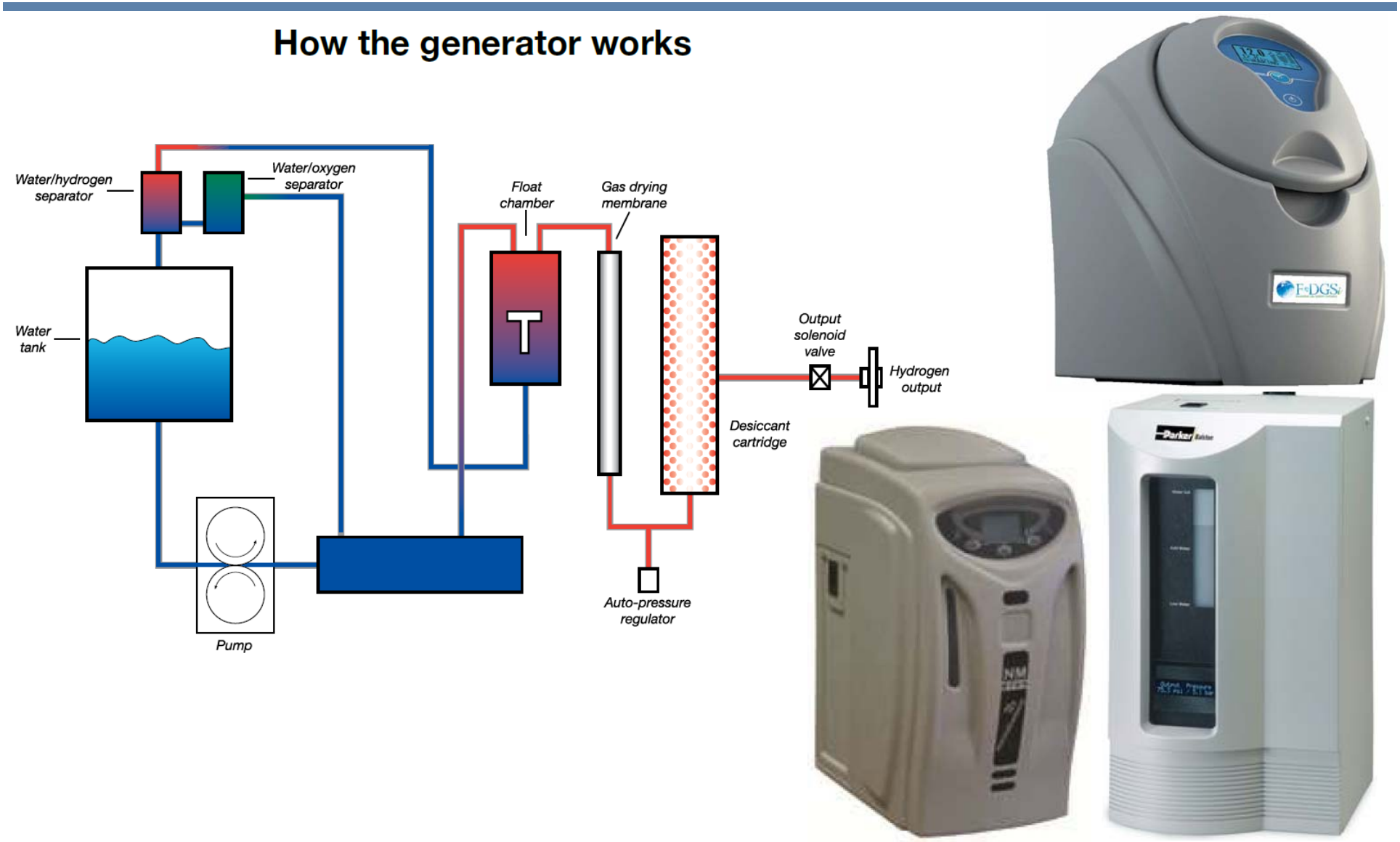
- **GC-MS Hydrogen Generator**
- **O_2 < 0.01 ppm**
- **H_2O < 1 ppm**
- **THC N/A**

- **Hydrogen Grade 5.0 UHP**
- **O_2 < 1 ppm**
- **H_2O < 3 ppm**
- **THC < 0.1 ppm**

- **Hydrogen FID Fuel Grade**
- **O_2 < 1 ppm**
- **H_2O < 3 ppm**
- **THC < 0.5 ppm**

- **Hydrogen Grade 6.0 UHP**
- **O_2 < 0.1 ppm**
- **H_2O < 0.5 ppm**
- **THC < 0.1 ppm**

Hydrogen Generators: Choose the Best



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Understanding Hydrogen Plumbing

- Gas Filter, triple stage

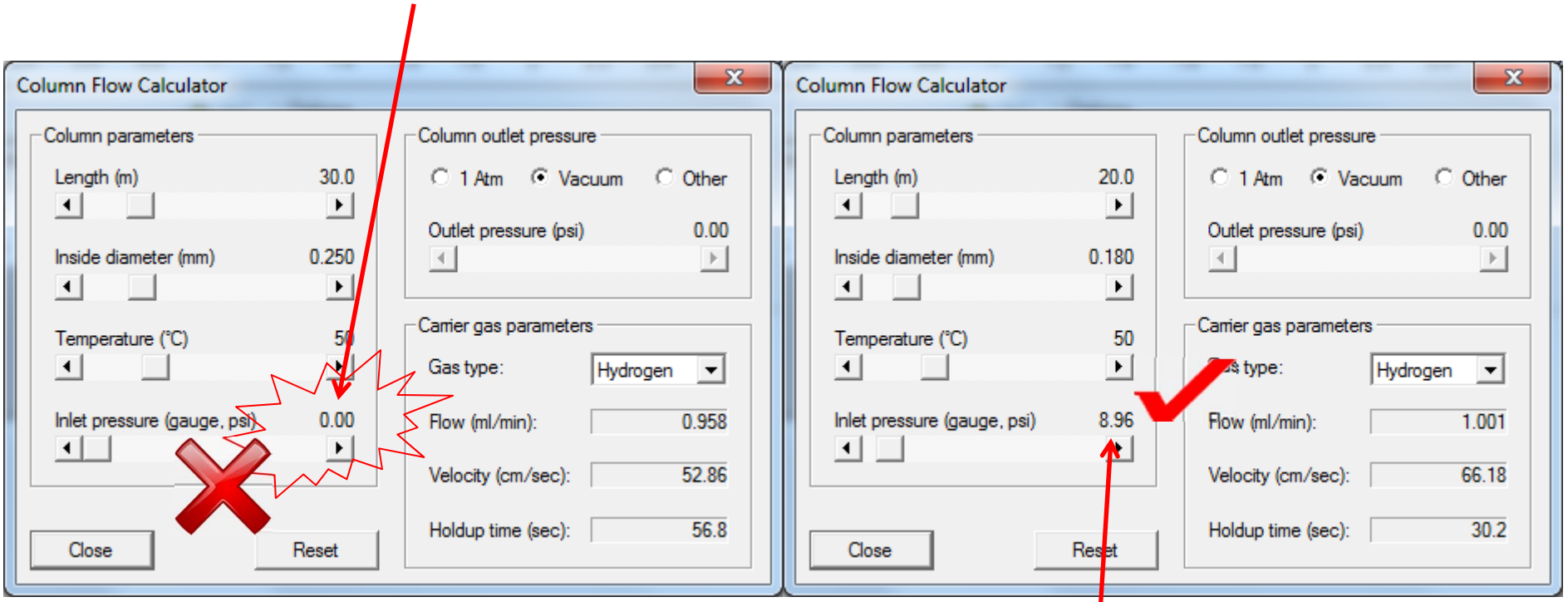
- Tubing
- Stainless steel preferred
- 1/8” pre-cleaned
- New tubing is preferred over used with He

- Filter – only need with tanks
- For removal of water, oxygen and hydrocarbons

What you need to know about plumbing up hydrogen to your GC

Limits on Hydrogen Flow and Column Selection

1 mL/min hydrogen on 0.25 mm × 30 m column



1 mL/min hydrogen on 0.18 mm × 20 meter column

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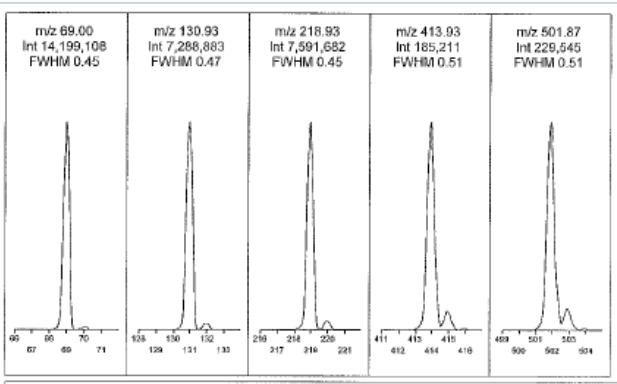
Tuning Report: He vs. H_2



