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

Issues	Solutions
1. Sensitivity	1. LVI with PTV and/or SIM
2. Identification	2. RTL and DRS
3. Sensitivity and Unknowns	3. Synchronous SIM/scan
4. Analysis time	4. Narrower bore column
5. Cycle Time	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

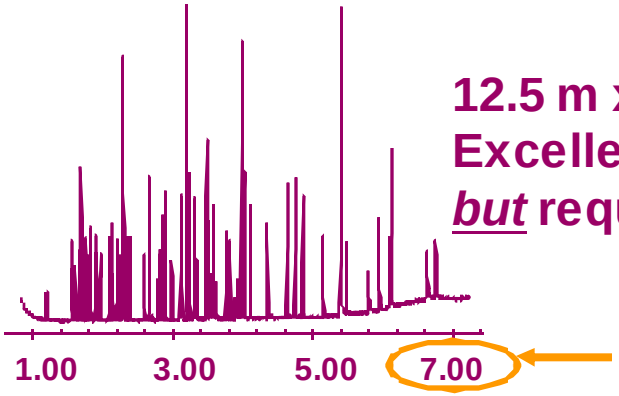
- **Agilent 6890 or 7890 GC & 5975 MSD**
  - **S/SL inlet, direct connect liner, no glass wool, P/N *G1544-80730***
  - **20 m x 180 µm x 0.36 µm DB-5.625, P/N *121-5622* – faster runs**

  or

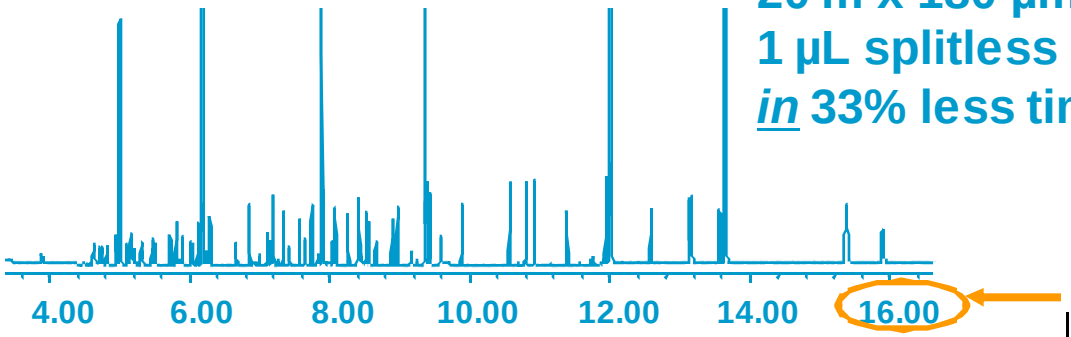
  - **PTV inlet, multi-baffle liner, no glass wool, P/N *5183-2037***
  - **30 m x 250 µm x 0.25 µm HP-5ms, P/N *19091S-433***

83 Semivolatiles on 3 Different Columns.

Significant Time Savings, Possible Trade-offs

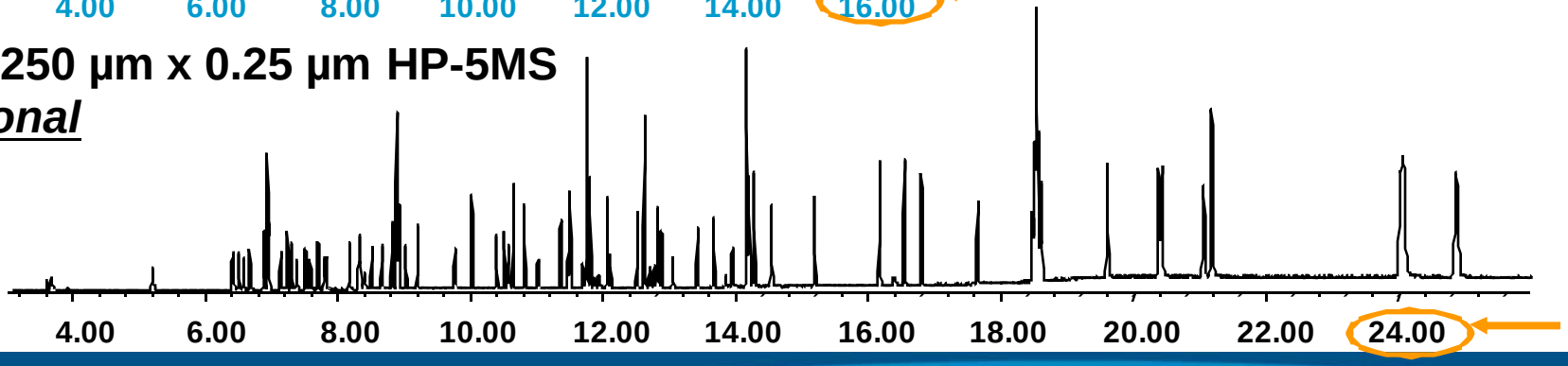


12.5 m x 100 µm x 0.1 µm HP- 5ms
Excellent for rapid screening
but **requires minimum 10:1 split injection.**



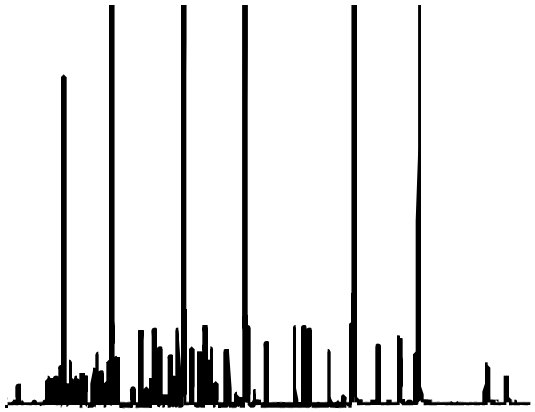
20 m x 180 µm x 0.36 µm DB-5.625
1 µL splitless injections maintain MDLs
in **33% less time.**

