

Semivolatiles Analysis by GC/MSD

Drinking Water and Wastewater



Semivolatiles – The Main Classes of Compounds from Various Methods

Drinking Water

- Pesticides
- Herbicides
- PAHs
- Phthalates
- Aroclors - PCBs
- Nitrotoluenes

Waste Water

- PAHs
- Chloro- PAHs, ethers, phenols
- Nitro- phenols, amines, toluenes
- Pesticides & Herbicides
- Aroclors - PCBs
- Misc Industrial Chemicals





Drinking Water Analysis Issues and Solutions

1. Sensitivity
2. Identification
3. Sensitivity and Unknowns
4. Analysis time
5. Cycle Time

1. LVI with PTV and/or SIM
2. RTL and DRS
3. Synchronous SIM/scan
4. Narrower bore column
5. Faster Oven Cooldown





Wastewater Analysis Issues and

Solutions

1. Sensitivity
2. Identification
3. Analysis time
4. Nonproductive Time
 - Matrix bakeout
 - Instrument maintenance
5. Cycle Time

1. Sample Cleanup such as GPC
2. RTL and DRS
3. Narrower bore column
4. Capillary Flow Technology
 - backflushing
5. Faster Oven Cooldown





Semivolatiles Instrument Configuration for Wastewater

- **Agilent 6890 or 7890 GC & 5975 MSD**
 - S/SL inlet, single-taper liner, no glass wool, P/N **5181-3316**
 - 20 m x 180 μm x 0.36 μm DB-5.625, P/N **121-5622** – faster runs
 - QuickSwap for column maintenance/replacement without venting the 5975 or cooling the transfer line
 - 5975 mounted in rear position of 7890 allows use of the optional oven insert.
 - Faster ramp rates
 - Faster cool down





Semivolatiles Instrument Configuration for Drinking Water

- **Agilent 6890 or 7890 GC & 5975 MSD**
 - S/SL inlet, direct connect liner, no glass wool, P/N **G1544-80730**
 - 20 m x 180 μm x 0.36 μm DB-5.625, P/N **121-5622** – faster runs

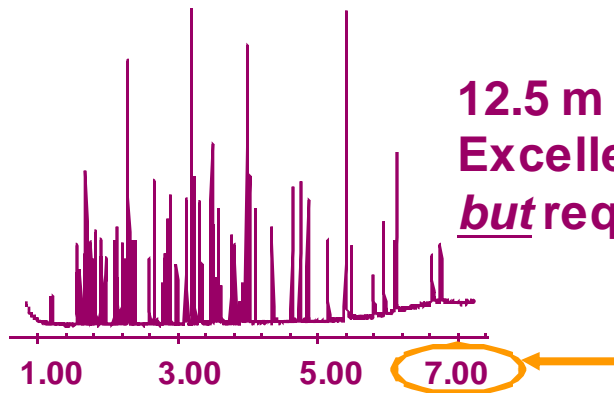
or

 - PTV inlet, multi-baffle liner, no glass wool, P/N **5183-2037**
 - 30 m x 250 μm x 0.25 μm HP-5ms, P/N **19091S-433**

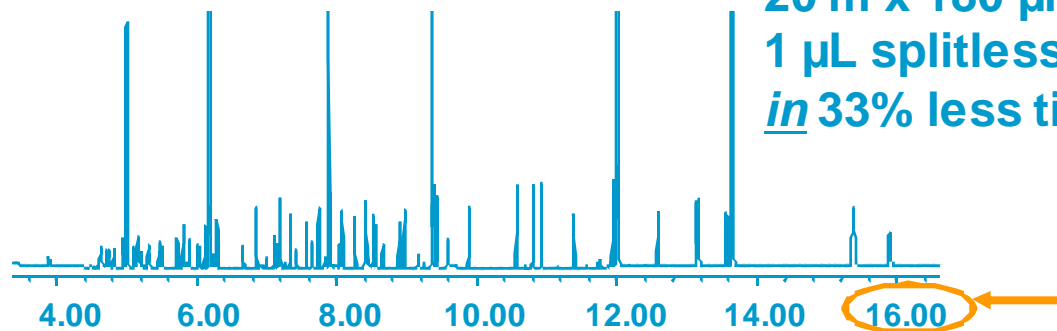


83 Semivolatiles on 3 Different Columns.

Significant Time Savings, Possible Trade-offs

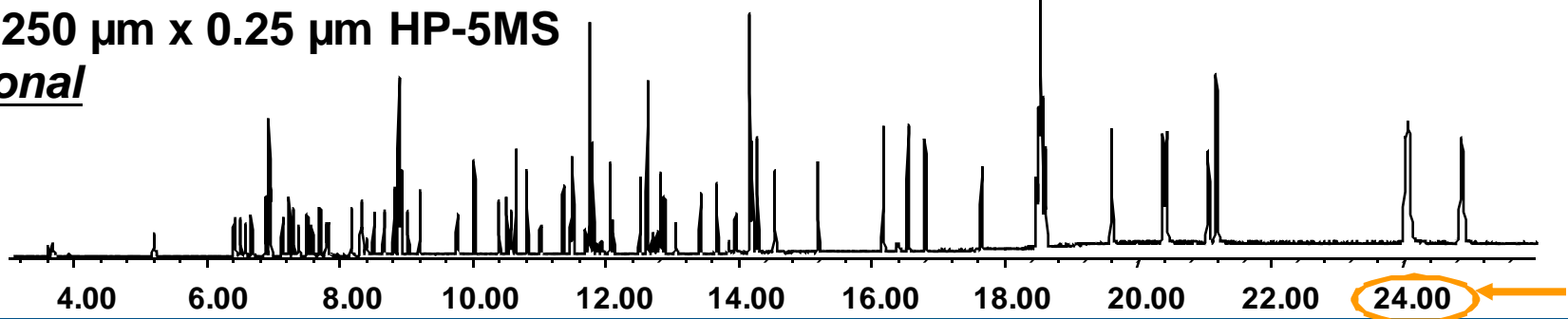


12.5 m x 100 μm x 0.1 μm HP- 5ms
Excellent for rapid screening
but requires minimum 10:1 split injection.



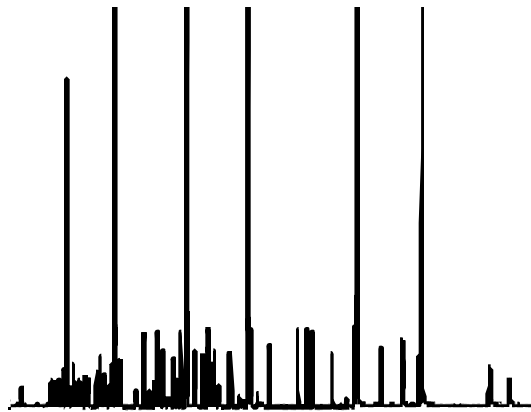
20 m x 180 μm x 0.36 μm DB-5.625
1 μL splitless injections maintain MDLs
in 33% less time.