Polarity	Positive
Electron Lens Voltage	15 V
Electron Energy	70 eV
Emission Current	50 µA
Ion Guide Frequency	1618.6
Q1 Frequency	1080.9
Multiplier Voltage	1754.8 V
Detector Gain	3.0 × 10 ^ 5
MS Transfer Line	310.0 °C
Filament Selection	1
Ion Source Temperature	250.0 °C
Foreline Pressure	75 mTorr
Ion Gauge Pressure	1.3 × 10 ^ -5 Torr

Full Scan Spectrum Not Acquired

Mass	Theory	Abundance	Relative Abundance	Isotope Mass	Theoretical Isotope Mass	Isotope Abundance	Isotope Ratio
69.03	69.00	4,973,356	100.00	69.98	70.00	73,396	1.48
131.00	130.99	2,607,640	52.43	131.95	131.99	113,566	4.36
219.01	218.99	2,591,609	52.11	219.95	219.99	150,777	5.82
413.98	413.98	79,576	1.60	415.07	414.98	8,789	11.04
502.06	501.97	120,545	2.42	503.00	502.97	9,527	7.90

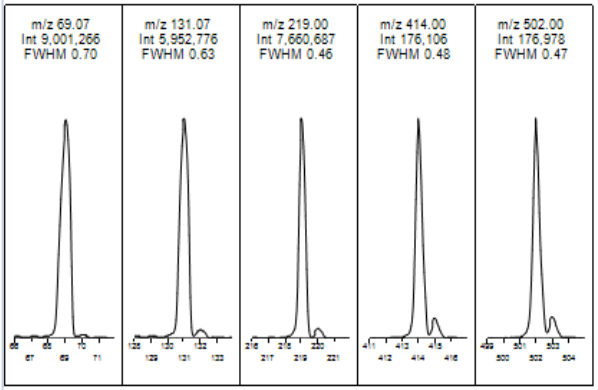
Air/ Water Check:			
	H2O	(%18/69)	20.12
	N2	(%28/69)	58.70
	O2	(%32/69)	4.24
	CO2	(%44/69)	2.20
	N2 / H2O	(%28/18)	2.92

Leak check not performed

Target Tune Factors:

Mass	50	69	131	219	414	502
Scale	1	0.49	0.41	0.29	0.12	0.13

Signature: _____



EI Ion Source Type	EI
Polarity	Positive
Electron Lens Voltage	15 V
Electron Energy	70 eV
Emission Current	50 µA
Ion Guide Frequency	1599.5
Q1 Frequency	1097.1
Multiplier Voltage	1431.1 V
Detector Gain	3.0 × 10 ^ 5
MS Transfer Line	310.0 °C
Filament Selection	1
Ion Source Temperature	325.0 °C
Foreline Pressure	51 mTorr
Ion Gauge Pressure	9.6 × 10 ^ -6 Torr

Full Scan Spectrum Not Acquired

Mass	Theory	Abundance	Relative Abundance	Isotope Mass	Theoretical Isotope Mass	Isotope Abundance	Isotope Ratio
68.98	69.00	6,210,659	100.00	70.07	70.00	78,224	1.26
130.99	130.99	3,716,974	59.85	132.03	131.99	133,679	3.60
219.04	218.99	3,676,688	59.20	220.06	219.99	157,409	4.28
414.00	413.98	90,746	1.46	415.02	414.98	7,855	8.66
502.00	501.97	92,223	1.48	503.04	502.97	8,481	9.20

Air/ Water Check:			
	H2O	(%18/69)	50.06
	N2	(%28/69)	22.70
	O2	(%32/69)	6.34
	CO2	(%44/69)	5.42
	N2 / H2O	(%28/18)	0.45

Leak check not performed

Target Tune Factors:

Mass	50	69	131	219	414	502
Scale	1	0.56	0.82	0.91	0.42	0.44

Signature: _____

He

H_2

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EPA Methods 524 and 525

- **EPA Method 524**
  - Purge & Trap
  - BFB Tuning Criteria
  - 5 mL sample volume
  - Calibration (0.4 – 200 ppb)

- **EPA Method 525**
  - Direct 1 µL liquid injection
  - DFTPP Tuning Criteria
  - 1 liter sample volume
  - Calibration (0.1 – 10 ppm)

Volatile and Semi-volatile Organics

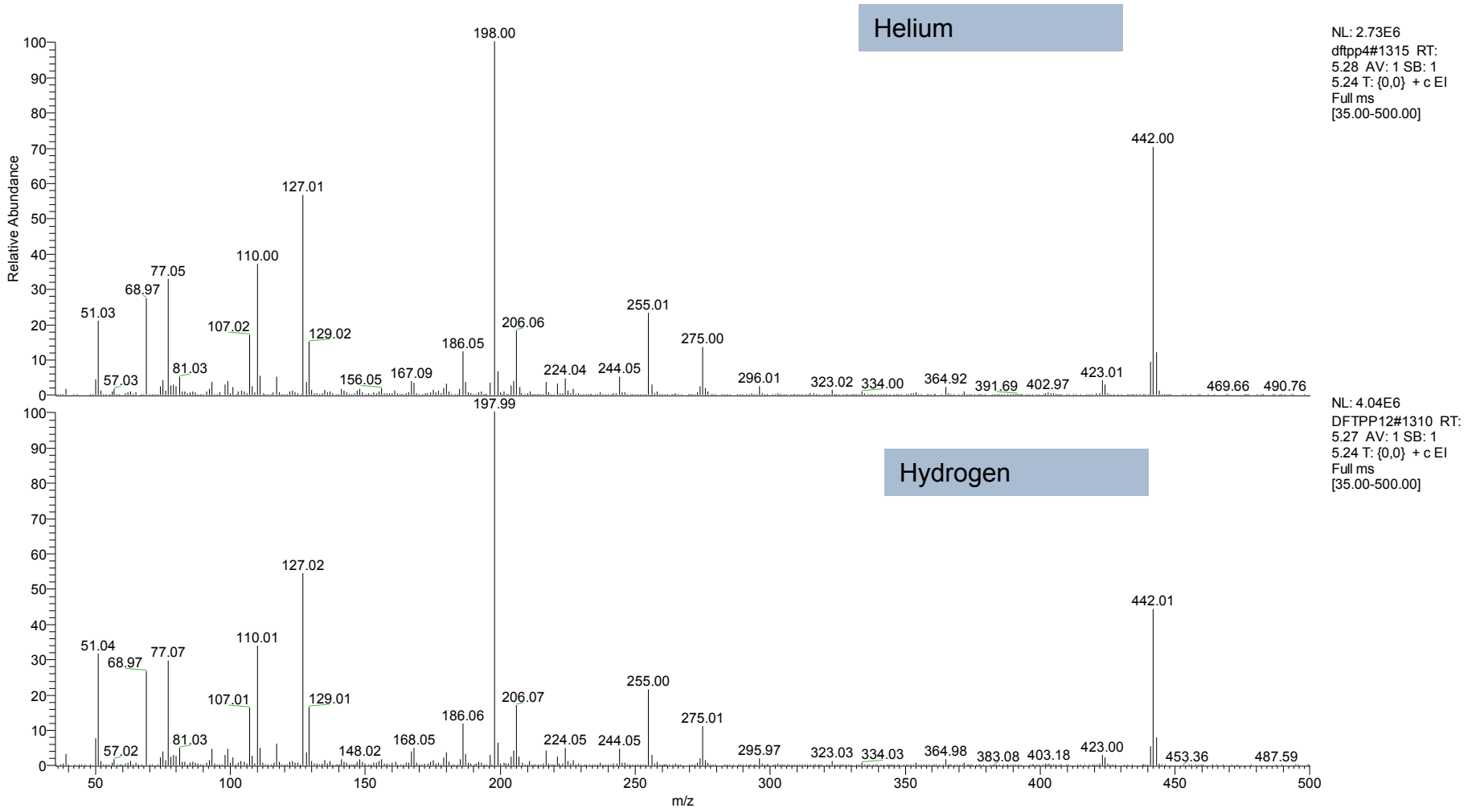
EPA Method 8270

- **EPA Method 8270**
  - Direct 1 µL liquid injection
  - Calibration (1 – 200 ppm)
  - More than 120 compounds
  - Surrogates = 40 ppm
  - Internal Standards = 40 ppm