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

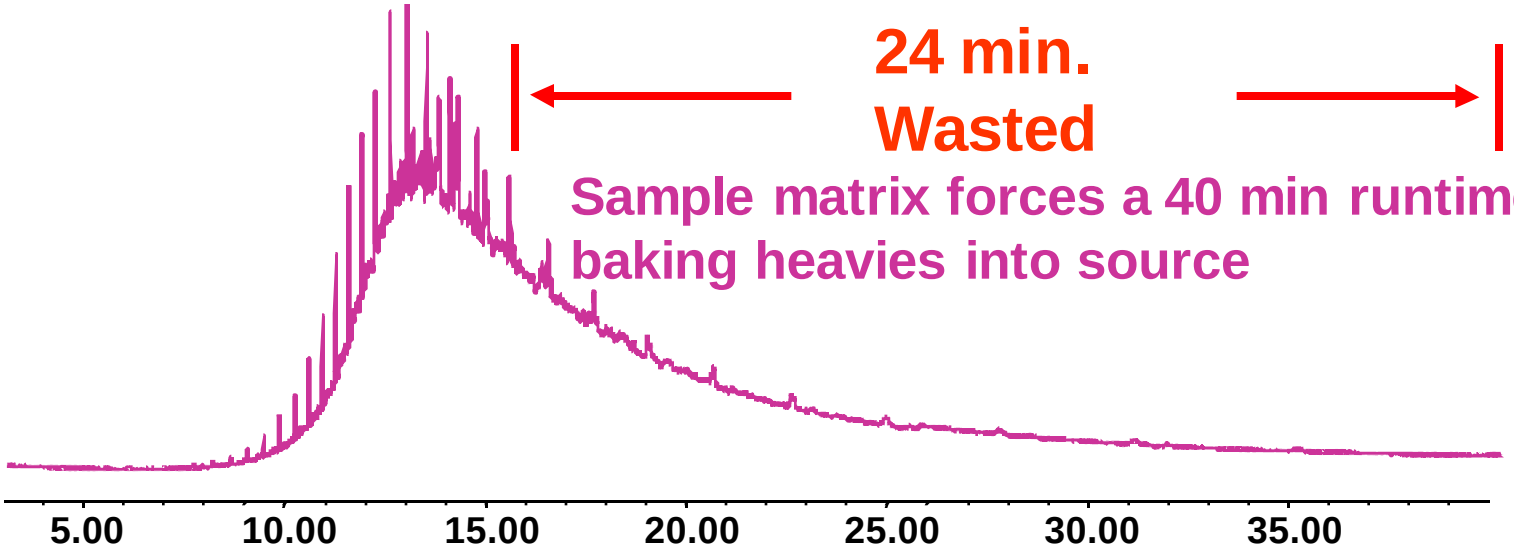


Run Time and Cycle time Wasted

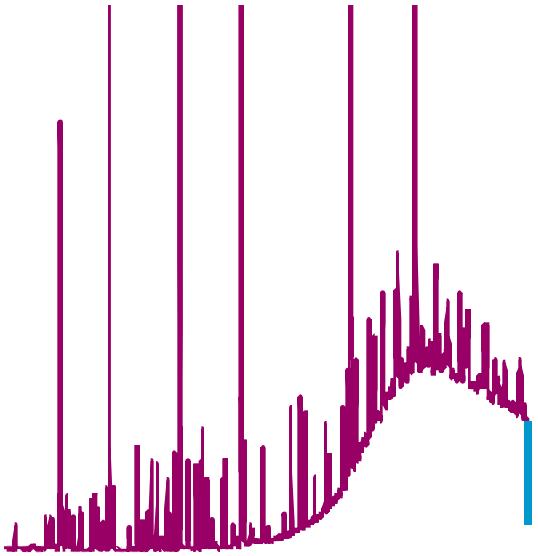
Due to Matrix Bakeout



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



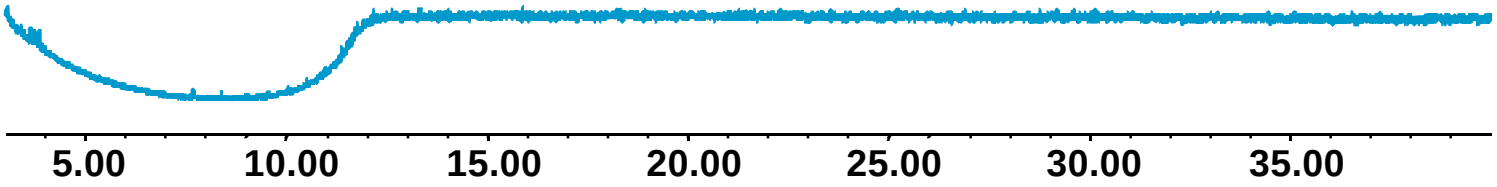
Spiked Sample

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 µm *vs* 180 µm column	25	17	8
Run time, matrix bake-out *vs* 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

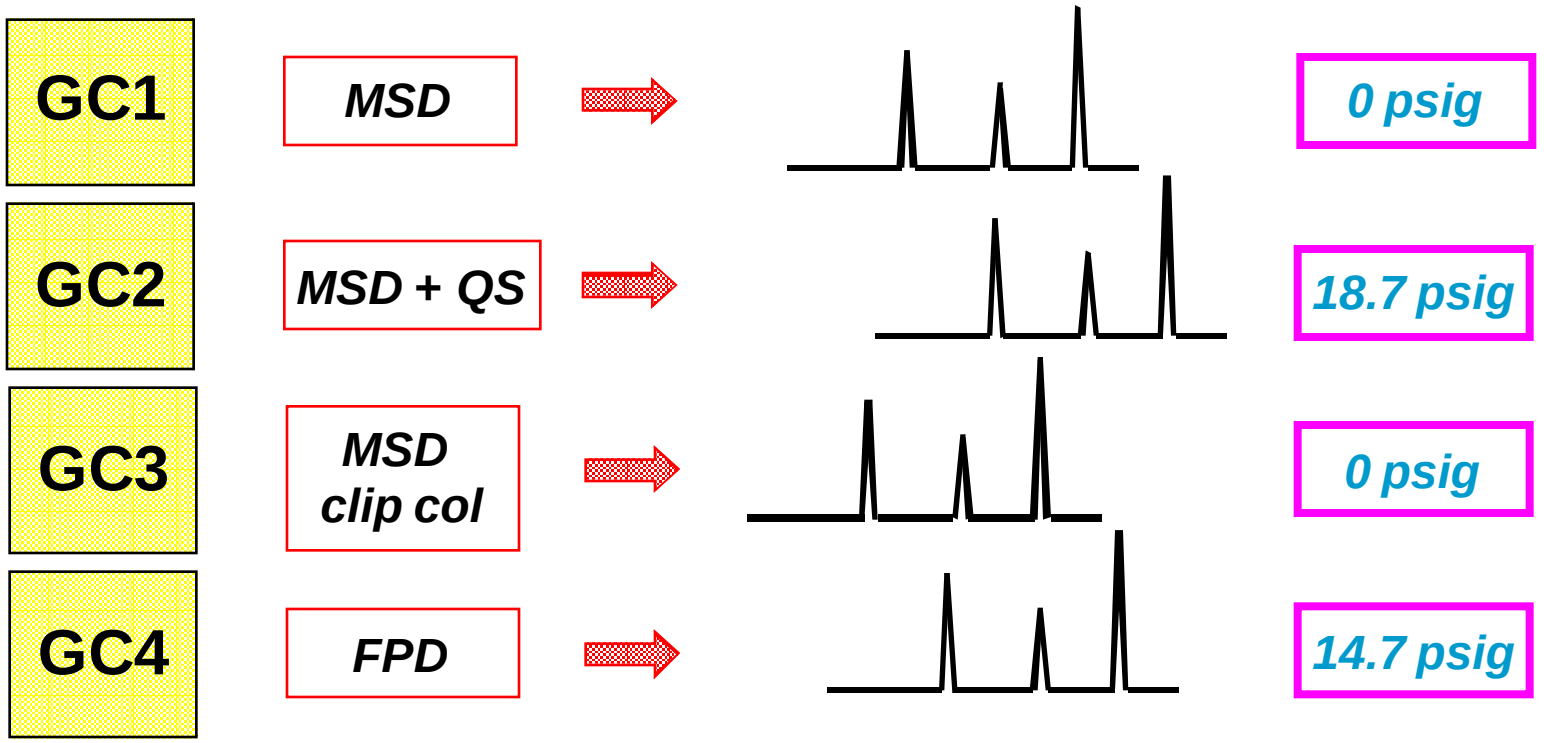
Time Savings > 50 % => Run Twice the Samples/Day =>……