30 m x 250 μm x 0.25 μm HP-5MS
Traditional

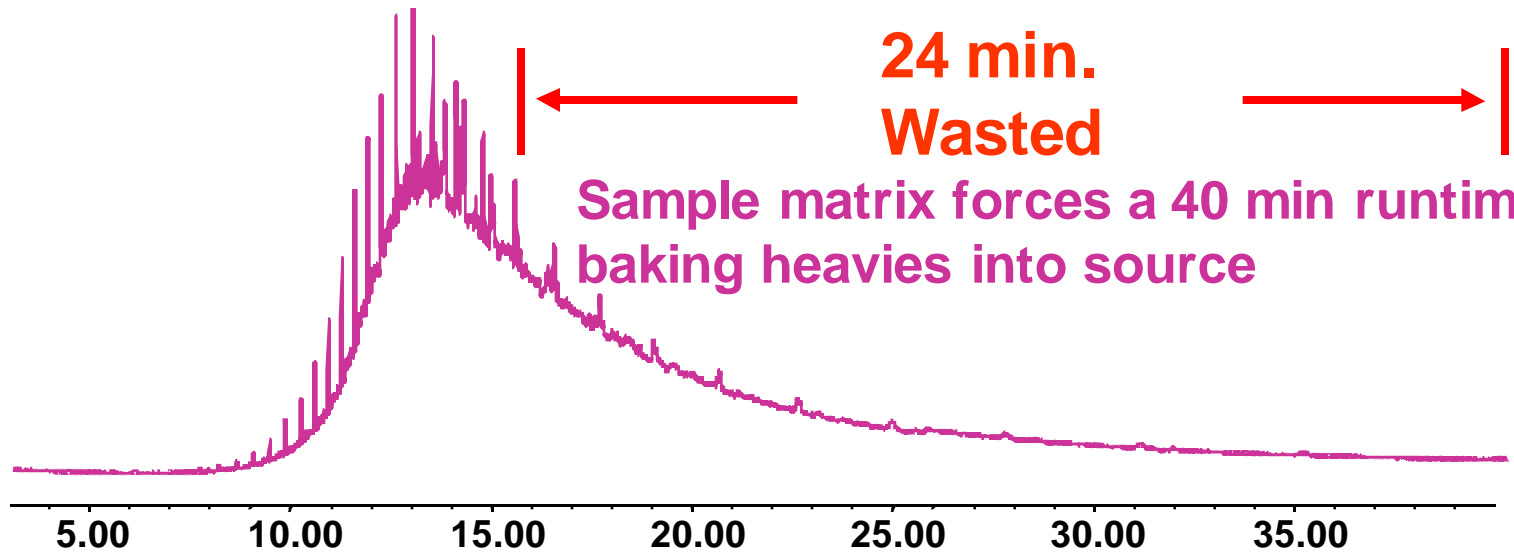


Run Time and Cycle time Wasted

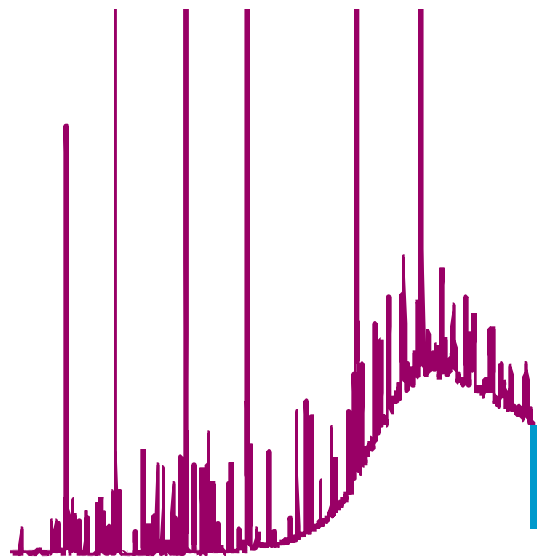
Due to Matrix Bakeout



**5 ppm semivolatiles standard,
run time = 16 min.
77 analytes plus 6 ISTDs at 40 ppm**



Cycle Time and Instrument Maintenance Time Savings with Capillary Flow Technology and Backflush



Spiked Sample

4 min. Backflush

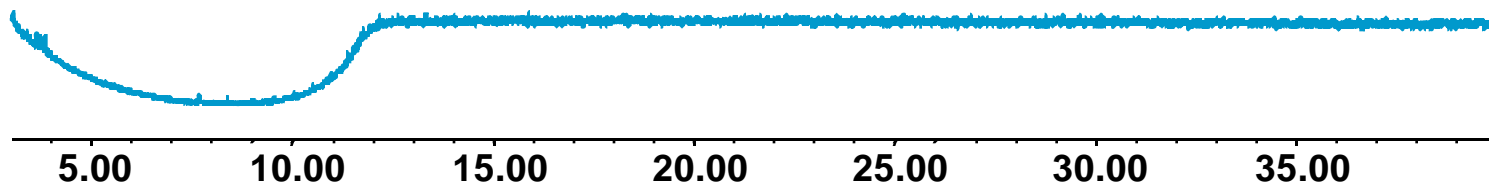


20 min. Saved



Scale 20x more sensitive than above

Solvent injection after above 4 min backflush run. Inlet and column clean.



Cycle Time Reduction = Productivity Gain



	Yesterday's Typical System	Today's 7890 5975	Minutes Saved
Run Time, 250 μ m <u>vs</u> 180 μ m column	25	17	8
Run time, matrix bake-out <u>vs</u> Capillary Flow Tech	50	21	29
Cool down time from 320 °C to 40 °C	7	3.3	3.7
Total time savings using a 7890-5975, narrower bore column and Quickswap	57	24.4	32.6

Time Savings > 50 % => Run Twice the Samples/Day =>.....



Performance is Maintained with Capillary Flow Technology

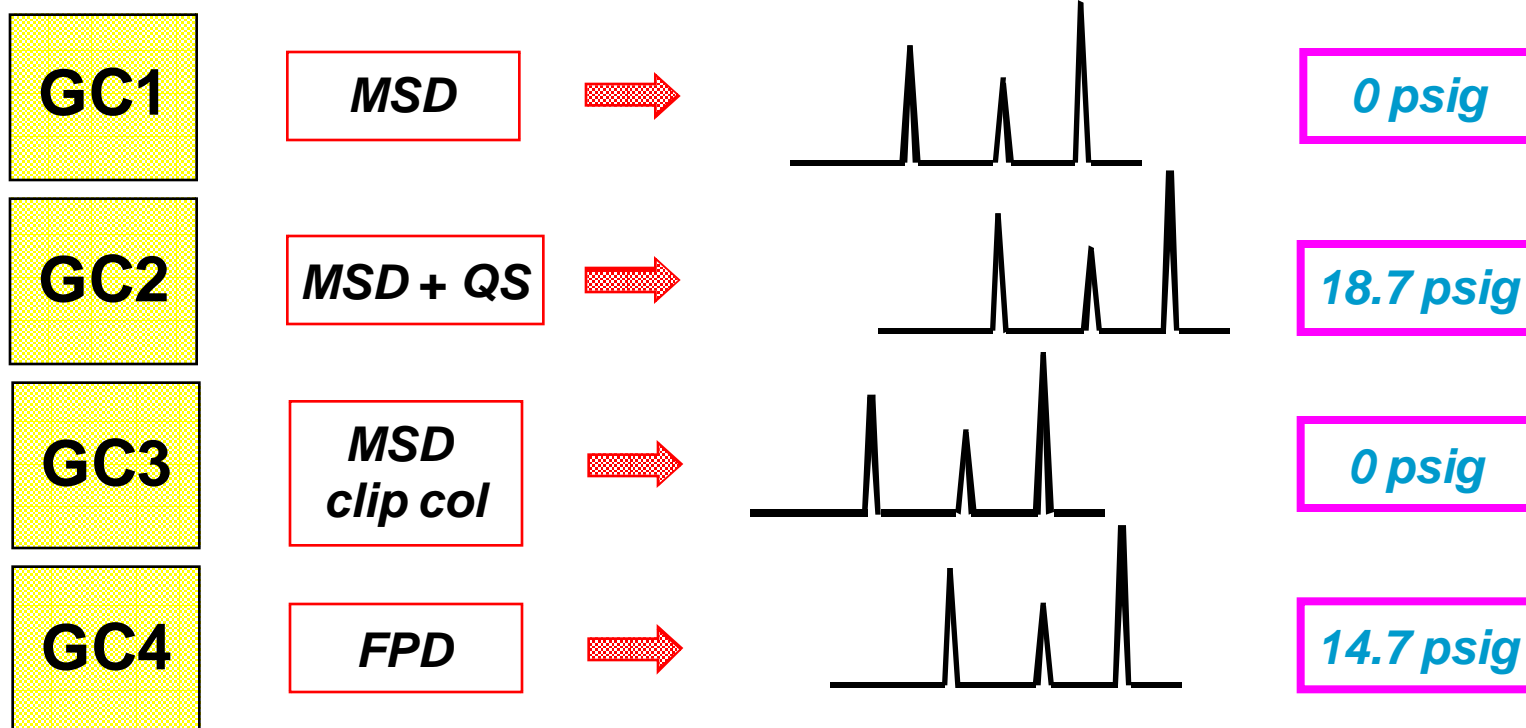


- As measures of performance, criteria from the widely used US EPA Method 8270 were measured. The System Performance Check Compounds are active and therefore have minimum response requirements. The Calibration Check Compounds are from various classes and are used to check overall system linearity