- **Goals**
  - Improve peak shape and resolution
  - Improve method runtime (<15 minutes)

Semi-volatile Organics

DFTPP (Decafluorotriphenylphosphine) Spectrum



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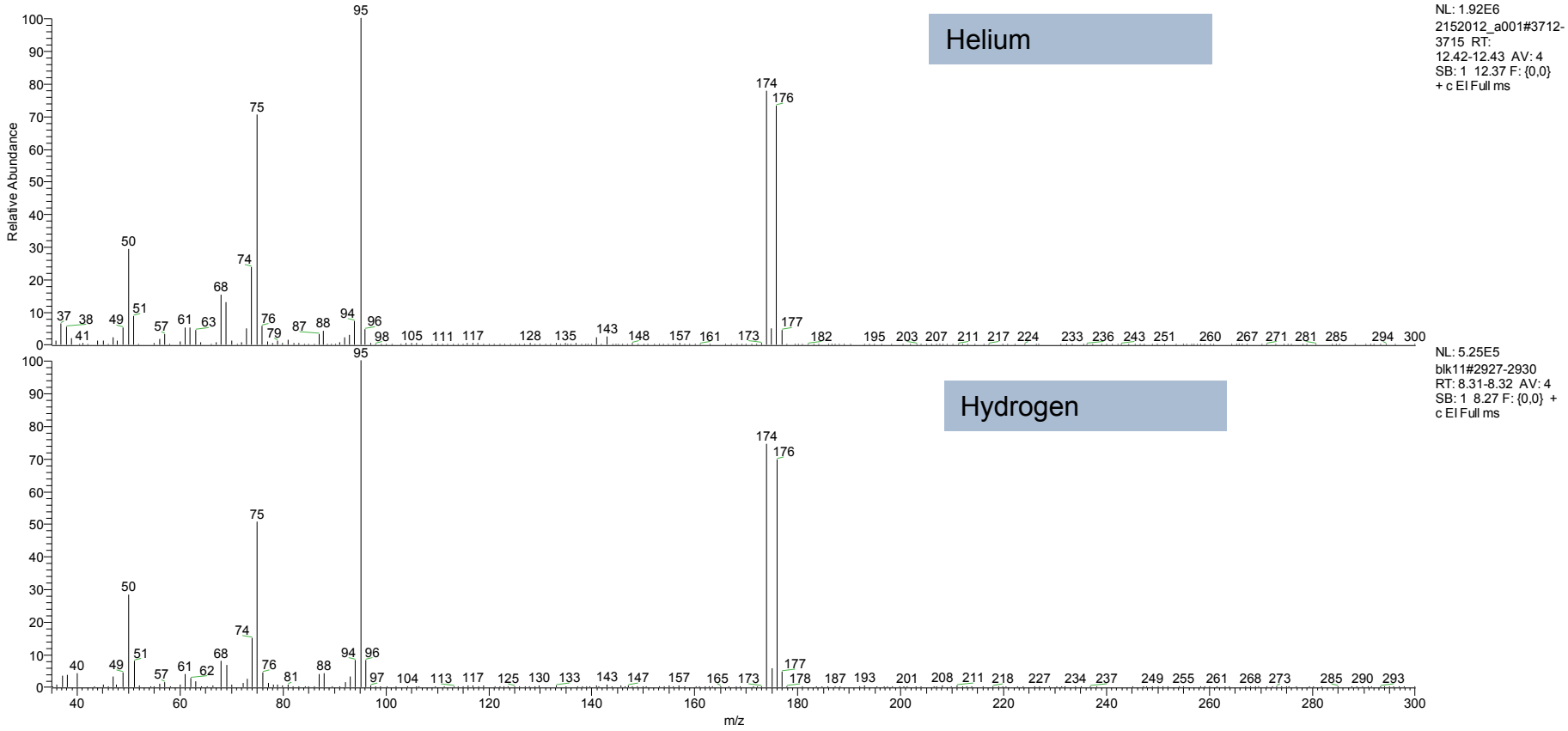
BFB (1-bromo-4-fluorobenzene)



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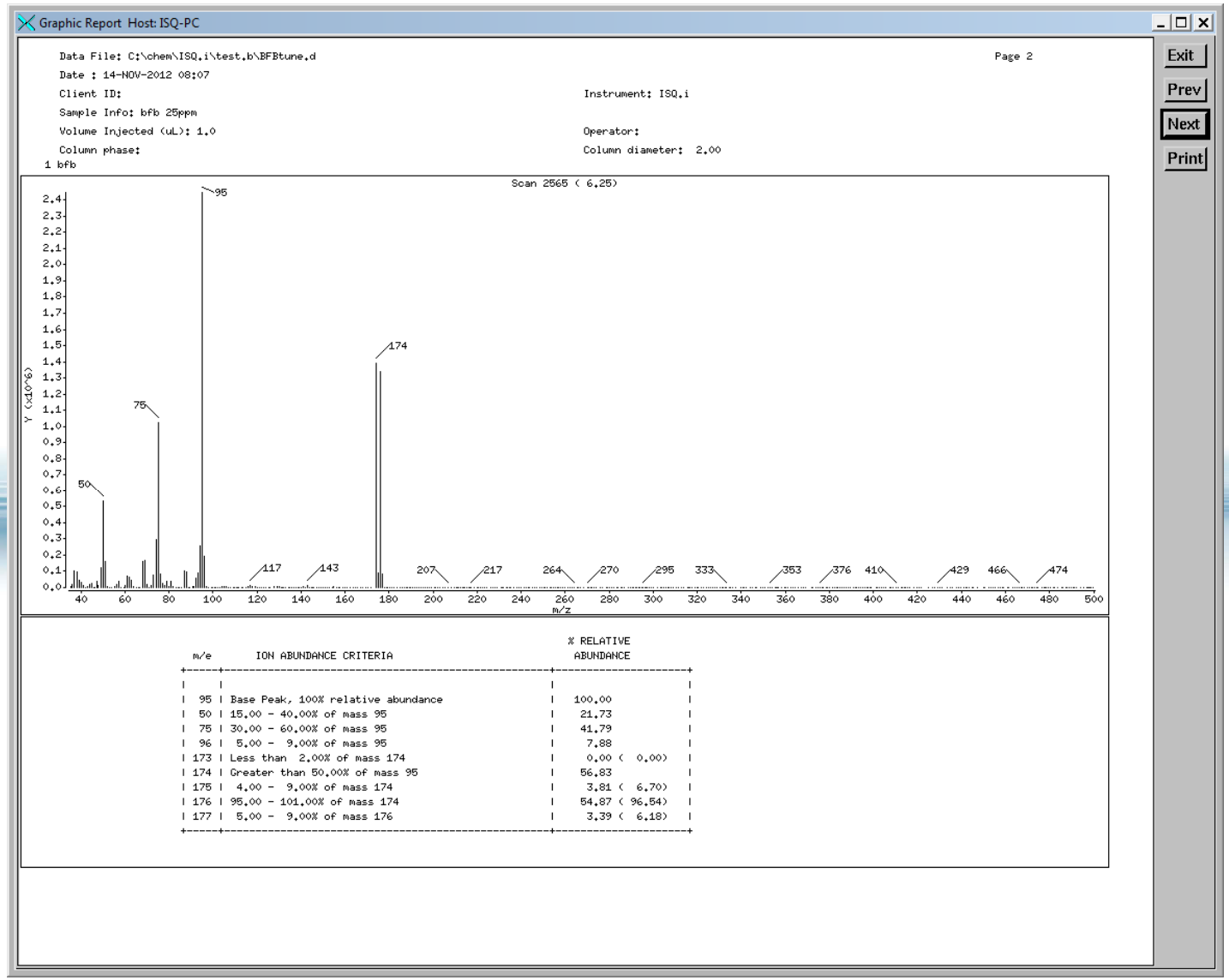
BFB H_2 Tuning Report in Target Software



m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
95	Base Peak, 100% relative abundance	100.00
50	15.00 - 40.00% of mass 95	21.73
75	30.00 - 60.00% of mass 95	41.79
96	5.00 - 9.00% of mass 95	7.88
173	Less than 2.00% of mass 174	0.00 (0.00)
174	Greater than 50.00% of mass 95	56.83
175	4.00 - 9.00% of mass 174	3.81 (6.70)
176	95.00 - 101.00% of mass 174	54.87 (96.54)
177	5.00 - 9.00% of mass 176	3.39 (6.18)