Performance is Maintained with Capillary Flow Technology

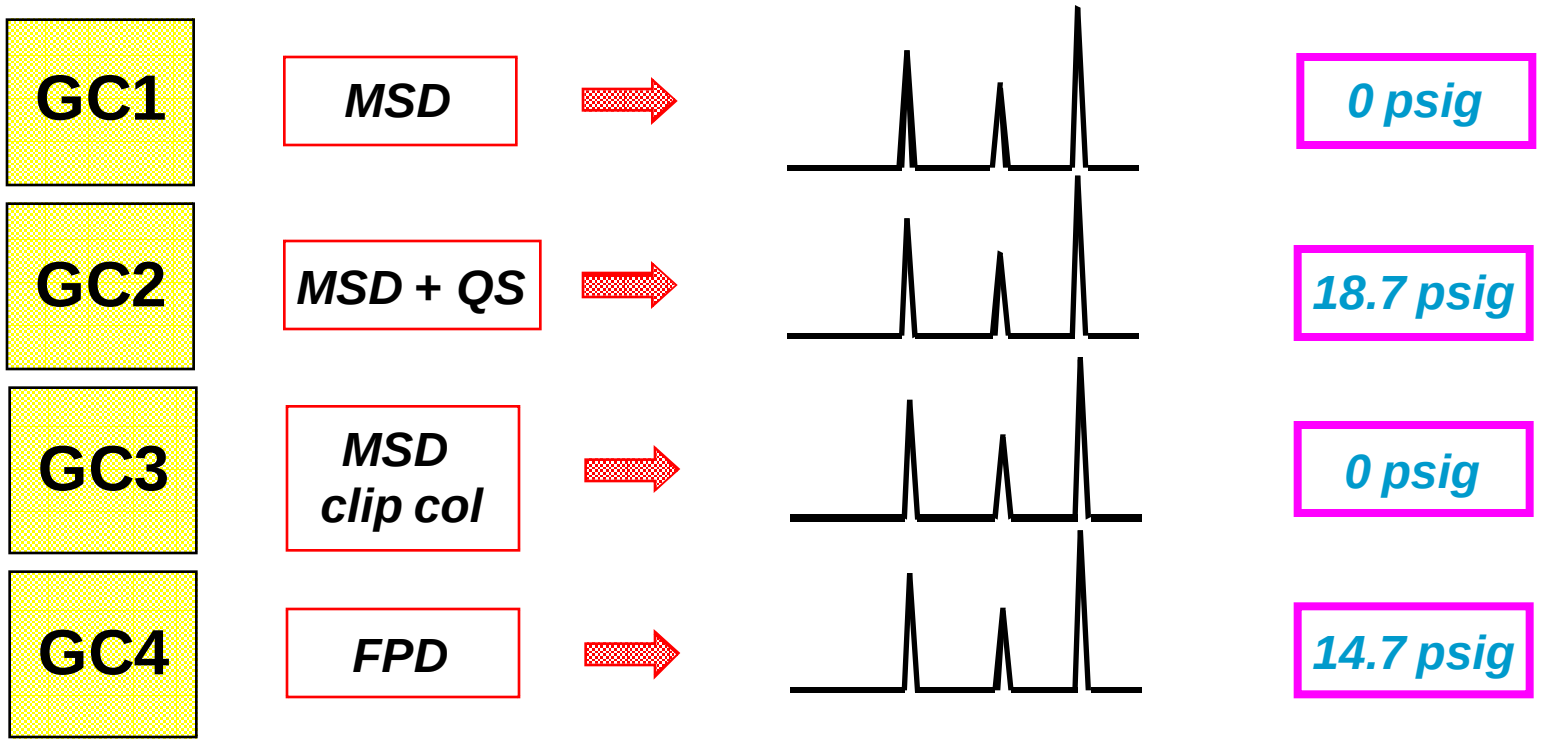
- **As measures of performance, criteria from the widely used US EPA Method 8270 were measured. The System Performance Check Compounds are active and therefore have minimum response requirements. The Calibration Check Compounds are from various classes and are used to check overall system linearity**