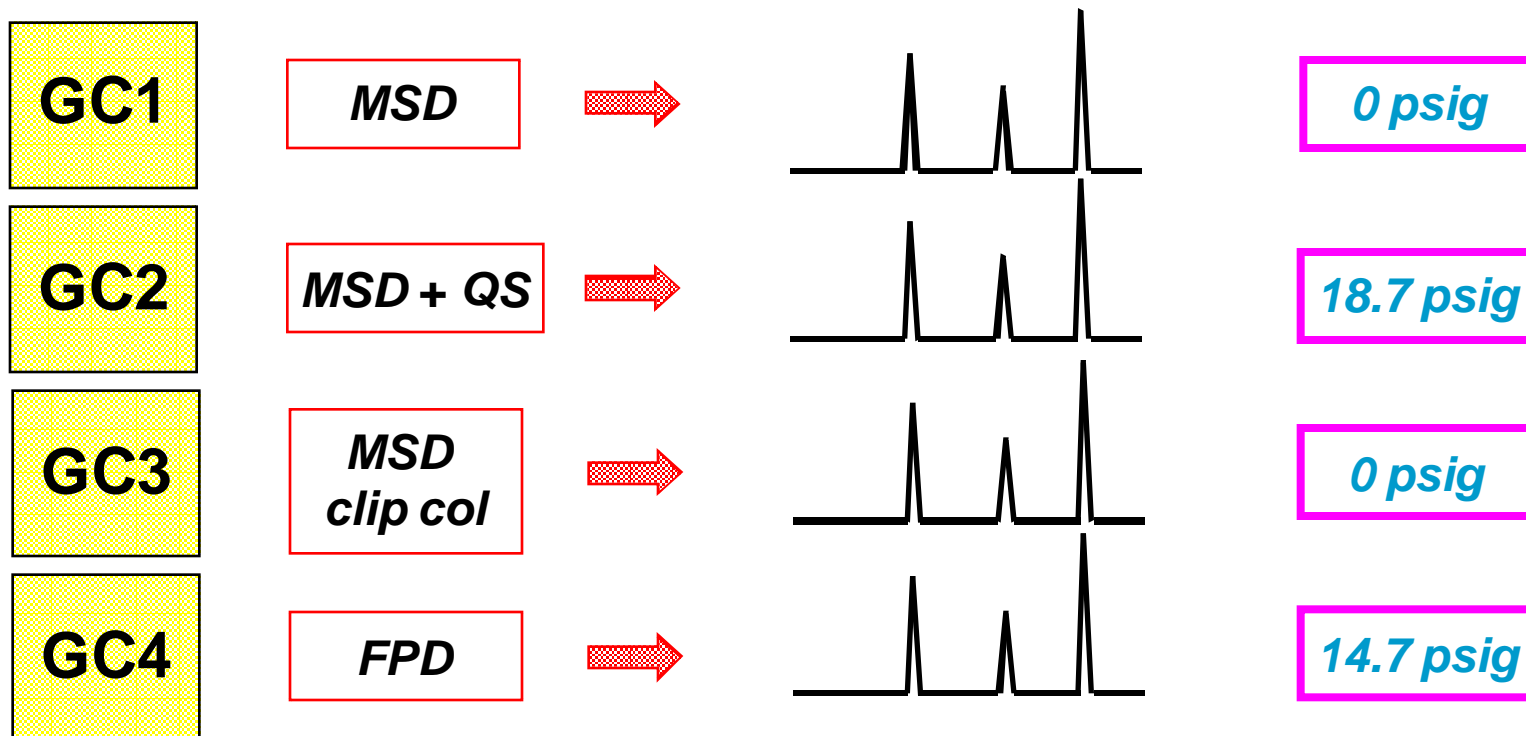
	8270 criteria	7890- 5975 w/QS (range)
4 SPCCs minimum avg RRF	0.050	0.114 - 0.405
13 CCCs %RSD	< 30 %	2% - 20%



Different GCs, Columns and Detectors Retention Times Vary Widely



Retention Time Locking (RTL) Precisely Matches RTs in Any System



Benefits of RTL

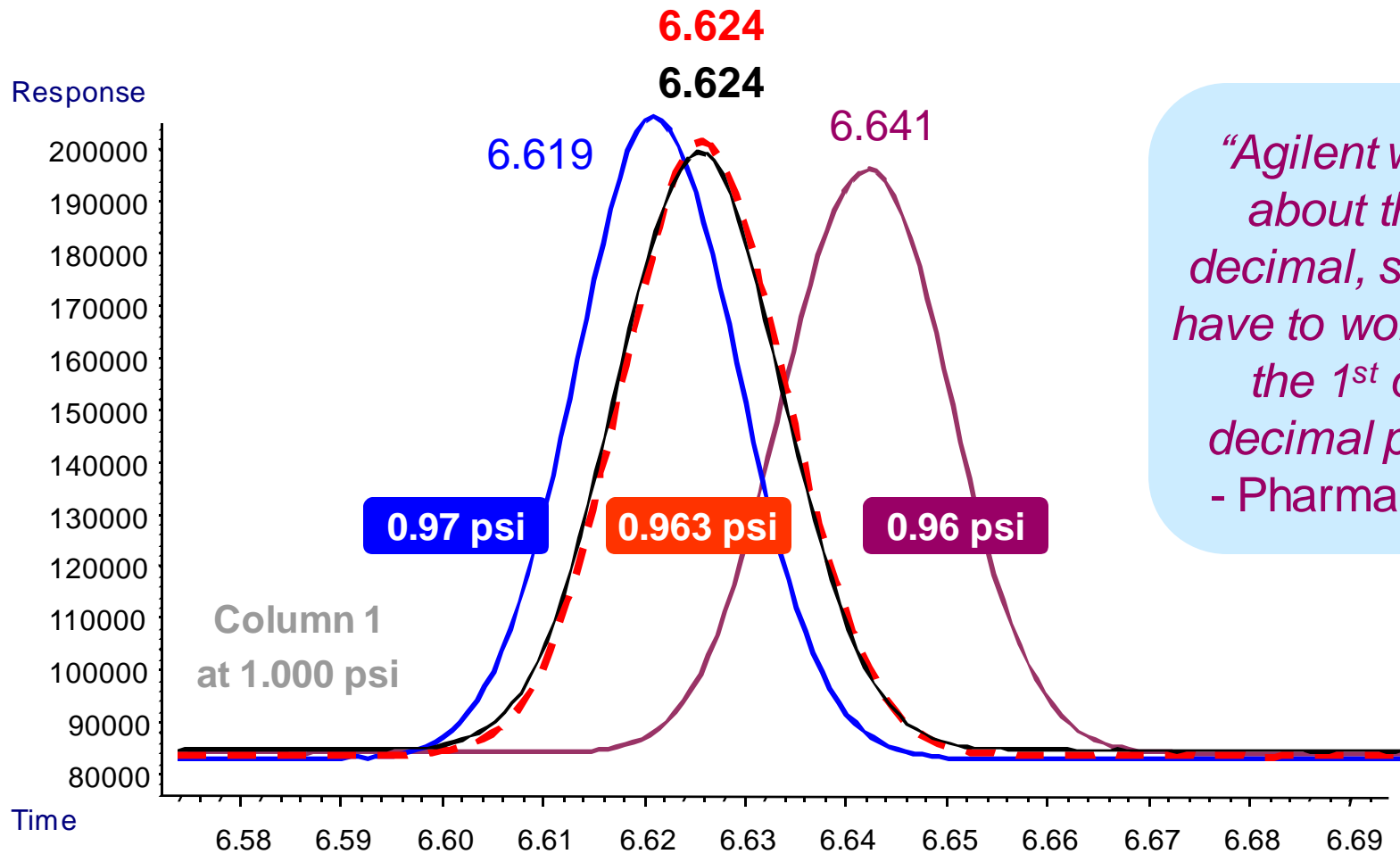


- Databases with precise retention times can be built and used with deconvolution for rapid data analysis
- Never have to change SIM group times
- Never have to change integration events
- Never have to change ion extraction windows
- Rapid data comparison, uniform methods and method transfer
- Leak detection



7890 can control the precision of 1/1000 psi

Key to even better Retention Time Locking (RTL)



“Agilent worries about the 3rd decimal, so I don’t have to worry about the 1st or 2nd decimal point...”
- Pharma (USA)



RTL is more flexible now...