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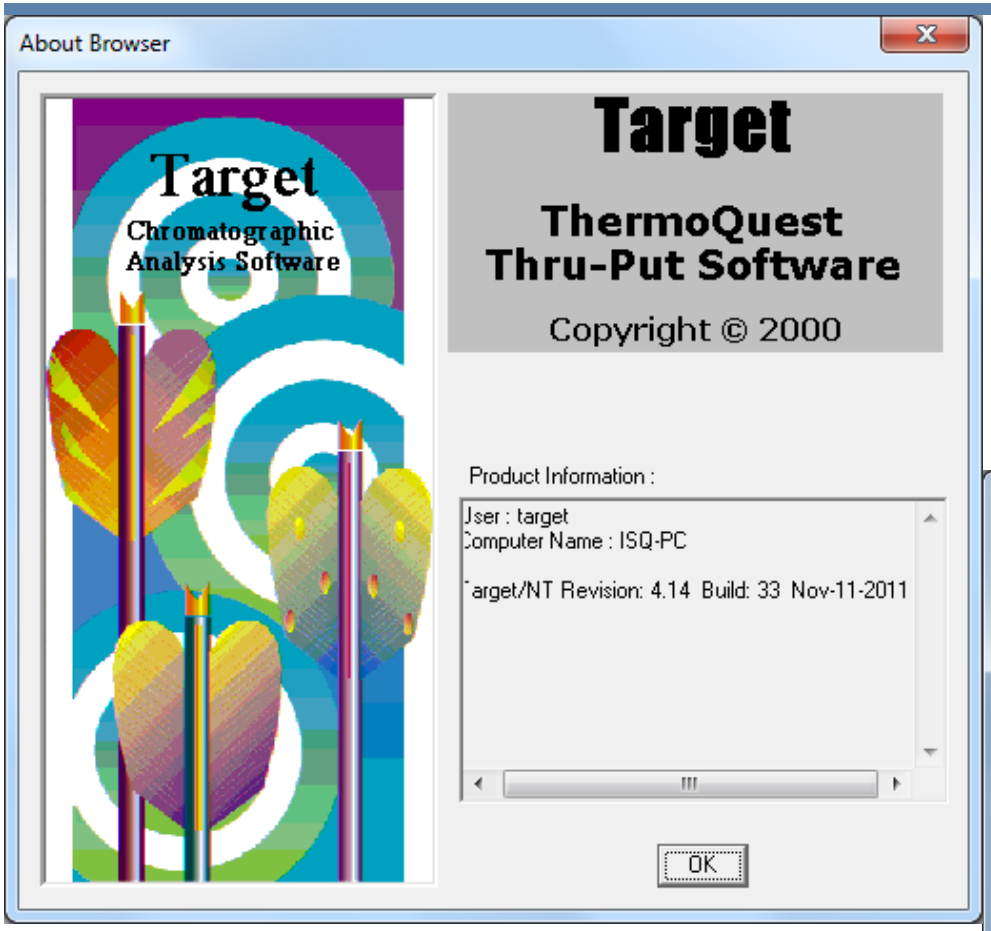
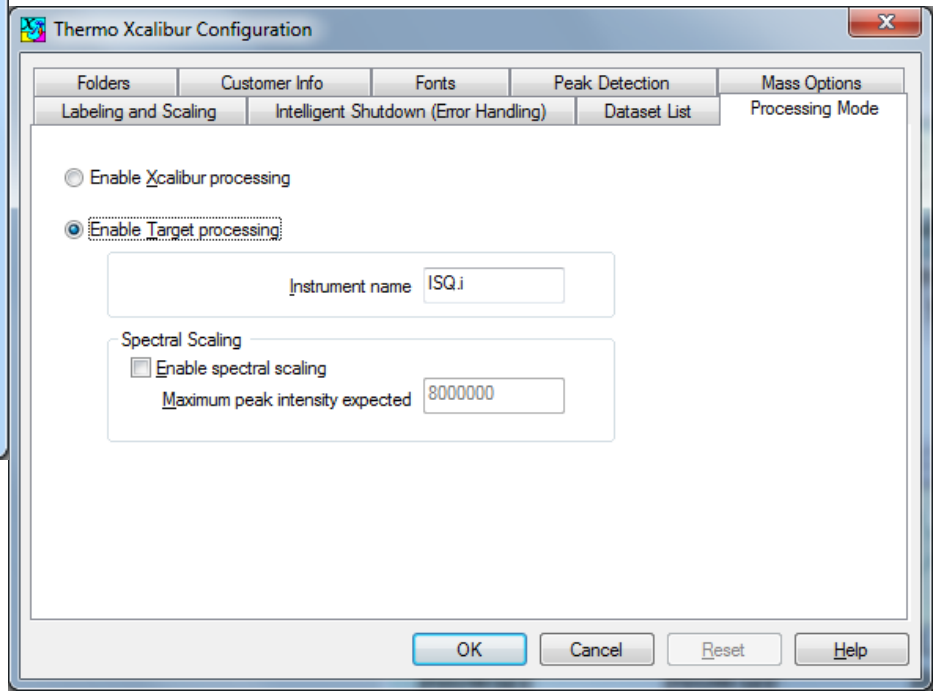
Thermo Scientific Target Software – Still Viable Product





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Ion Ratio Stability for DFTPP

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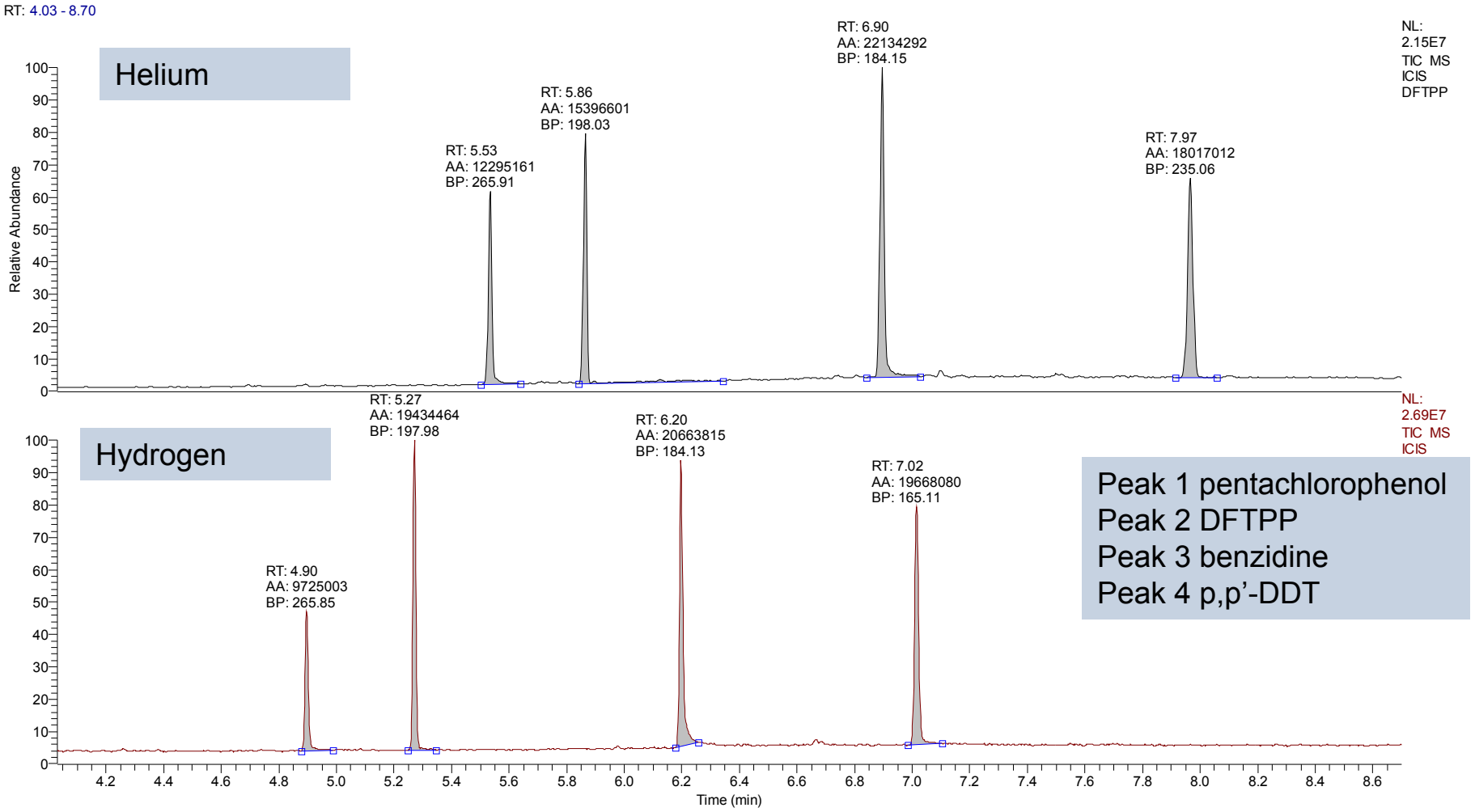
BFB Ion Ratio Stability