	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

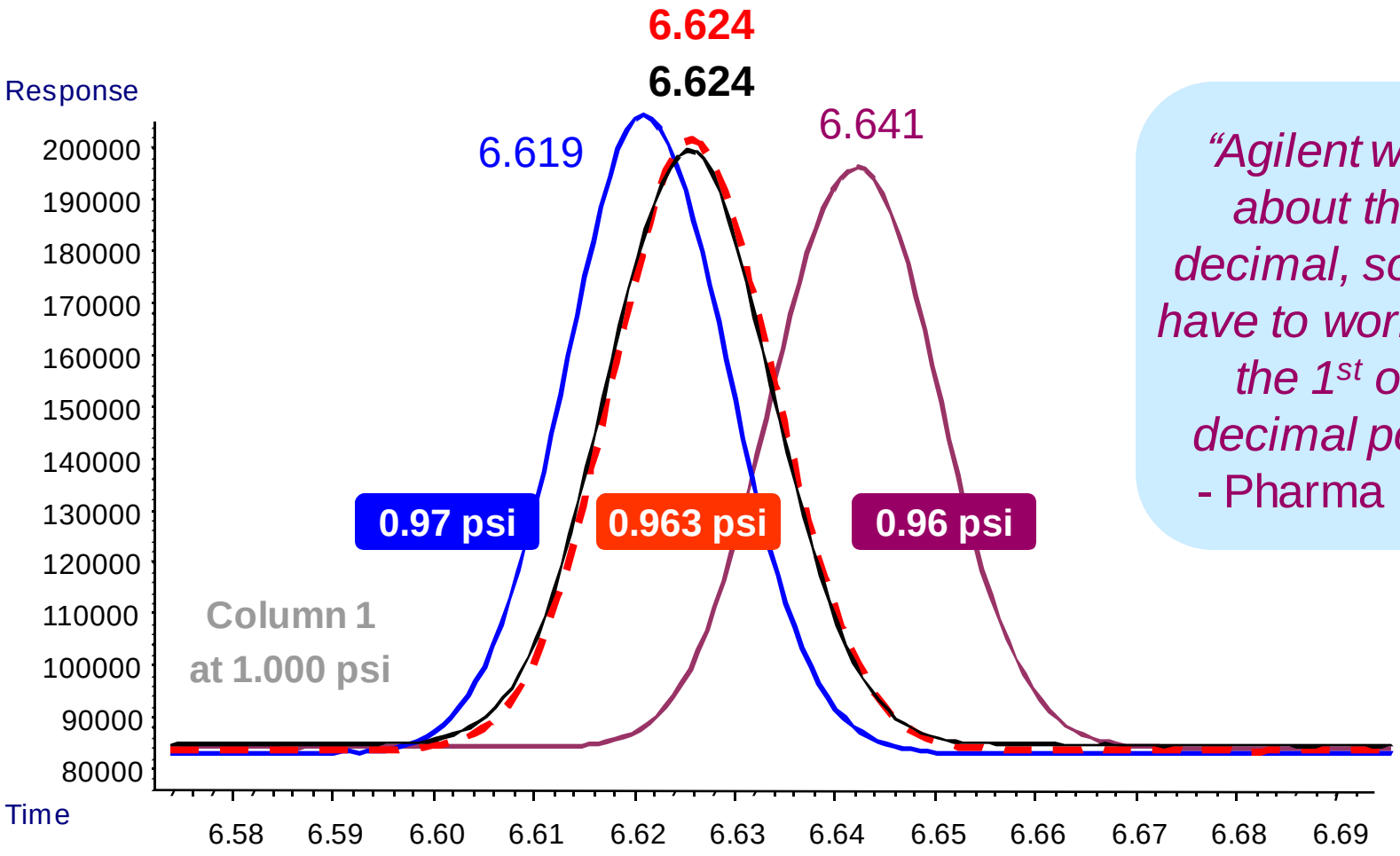


Benefits of RTL

- 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

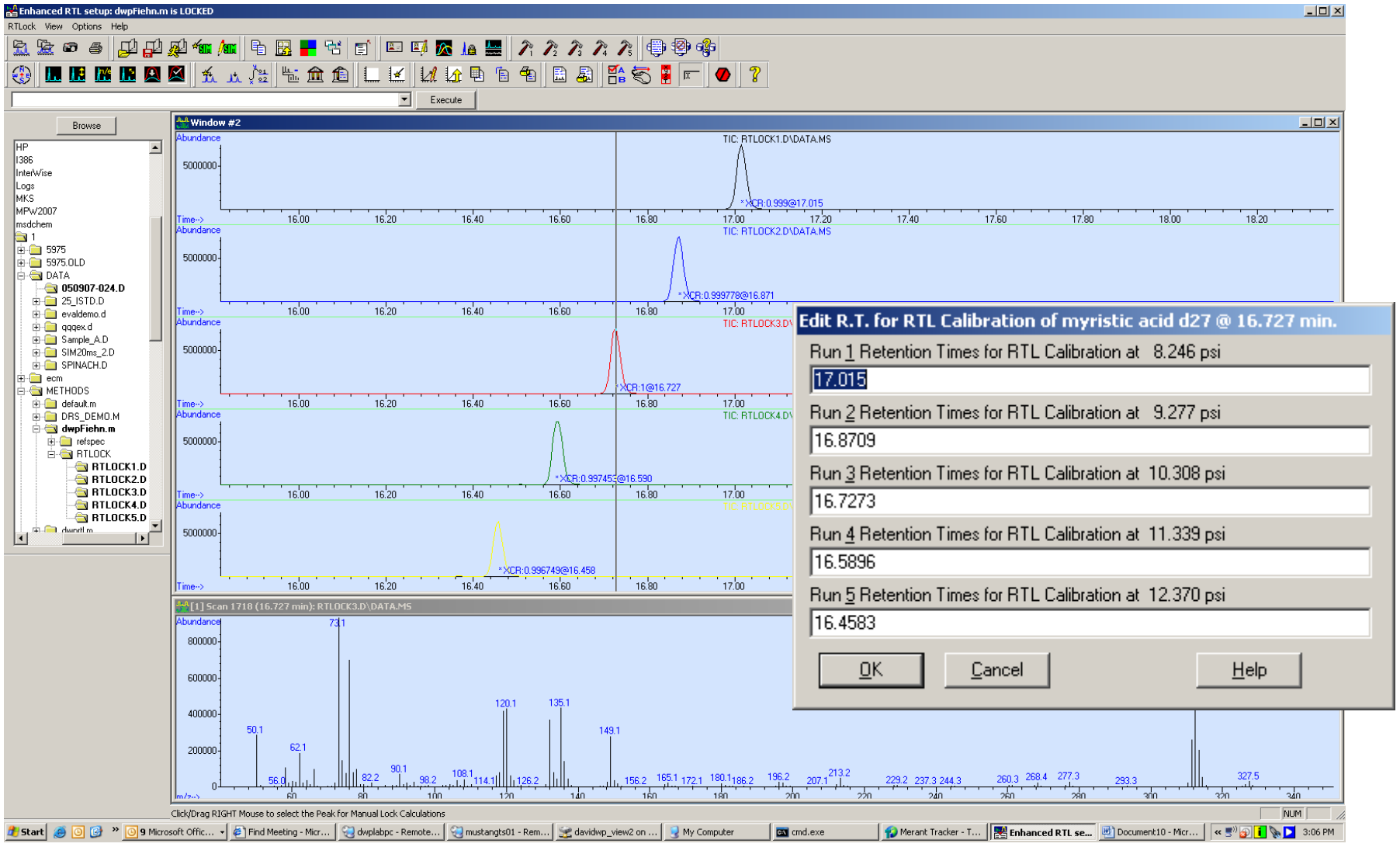
7890 can control the precision of 1/1000 psi

Key to even better Retention Time Locking (RTL)