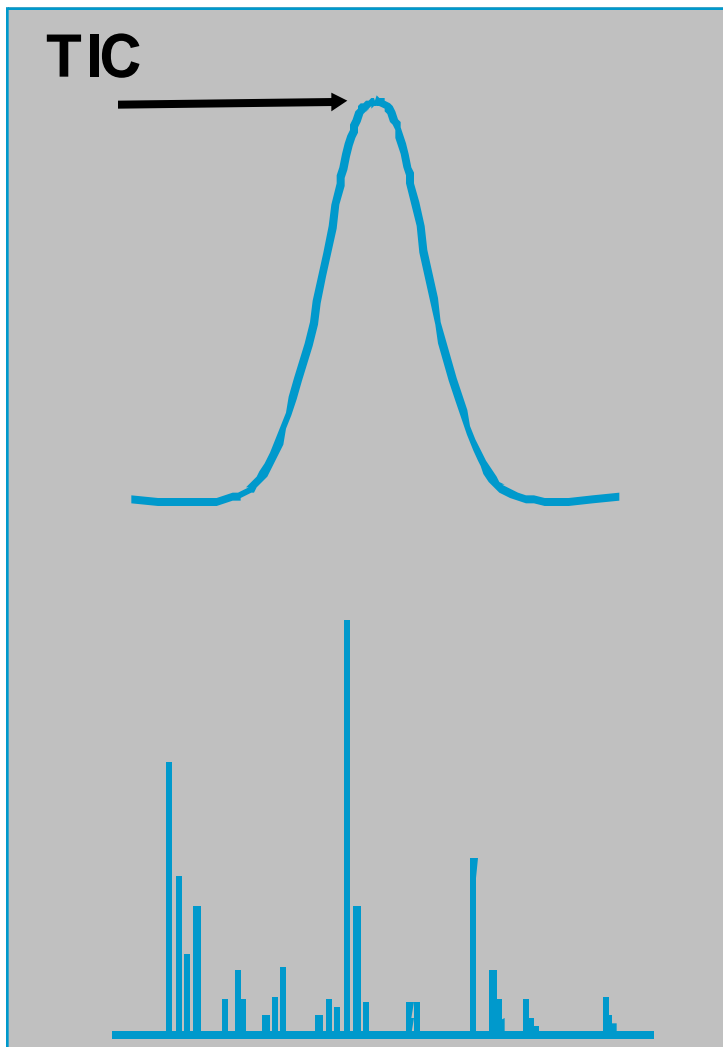
The screenshot displays the 'Enhanced RTL setup: dwpFiehn.m is LOCKED' window. On the left is a file tree showing folders like 'HP', 'IntelWise', 'Logs', 'MKS', 'MPW2007', 'msdchem', '1', '5975', '5975.OLD', 'DATA', '050907-024.D', '25_ISTD.D', 'evaldemo.d', 'ggqex.d', 'Sample_AD', 'SIM20ms_2.D', 'SPINACH.D', 'ecm', 'METHODS', 'default.m', 'DRS_DEMO.M', 'dwpFiehn.m', 'refspec', 'RTLOCK', and 'RTLOCK1.D' through 'RTLOCK5.D'. The main area shows five stacked Total Ion Chromatograms (TIC) for RTLOCK1.D through RTLOCK5.D. Each plot shows Abundance vs. Time (min) with a peak labeled with its retention time and XCR value. For example, RTLOCK1.D has a peak at 17.015 min with XCR 0.999. RTLOCK2.D has a peak at 16.871 min with XCR 0.999778. RTLOCK3.D has a peak at 16.727 min with XCR 1.0. RTLOCK4.D has a peak at 16.590 min with XCR 0.99745. RTLOCK5.D has a peak at 16.458 min with XCR 0.996749. At the bottom, a mass spectrum for Scan 1718 (16.727 min) is shown with Abundance vs. m/z, featuring major peaks at 731, 120.1, 135.1, and 149.1. A dialog box titled 'Edit R.T. for RTL Calibration of myristic acid d27 @ 16.727 min.' is overlaid on the right, listing retention times for five runs at different pressures: Run 1 (8.246 psi) with value 17.015, Run 2 (9.277 psi) with value 16.8709, Run 3 (10.308 psi) with value 16.7273, Run 4 (11.339 psi) with value 16.5896, and Run 5 (12.370 psi) with value 16.4583. The dialog includes 'OK', 'Cancel', and 'Help' buttons.



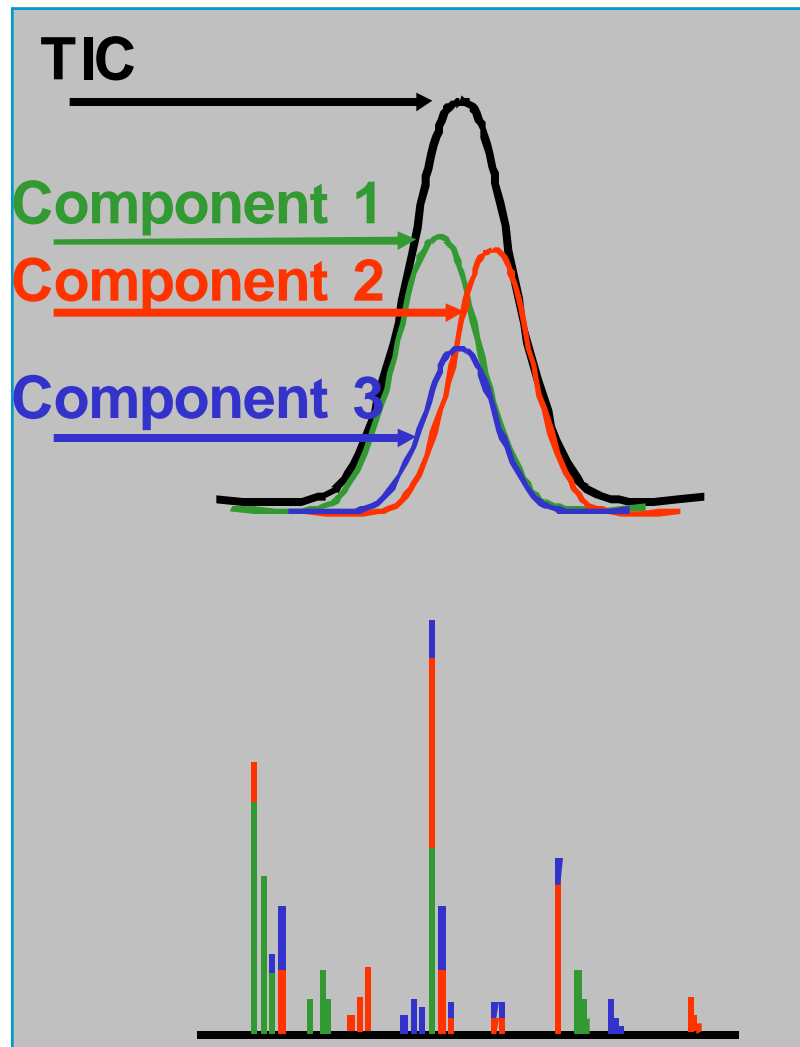
A Single Chromatographic Peak May Contain Multiple Components