m/z	Criteria	run01	run02	run03	run04	run05	run06	run07	run08	run09	run10	run11
50	15-40%	28	26	26	24	27	26	25	26	28	25	25
75	>30%	52	51	48	48	51	52	49	48	48	50	53
95	100%	100	100	100	100	100	100	100	100	100	100	100
96	5-9%	8.0	7.3	7.9	7.7	8.2	7.2	7.7	7.4	7.8	7.5	7.7
173	< 2% of 174	0.4	0.6	0.7	1.5	0.4	0.4	0.8	0.7	0.5	1.1	0.3
174	>50%	76	75	69	69	75	70	72	72	71	74	72
175	5-9% of 174	7.3	7.4	7.4	5.9	7.6	8.5	6.4	7.7	6.8	6.4	6.7
176	95-101% of 174	96	95	100	96	93	96	98	95	96	101	96
177	5-9% of 176	5.1	6.3	6.6	5.2	6.4	6	5.1	5.5	6.6	6.5	6

EPA Method 8270 Performance Mix



Peak 1 pentachlorophenol
Peak 2 DFTPP
Peak 3 benzidine
Peak 4 p,p'-DDT

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Method Parameters: EPA Method 524.2

- **Purge & Trap: 5 mL sample**

VOCARB	Purge	11 min
	Dry Purge	1 min
Desorb	240°	2 min

- **Oven**

50°	1 min.	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	

- **Inlet**
  - S/SL: 200°
  - Split : 40:1
- **Carrier: 0.7 mL/min H_2**
- **Column: TG VMS 0.18 mm x 20 m x 1.0 µm**

- **MS**

Source	275°
EC	25 uamps
FS 0.8-1.6 1.6- 15 min	47-300 35-300
Scan Speed	1,687 u/s

Method Parameters: EPA Method 525.2

- **Standards**
  - Prepared in ethyl acetate
  - Calibration curve (0.1, 0.5, 1.0, 2.0, 5.0, 10 ug/mL)

- **Inlet**
  - S/SL: 325°C
  - Split Mode: 15:1
- **Carrier: 1 mL/min H_2**
- **Column**
  - TG-5 SilMS 20m x 0.18mm x 0.36 µm

- **Oven:**

50°	1 min	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	20°/min

- **MS**

Source	325°
EC	15 uamps
Full Scan	35-500
Scan speed	4,650 u/ s

Method Parameters: EPA Method 8270D

- **Standards**
  - Prepared in ethyl acetate
  - Calibration curve (1.0, 2.0, 5.0, 10, 50, 100, 200 ug/mL)

- **Inlet**
  - S/SL: 325°C
  - Split Mode: 15:1
- **Carrier: 1 mL/min H_2**
- **Column**
  - TG-5 SilMS 20m x 0.18mm x 0.36 µm

- **Oven:**

50°	1 min.	30°/min
150°	0 min	20°/min
200°	0 min	30°/min
300°	0 min	20°/min
350°	0.5 min	

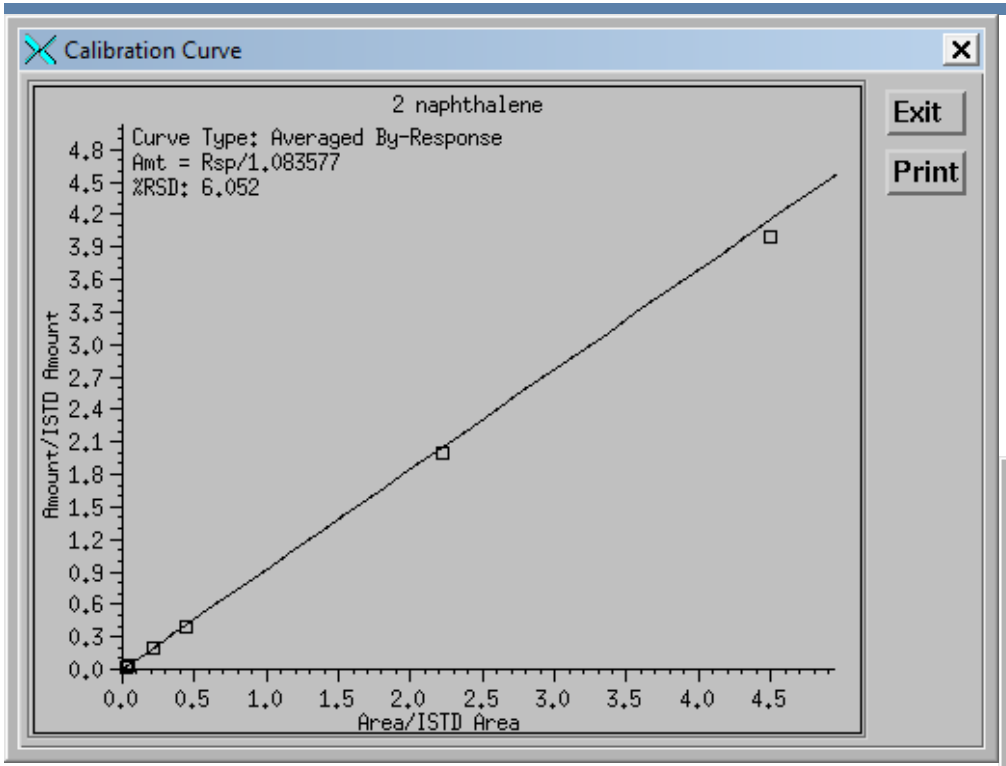
- **MS**

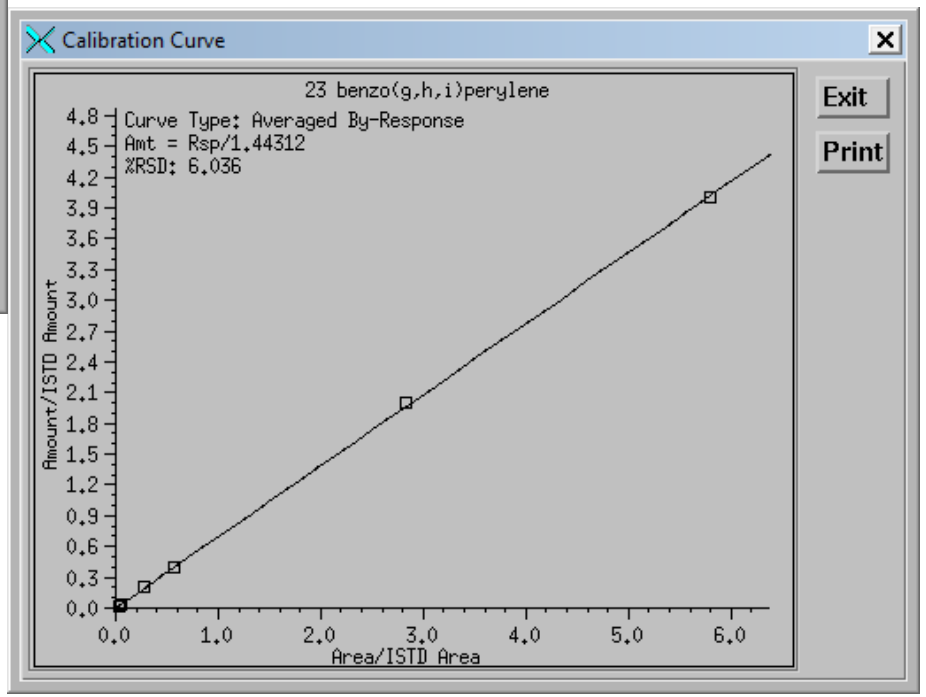
Source	325°
EC	15 uamps
Full Scan	35-500
Scan speed	4,650 u/ s