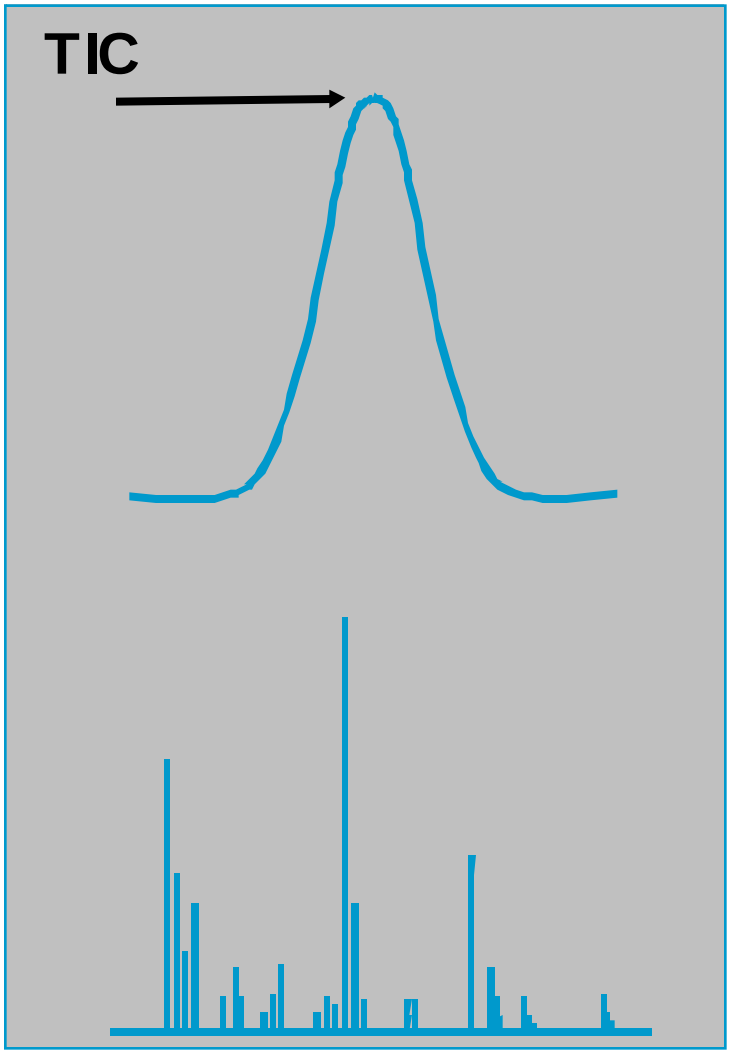
"Agilent worries about the 3rd decimal, so I don't have to worry about the 1st or 2nd decimal point…"
- Pharma (USA)