TIC & Spectrum



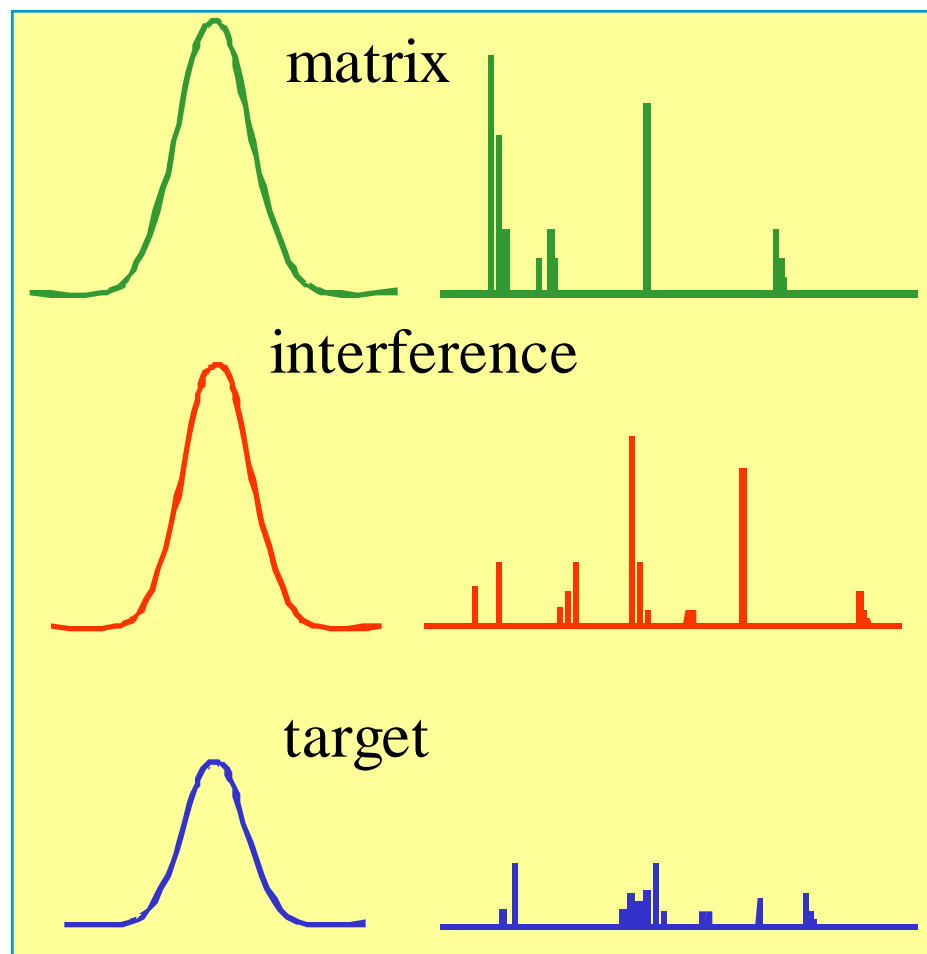
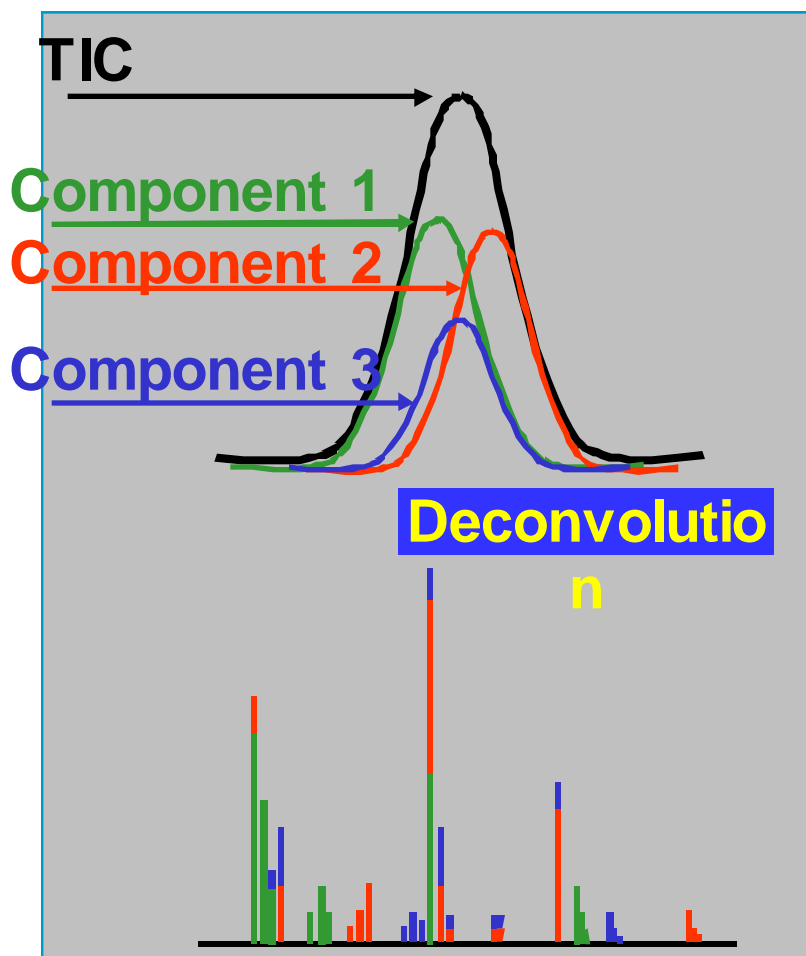
Components and Mixed Spectra



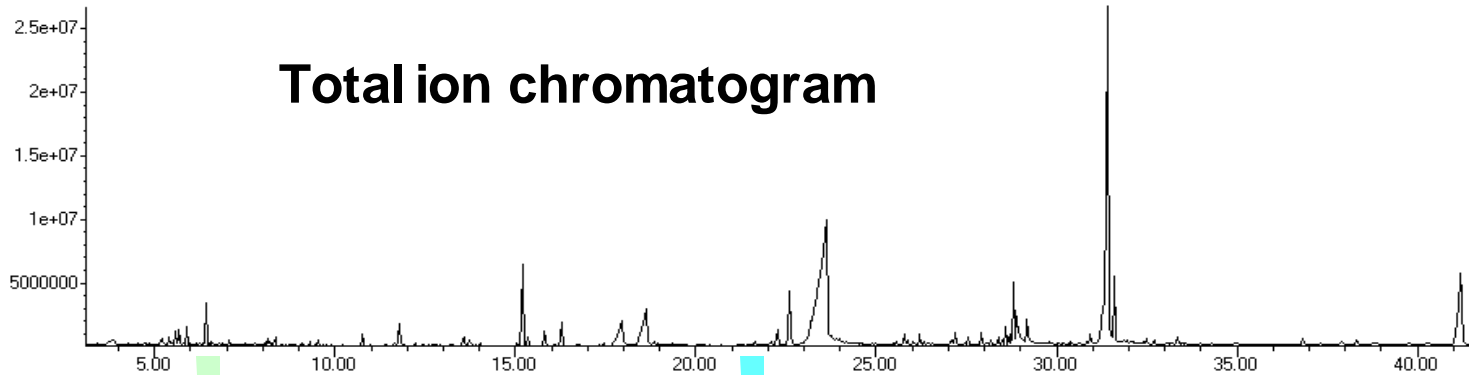
AMDIS Deconvolution Pulls Out Individual Components and their Spectra



Components and Mixed Spectra Deconvoluted peaks and spectra



DRS = 3 Distinct but Integrated Processes



Targets are identified by comparison to locked R.T.s and 3 qualifier ion ratios, then quantified using target ion area vs ISTD calibration Results

AMDIS 32 deconvolutes component spectra and searches target MS database using locked RT used as a qualifier

Deconvoluted Target spectra confirmed by AMDIS, searched against NIST05 MS database

Confirmed AMDIS hits

Confirmed NIST05 hits

Combined quantitative and qualitative Summary report





Partial DRS Report of Semivolatiles Spiked In 5000 ppm Gasoline-Kerosene-Diesel Mix

MSD Deconvolution Report

Sample Name: Short Mix + 50GKD

Data File: C:\msdchem\1\DATA\Semivolatiles Spike

Date/Time: 09:39 AM Tuesday, Dec 11 2007

Importance of RTL

The NIST library was searched for the components that were found in the AMDIS target library.

R.T.	Cas #	Compound Name	Agilent	AMDIS		NIST	
			ChemStation Amount (ng)	Match	R.T. Diff/sec.	Reverse Match	Hit Num.
2.8499	62759	N-Nitrosodimethylamine	5.55	93	-0.5	96	1
4.730	62533	Aniline		98	4.2	96	1
5.0358	3855821	1,4-Dichlorobenzene-d4	40	99	-0.2	93	1
5.214	106445	4-Methylphenol		66	-7.7	89	1
6.2476	1146652	Naphthalene-d8	40	99	-0.1	86	1
6.2679	91203	Naphthalene	3.77	58	-0.1	81	1
6.944	91576	2-methylnaphthalene		97	0.1	91	1
7.9945	15067262	Acenaphthene-d10	40	96	-0.1	91	1
8.0256	51285	2,4-Dinitrophenol		58	-0.0	68	1
8.0572	100027	4-Nitrophenol	2.44	81	-0.1	92	1
8.3833	84662	Diethyl phthalate	0.23	78	-0.2	75	1
8.542	86737	fluorene		56	0.0	80	58
8.5644	534521	4,6-Dinitro-2-methylphenol	3.99	89	-0.1	88	1
9.2806	92671	4-Aminobiphenyl	6.1	94	-0.1	89	2
9.2829	87865	Pentachlorophenol	4.1	91	-0.1	66	11
9.4964	1517222	Phenanthrene-d10	40	97	-0.1	86	1



DRS A.04 - enhanced for more effective review



- QEdit enhanced to:
 - Import AMDIS results into MSD ChemStation
 - Quantitate
 - Display AMDIS Results
 - Manually Integrate
- Enhanced DRS capabilities/Report
- Requires G1701EA E.02



QEdit - before DRS importing



Import Results to bring AMDIS deconvolved data into QEdit for quantitation.