Linear Fit of Low Level PAHs in SIM (0.05 to 10 ppm)

Compound	%RSD	Compound	%RSD
naphthalene	6.1	flouranthene	6.7
2-methylnaphthalene	8.7	benzo(a)anthracene	8.2
1-methylnaphthalene	7.7	chrysene	5.9
acenaphthylene	8.5	benzo(b)fluoranthene	8.6
acenaphthene	8.5	benzo(k)fluoranthene	9.2
flourene	8.5	benzo(a)pyrene	7.8
phenanthene	3.8	indeno(1,2,3,c,d)pyrene	5.1
anthracene	7.0	dibenz(a,h)anthracene	5.4
pyrene	3.6	benzo(g,h,i)perylene	6.0
acenaphthene-d10	4.6	phenanthene-d10	4.5
chrysene-d12	9.7	perylene-d12	7.4

Cal Curves: Naphthalene & Benzo(g,h,i)perylene





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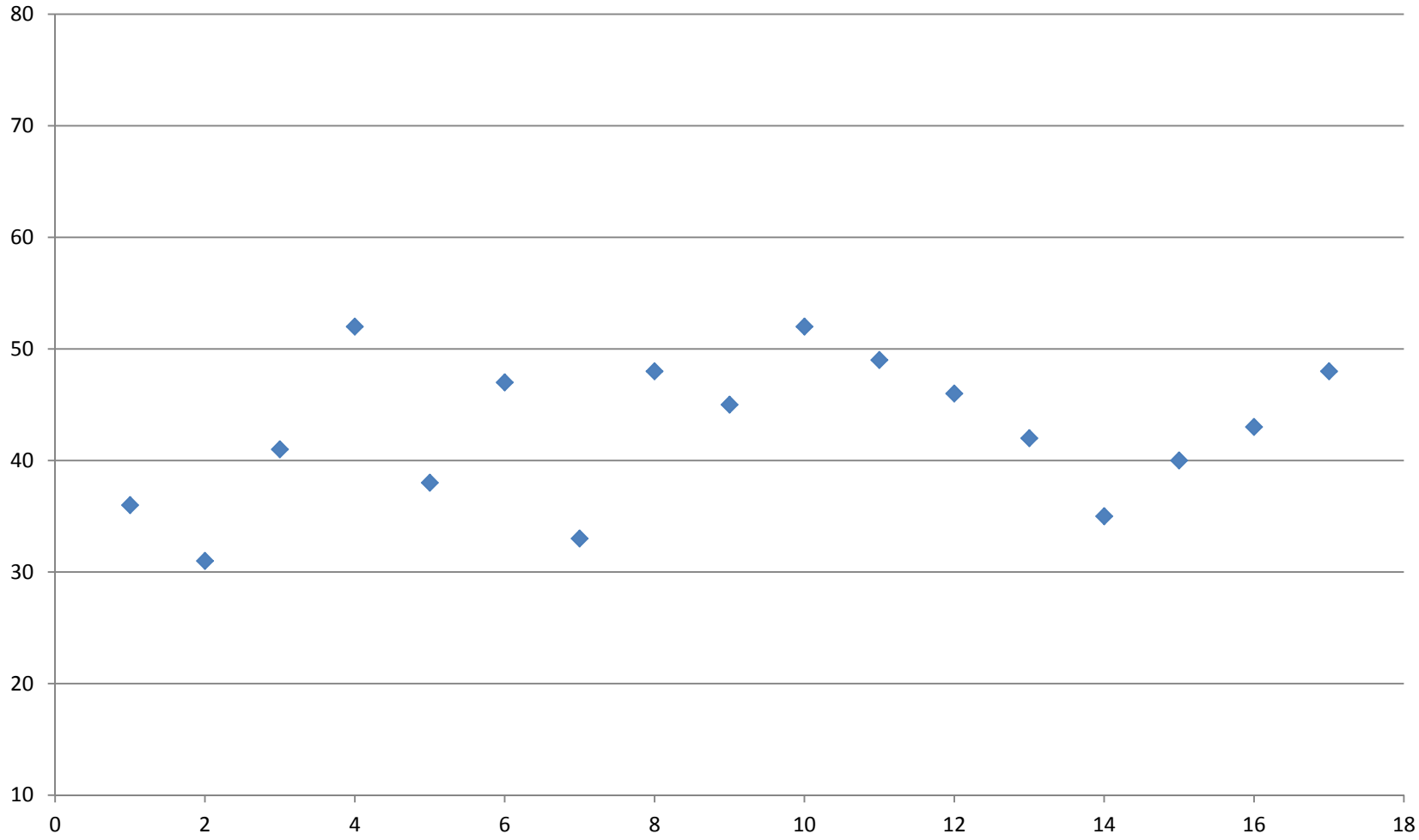
Low Level PNAs 50 ppb (+/- 50%) Accuracy



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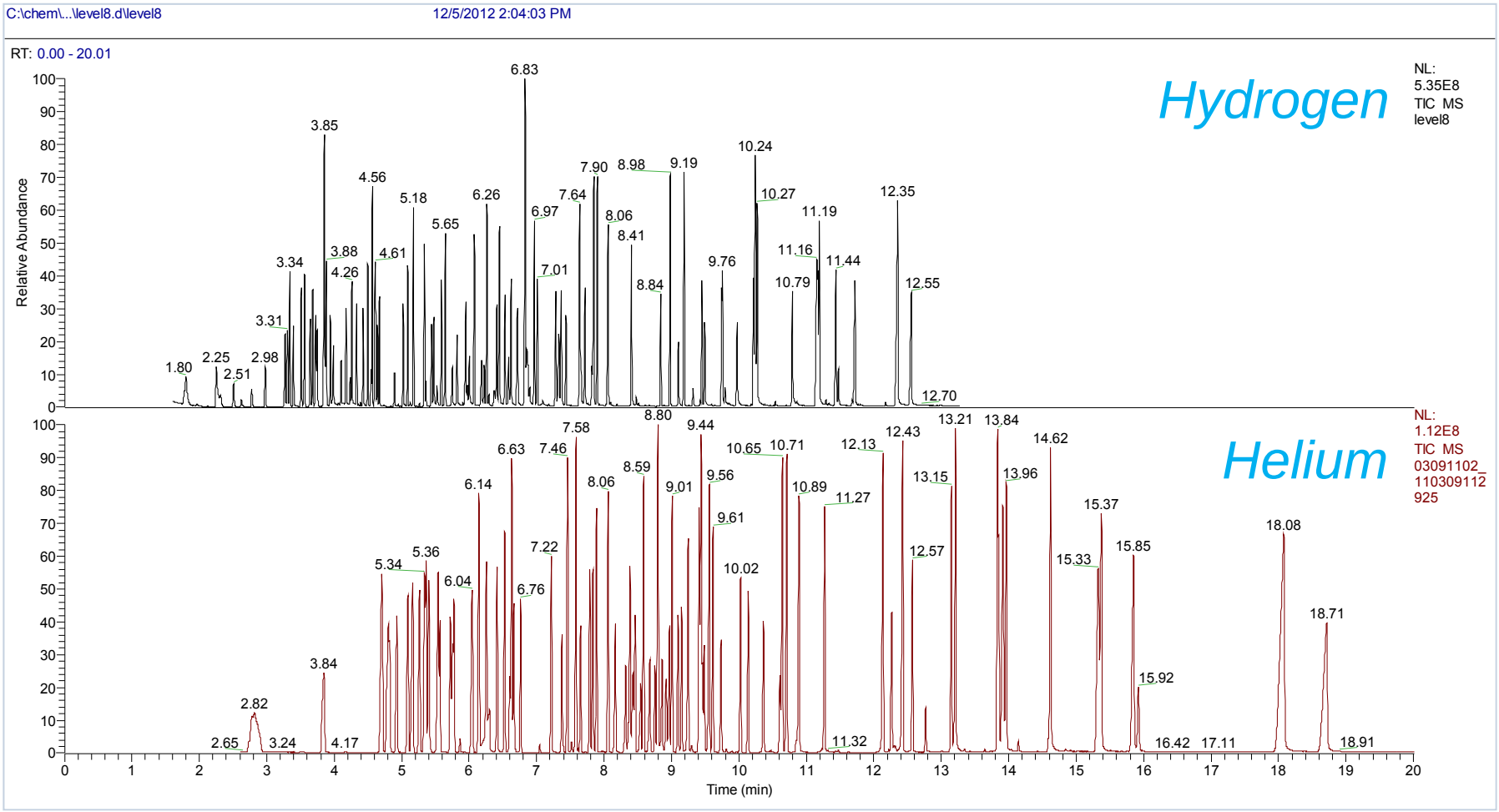
8270: Comparison of Hydrogen to Helium Run Times