RTL is more flexible now…

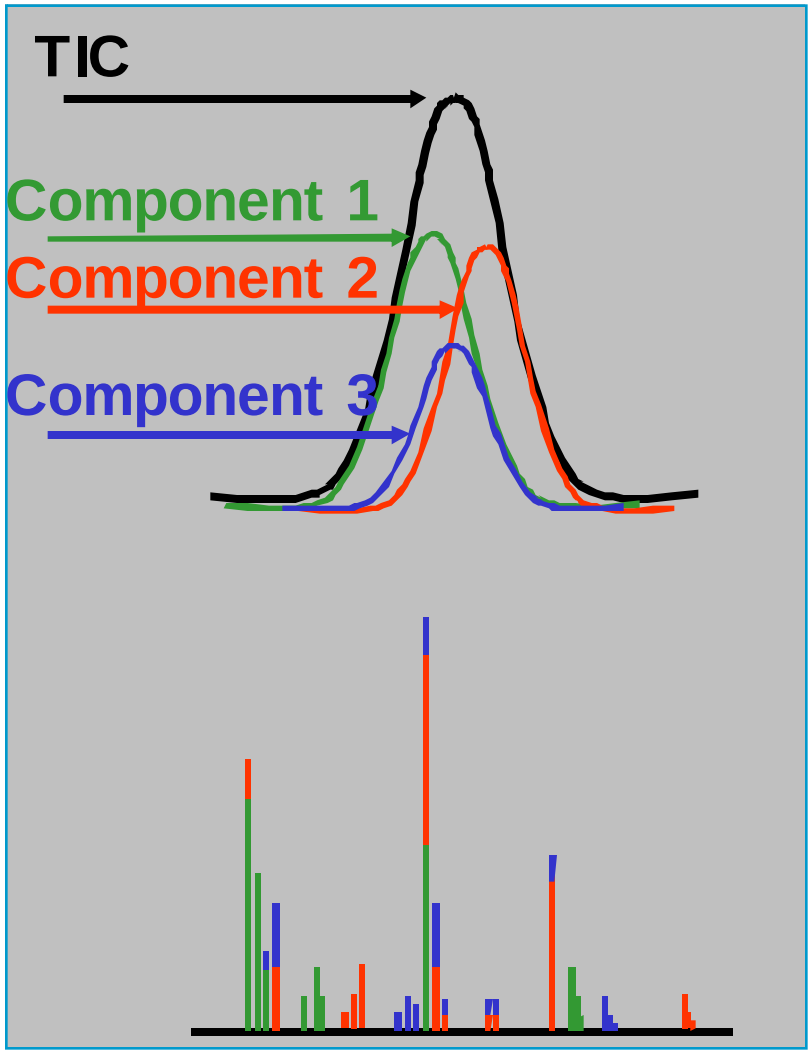


A Single Chromatographic Peak May Contain Multiple Components

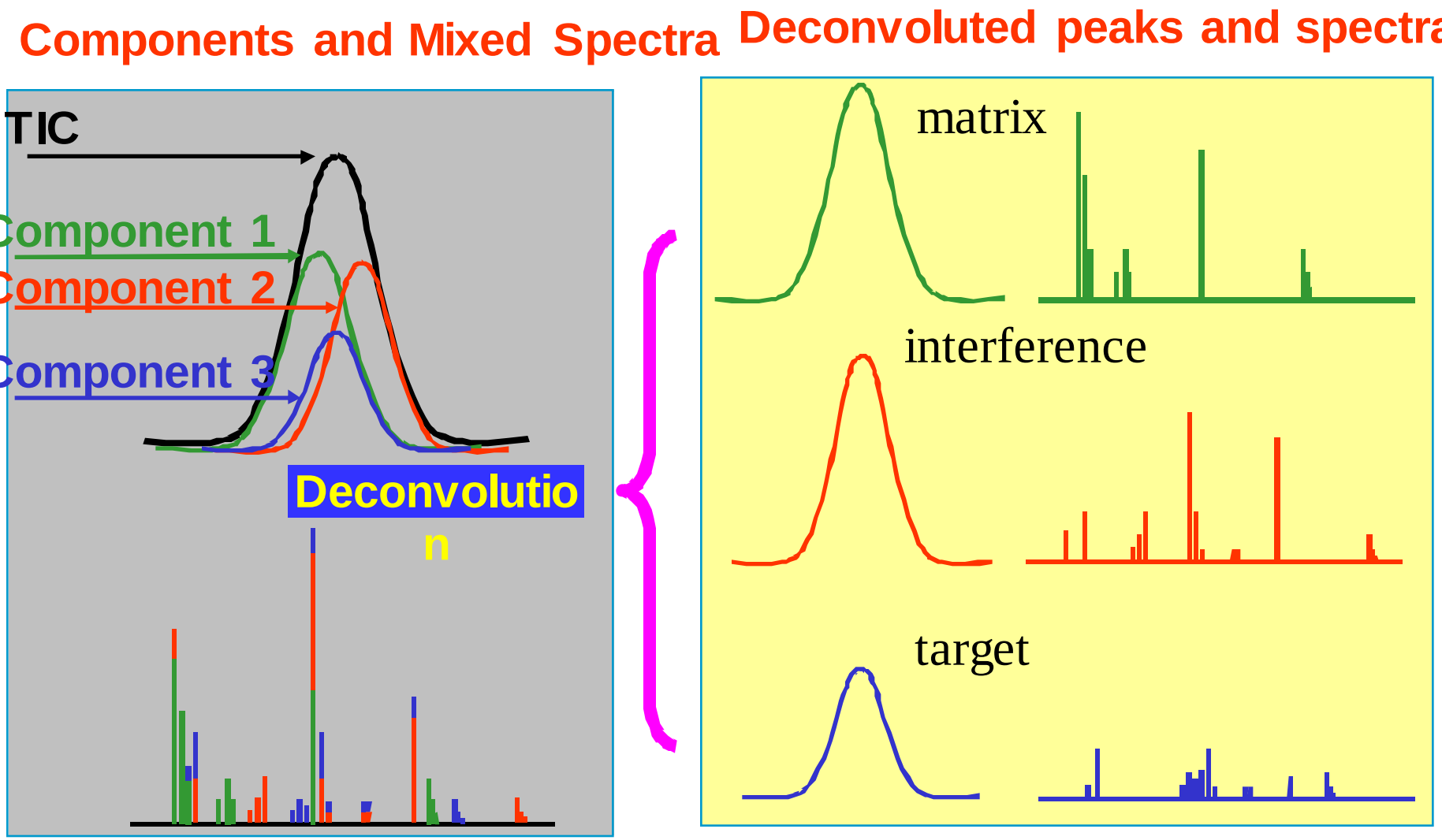
TIC & Spectrum



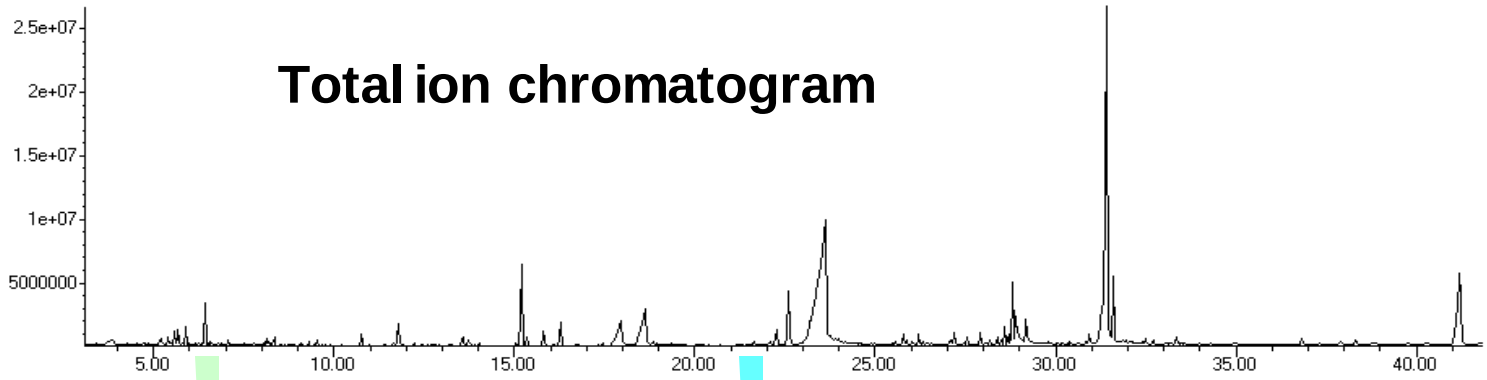
Components and Mixed Spectra



AMDIS Deconvolution Pulls Out Individual Components and their 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

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

Quant Results

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.

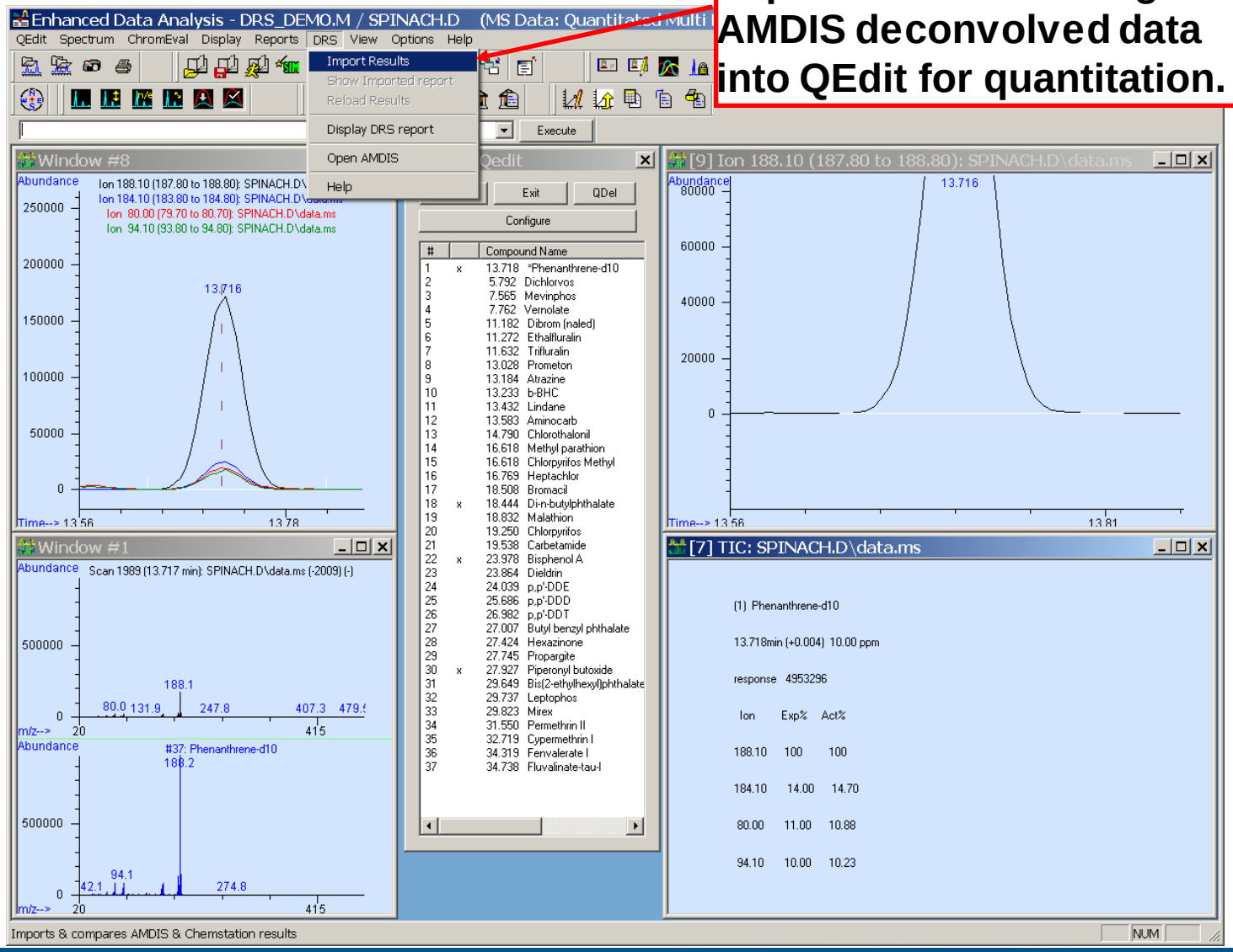
			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
2.8499	62759	N-Nitrosodimethylamine	5.55	93	-0.5	96	1
4.730	62533	Aniline		98	4.2	96	1
5.0358	3855821	1,4-Dichlorobenzene-d4	40	99	-0.2	93	1
5.214	106445	4-Methylphenol		66	-7.7	89	1
6.2476	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