The screenshot displays the QEdit software interface with several windows open:

- Window #8:** Total Ion Chromatogram (TIC) for SPINACH.D\data.ms. The x-axis is Time (min) from 13.56 to 13.78. The y-axis is Abundance from 0 to 250,000. A major peak is labeled at 13.716 minutes.
- Window #1:** Mass Spectrum for Scan 1989 (13.717 min). The x-axis is m/z from 20 to 415. The y-axis is Abundance from 0 to 500,000. The base peak is at m/z 188.1. Other labeled peaks include 80.0, 131.9, 247.8, 407.3, and 479.4.
- Window #7:** TIC: SPINACH.D\data.ms. The x-axis is Time (min) from 13.56 to 13.81. The y-axis is Abundance from 0 to 80,000. A peak is labeled at 13.716 minutes.
- Table:** A list of compounds with their retention times and identification status. The table is as follows:

#	Compound Name
1	x 13.718 *Phenanthrene-d10
2	5.792 Dichlorvos
3	7.565 Mevinphos
4	7.762 Vernolate
5	11.182 Dibrom (naled)
6	11.272 Ethalfuralin
7	11.632 Trifluralin
8	13.028 Prometon
9	13.184 Atrazine
10	13.233 b-BHC
11	13.432 Lindane
12	13.583 Aminocarb
13	14.790 Chlorothalonil
14	16.618 Methyl parathion
15	16.618 Chlorpyrifos Methyl
16	16.769 Heptachlor
17	18.508 Bromacil
18	x 18.444 Di-n-butylphthalate
19	18.832 Malathion
20	19.250 Chlorpyrifos
21	19.538 Carbetamide
22	x 23.978 Bisphenol A
23	23.864 Dieldrin
24	24.039 p,p'-DDE
25	25.686 p,p'-DDD
26	26.962 p,p'-DDT
27	27.007 Butyl benzyl phthalate
28	27.424 Hexazinone
29	27.745 Propargite
30	x 27.927 Piperonyl butoxide
31	29.649 Bis(2-ethylhexyl)phthalate
32	29.737 Leptophos
33	29.823 Mirex
34	31.550 Permethrin II
35	32.719 Cypermethrin I
36	34.319 Fenvalerate I
37	34.738 Fluralinate-tau-I
- Table #7:** A table showing quantitation results for Phenanthrene-d10.

Ion	Exp%	Act%
13.718min (+0.004)	100	100
188.10	100	100
184.10	14.00	14.70
80.00	11.00	10.88
94.10	10.00	10.23



QEdit - After DRS Import Result (butylbenzyl phthalate selected)

Overlay of target(s) and Deconvoluted ion plots

Spectral review: Before AMDIS After AMDIS AMDIS Library

**Hits
X = MSD
A = AMDIS**

Target ion plot

Deconvoluted ion plot

Areas & amounts from target ion and Deconvoluted ion

Ion	Exp%	Act%
149.00	100	100
91.00	60.00	125.86#
206.00	25.40	14.53#
104.00	16.20	33.38#

Enhanced DRS A.04 Capabilities



1) DRS quant results will appear in the Summary Quant Report

2) AMDIS libraries, quant database and screener database can be created from a user selected PBM library

3) Retention times in user selected AMDIS libraries can be updated with retention times from the currently loaded method quant database



Summary Quant Report with both MSD Chemstation and AMDIS results



Quant Time: Oct 25 07:32:46 2007
 Quant Method : C:\msdchem\1\METHODS\Trifecta\DRS_DEMO.M
 Quant Title :
 QLast Update : Mon Mar 12 08:59:53 2007
 Response via : Initial Calibration

Compound	R.T.	QIon	Response	Conc	Units	Dev (Min)
Internal Standards						
1) Phenanthrene-d10	13.718	188	4953296	10.00	ppm	0.00
Target Compounds						
18) Di-n-butylphthalate	18.444	149	968921	7.03	ppm	Qvalue 95
22) Bisphenol A	23.974	213	2314813m	16.80	ppm	
24) p,p'-DDE	24.060	246	89448m	0.65	ppm	
25) p,p'-DDD	25.705	235	22062m	0.16	ppm	
26) p,p'-DDT	26.998	235	20015m	0.15	ppm	
27) Butyl benzyl phthalate	27.009	149	42742m	0.31	ppm	
30) Piperonyl butoxide	27.927	176	5222839	37.91	ppm	93
31) Bis(2-ethylhexyl)phtha...	29.669	149	466583m	3.39	ppm	
34) Permethrin II	31.614	183	30828861m	223.78	ppm	

AMDIS Imported Quantitation Results

18) Di-n-butylphthalate	18.443	149	860786	6.25	ppm
22) Bisphenol A	23.975	213	1095930	7.96	ppm
27) Butyl benzyl phthalate	27.010	149	21499	0.16	ppm
30) Piperonyl butoxide	27.927	176	4451580	32.31	ppm
31) Bis(2-ethylhexyl)phtha...	29.669	149	369915	2.69	ppm
34) Permethrin II	31.613	183	27779700	201.65	ppm

(#) = qualifier out of range (m) = manual integration (+) = signals summed

partial report

DRS_DEMO.M Thu Oct 25 07:50:12 2007



DRS A.04 Report with both MSD ChemStation and AMDIS results



MSD Deconvolution Report

Sample Name: + 400 ppb ISTDs, 25 µL PTV
 Data File: C:\msdchem\1\DATA\Trifecta\SPINACH.D
 Date/Time: 08:14 AM Thursday, Oct 25 2007

Adjacent Peak Subtraction = 1
 Resolution = Medium
 Sensitivity = High
 Shape Requirements = Medium