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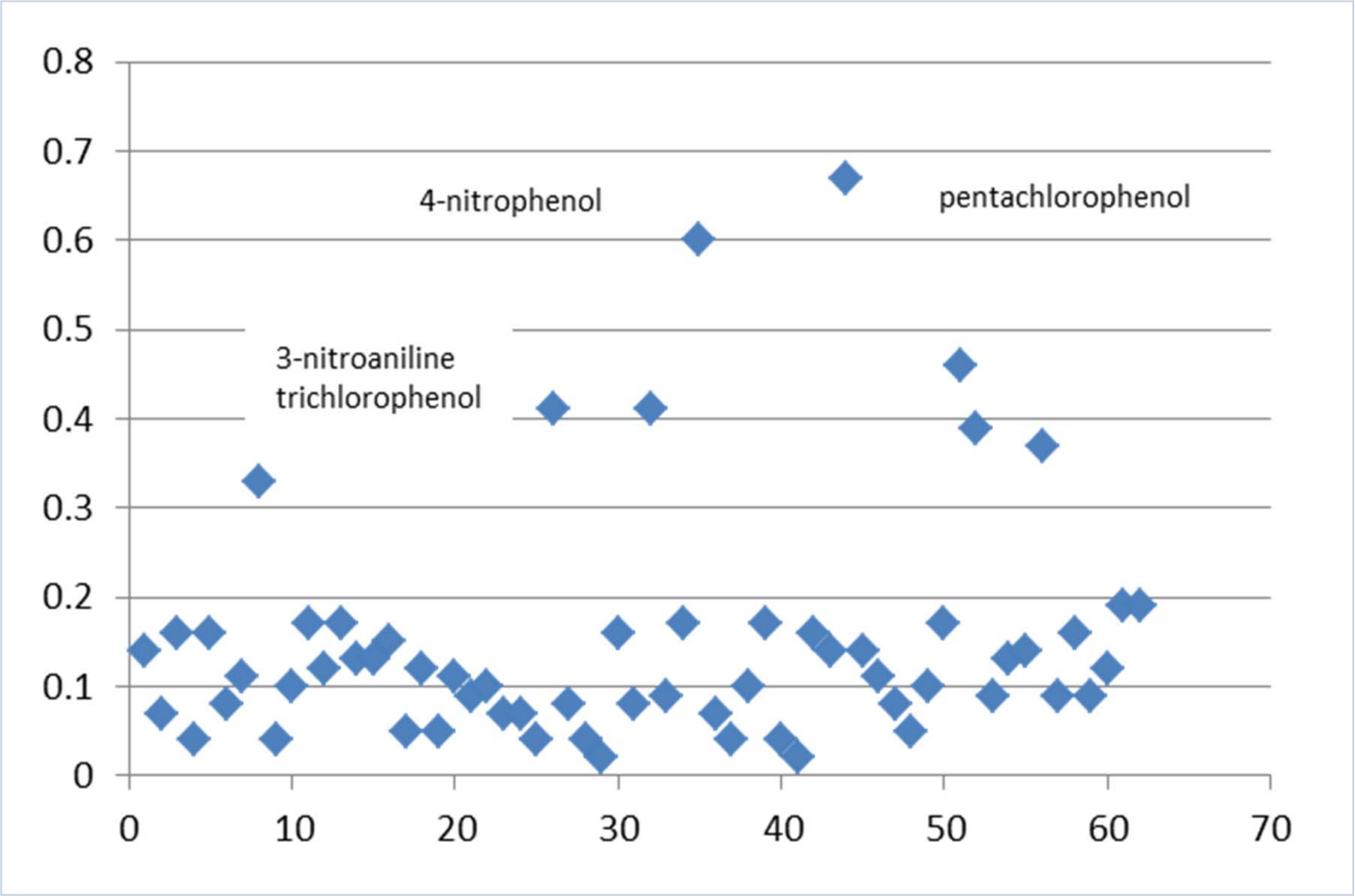
EPA Method 8270 MDLs



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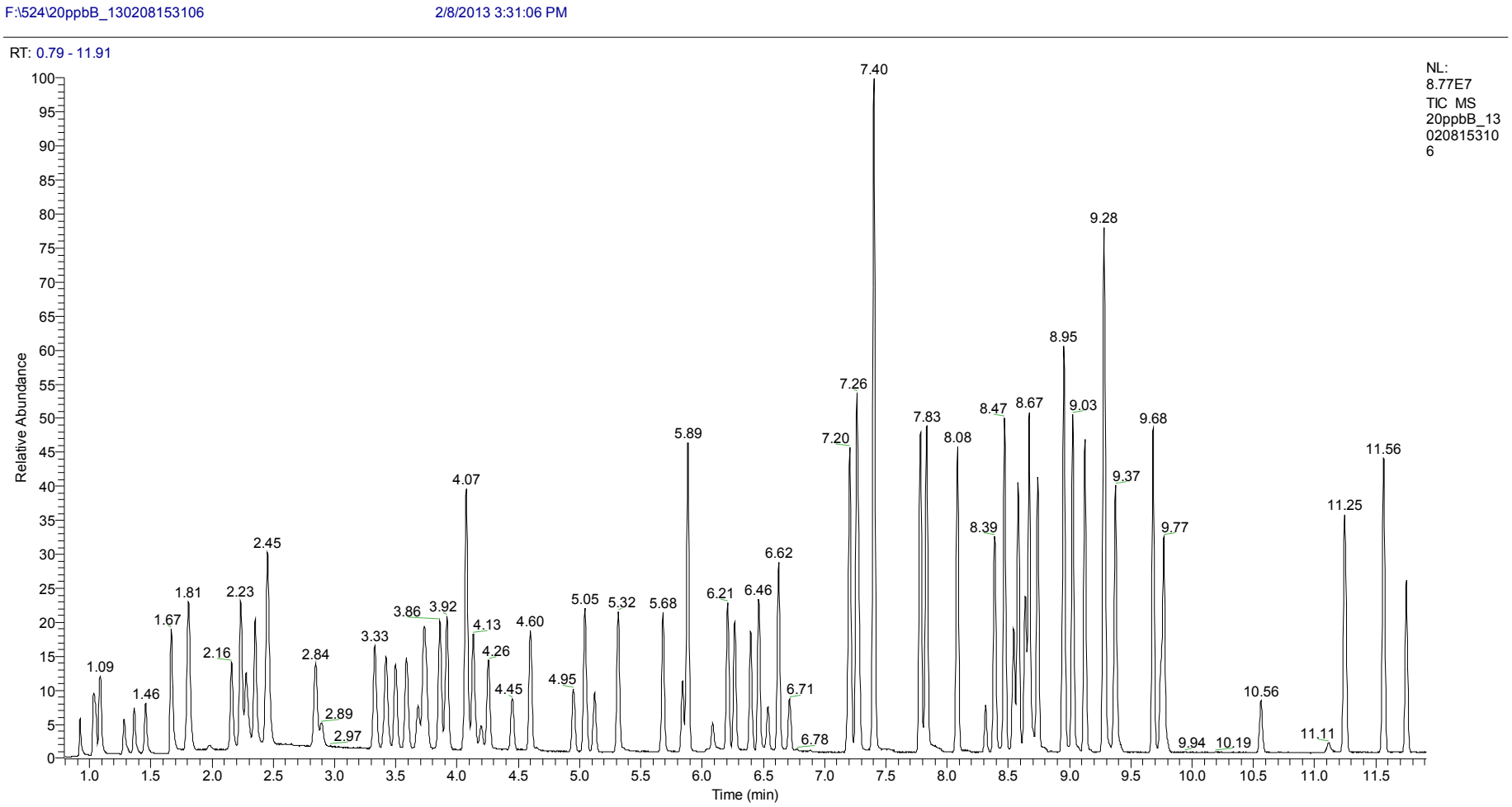
Performance: EPA Method 524 - 20 ppb Standard