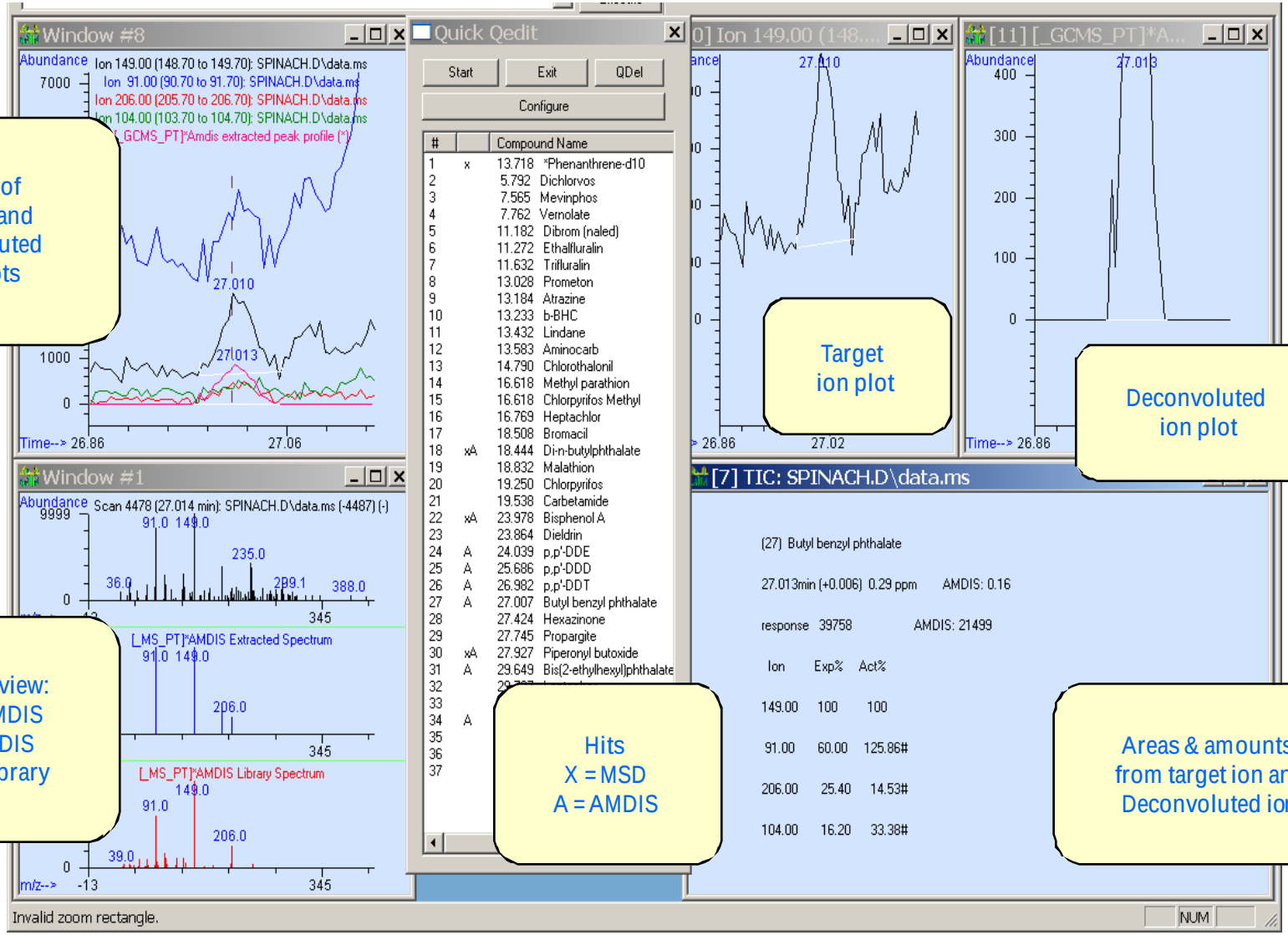
- QEdit enhanced to:
  - Import AMDIS results into MSD ChemStation
  - Quantitate
  - Display AMDIS Results
  - Manually Integrate
- Enhanced DRS capabilities/Report
- Requires G1701EA E.02

QEdit - before DRS importing

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



QEdit - After DRS Import Result (butylbenzyl phthalate selected)