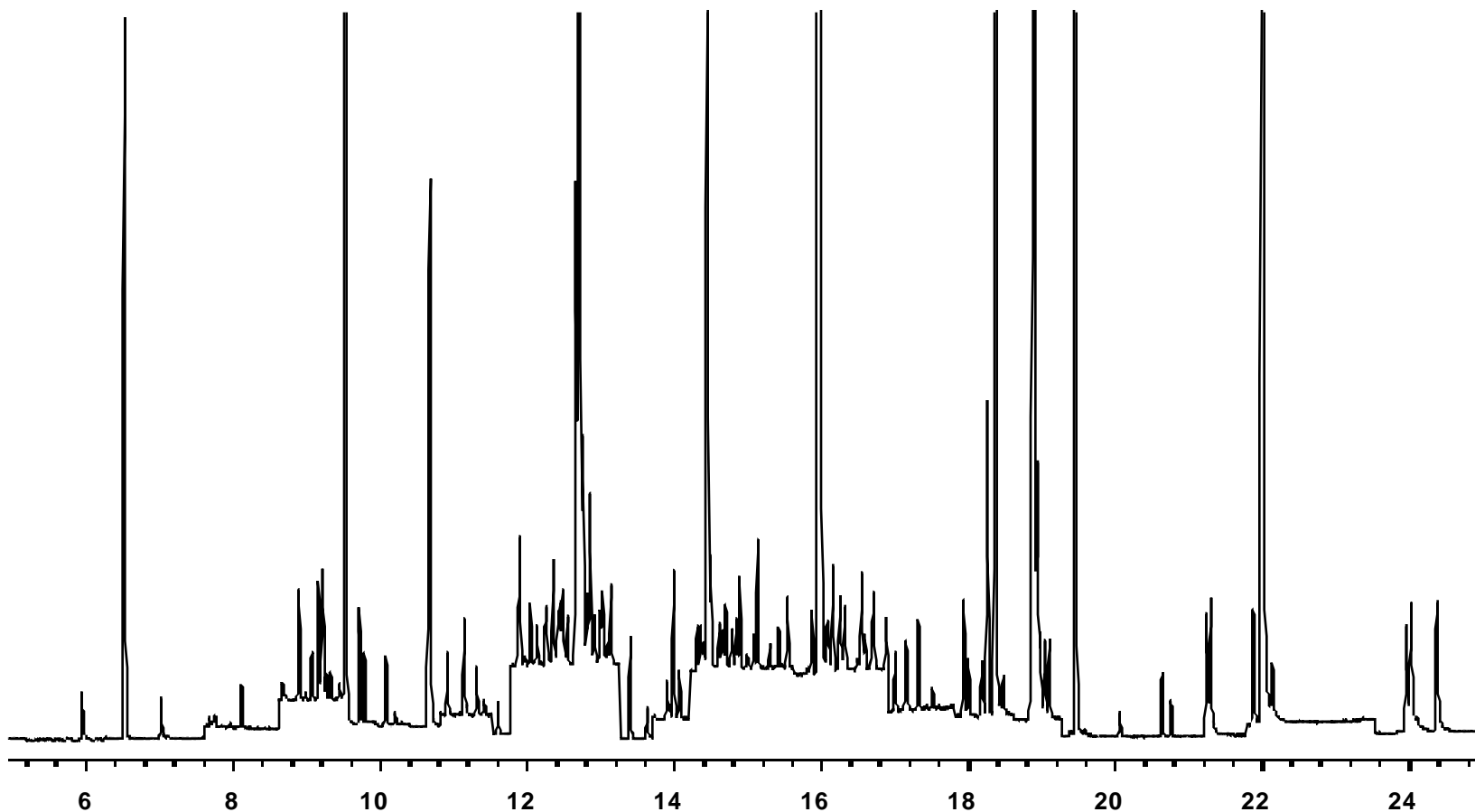
The NIST library was searched for the components that were found in the AMDIS target library.

R.T.	Cas #	Compound Name	Amount (ppm)		AMDIS		NIST	
			Chem station	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Num.
18.4431	84742	Di-n-butylphthalate	7.03	6.25	95	1.7	92	1
23.974	80057	Bisphenol A	16.8	7.96	97	8.7	91	1
24.0444	72559	p,p'-DDE	0.65		76	1.4	79	2
25.705	72548	p,p'-DDD	0.16	0.13	52	1.8	65	2
26.9932	50293	p,p'-DDT	0.15	0.09	53	0.7	43	6
27.009	85687	Butyl benzyl phthalate	0.31	0.16	54	0.2	57	25
27.9265	51036	Piperonyl butoxide	37.91	32.31	96	1.6	94	1
29.6685	117817	Bis(2-ethylhexyl)phthalate	3.39	2.69	93	1.2	85	3
31.6131	52645531	Permethrin II	223.78	201.65	90	3.8	91	3
13.718		Phenanthrene-d10	10					

p,p'-DDE target ion mismatch explained later



SIM TIC from Synchronous SIM/scan. 25 μ L LVI-PTV of a 180 ppb Semivolatiles Standard, 119 Compounds



Use PTV with SIM for the Best Sensitivity



	Traditional	Today's Lab	Today's Lab	Today's Lab
Inlet	S/SL	PTV	PTV	S/SL
Data Acquisition	Scan	SIM	Scan	SIM
~ Sample Concentration, ppb	0.1	0.0001	0.004	0.0025
~ Lowest cal level, ppb	100	0.1	4	2.5
Injection volume, uL	1	25	25	1



Save Time with Reduced Sample Preparation and LVI-PTV SIM



	Traditional	Today's Lab	Fast Prep	Quick Screen
Inlet	S/SL	PTV	PTV	PTV
Sample Concentration, ppb	0.1	0.0001	0.01	0.02
Lowest cal level, ppb	100	0.1	0.1	0.1
Sample size, mL	1000	1000	10	1.25
Extract volume, mL	1	1	1	0.25



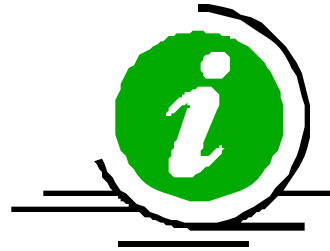


Optimizing Drinking Water and Wastewater Analyses for Semivolatiles

- Shorter narrow bore columns reduce runtime
- Backflush reduces cycle time and maintenance, while improving column life
- LVI-PTV gives better sensitivity and reduces sample prep
- RTL most fully utilizes the GC part of GC/MSD
- DRS significantly reduces data analysis time while providing the fewest number of false positives and false negatives



Thank you !!!