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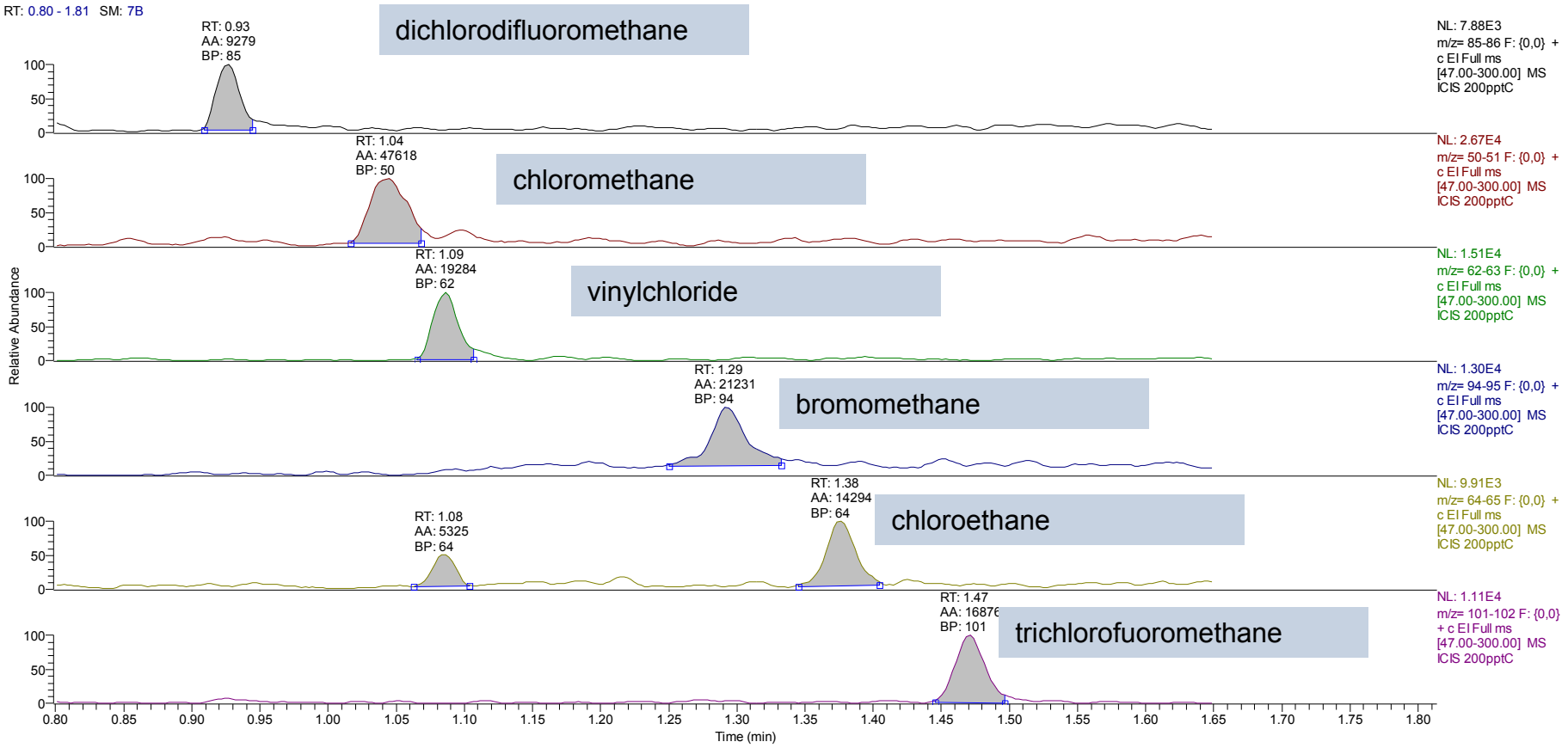
Gases at 200 ppt



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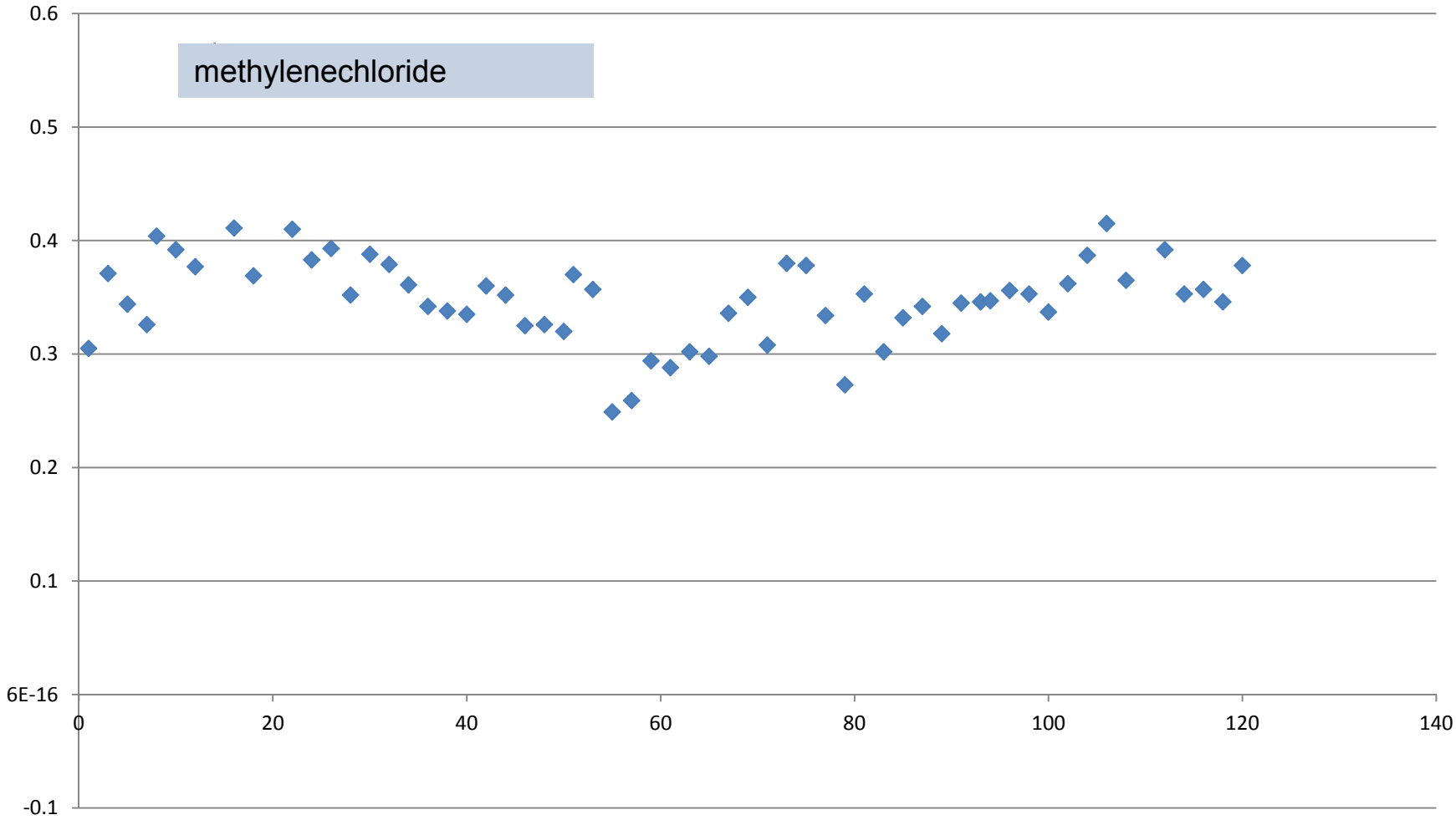
Accuracy of 400 ppt - Passed +/- 50%



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Moving To Hydrogen on the GC Side

- **Hydrogen Sensor is a *Must***
  - In GC oven
  - Possible on the hydrogen generator
  - May also be required at the ceiling of the lab
- **Expect Lower Inlet Pressure**
  - Due to viscosity differences of H_2 and He
  - Move to a smaller id column

Moving to Hydrogen on the MS Side

- ***NO*** **MS hardware change required to meet H_2 Installation Specs**
- **Maintain good vacuum**
  - Extended performance turbomolecular pumps
  - 9.8 x 10^{-6} Torr (1 ml/min hydrogen flow)
- **Higher initial background**
  - Minimized with stainless steel pre-cleaned tubing
  - UHP Grade 5.0 or better Hydrogen Source
  - Bake out source at 350°C for one hour with filament on
- **CI Effect on some compounds**
  - Require linear or quadratic fit
  - Reduce flow rate of H_2 into MS
- **Pressure dependency:**
  - Minimize solvent vapor with smaller id columns

ISQ Off-Axis Single Quadrupole GC-MS

Thank you for your attention!

Questions?

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