www.agilent.com/chem

... and browse our application warehouse for more pesticide analysis



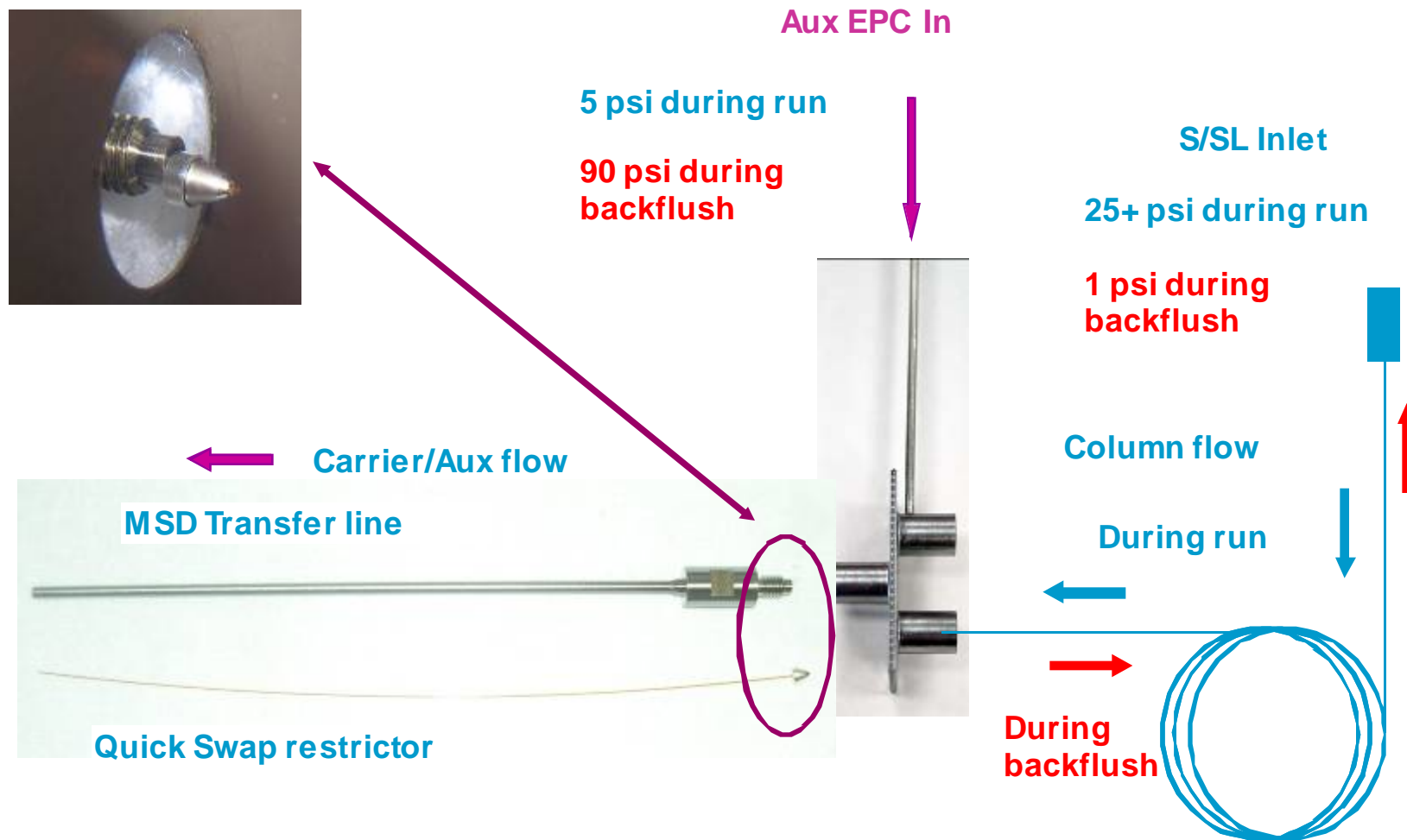
Backup Slides



Hidden slide



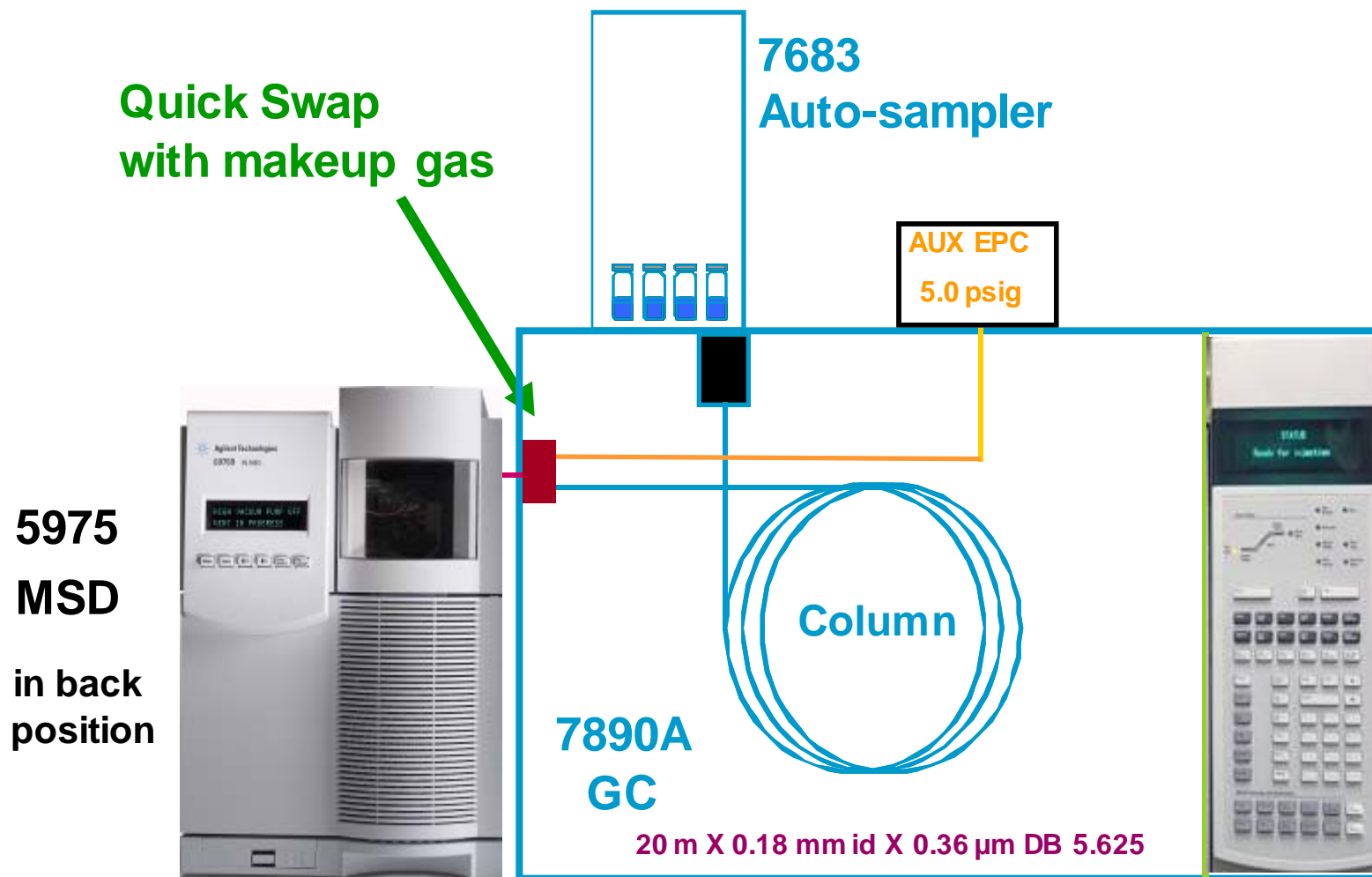
QuickSwap details



Hidden slide



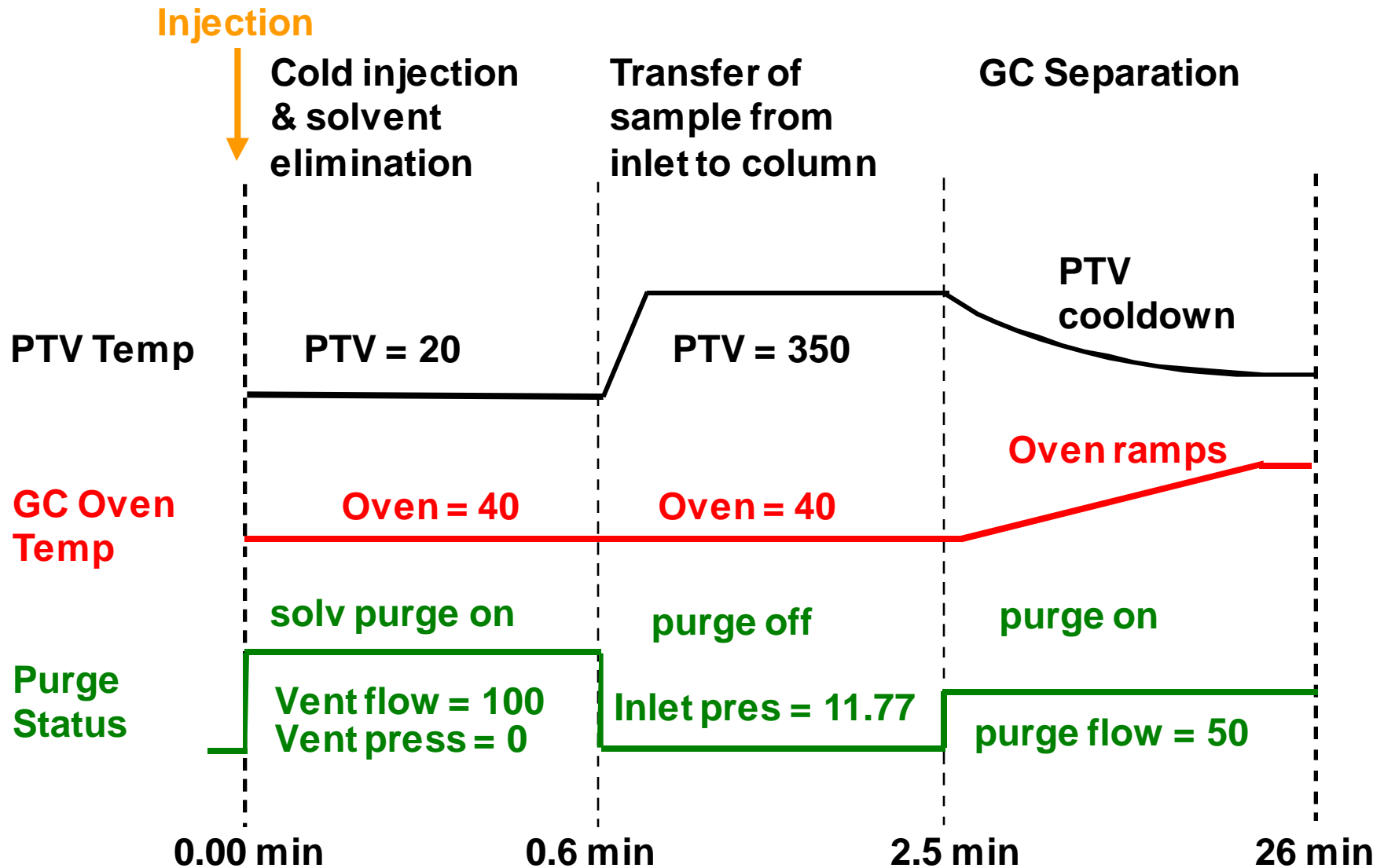
Semivolatiles Instrument



Hidden slide



PTV Temperature and Flow Programs



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