Overlay of target(s) and Deconvoluted ion plots

Target ion plot

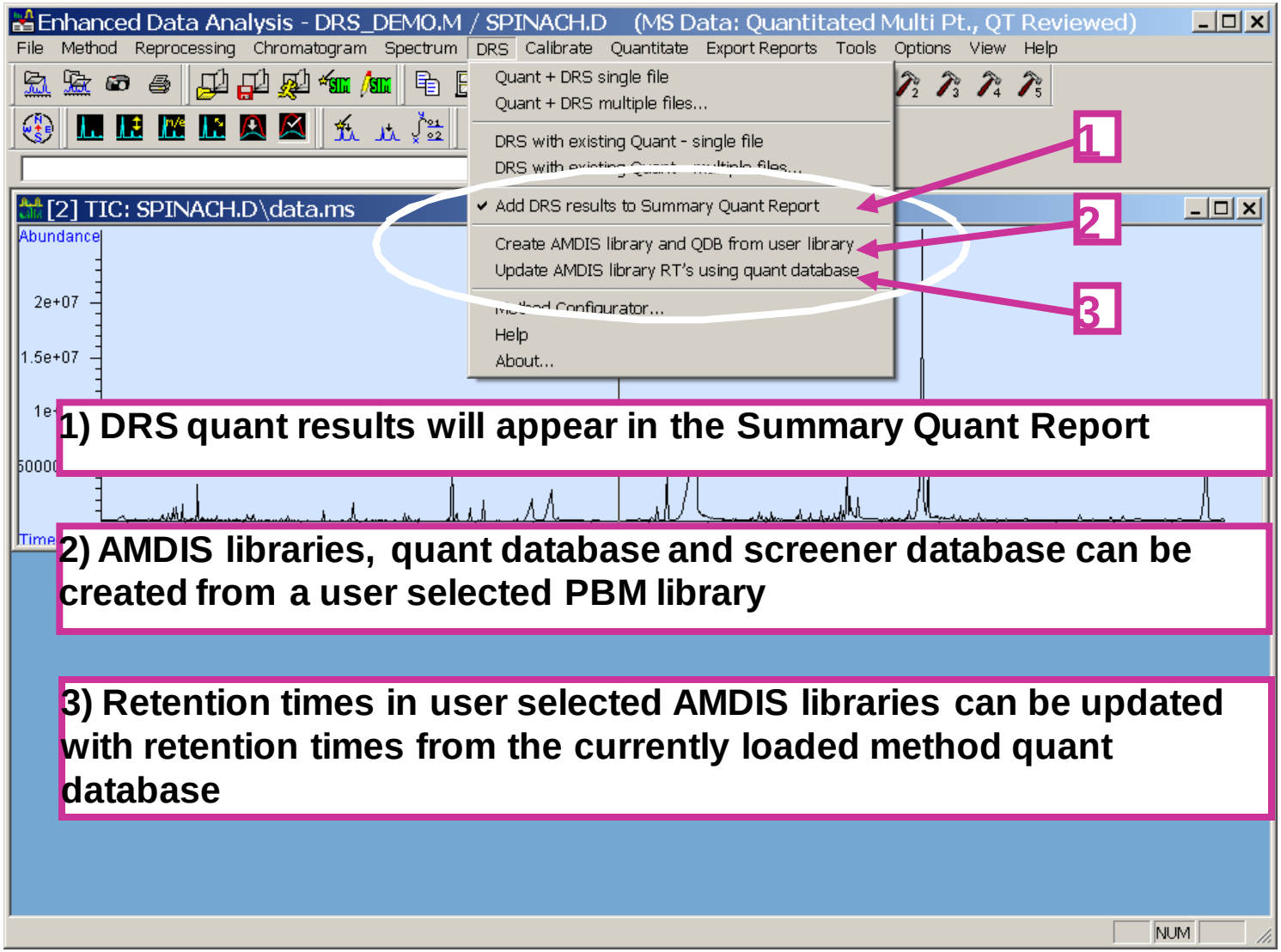
Deconvoluted ion plot

Spectral review:
Before AMDIS
After AMDIS
AMDIS Library

Hits
X = MSD
A = AMDIS

Areas & amounts from target ion and Deconvoluted ion

Enhanced DRS A.04 Capabilities



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						Qvalue
18) Di-n-butylphthalate	18.444	149	968921	7.03	ppm	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

)RS_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

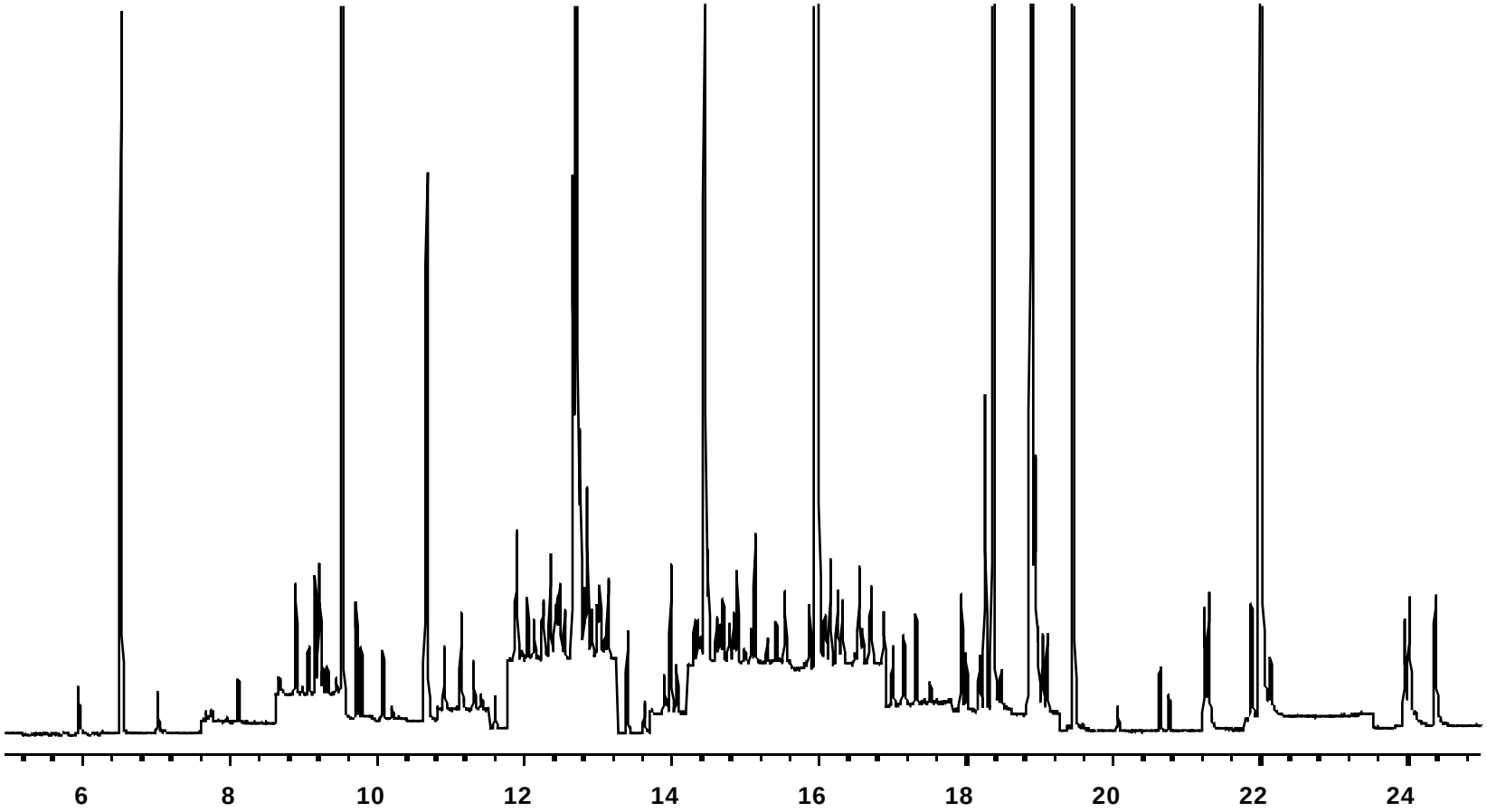
Adjacent Peak Subtraction = 1
Resolution = Medium
Sensitivity = High
Shape Requirements = Medium

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

			Amount (ppm)		AMDIS		NIST	
R.T.	Cas #	Compound Name	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 Synchonous SIM/scan. 25 µL 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 Acqusition	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 maintenace, 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

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QuickSwap details

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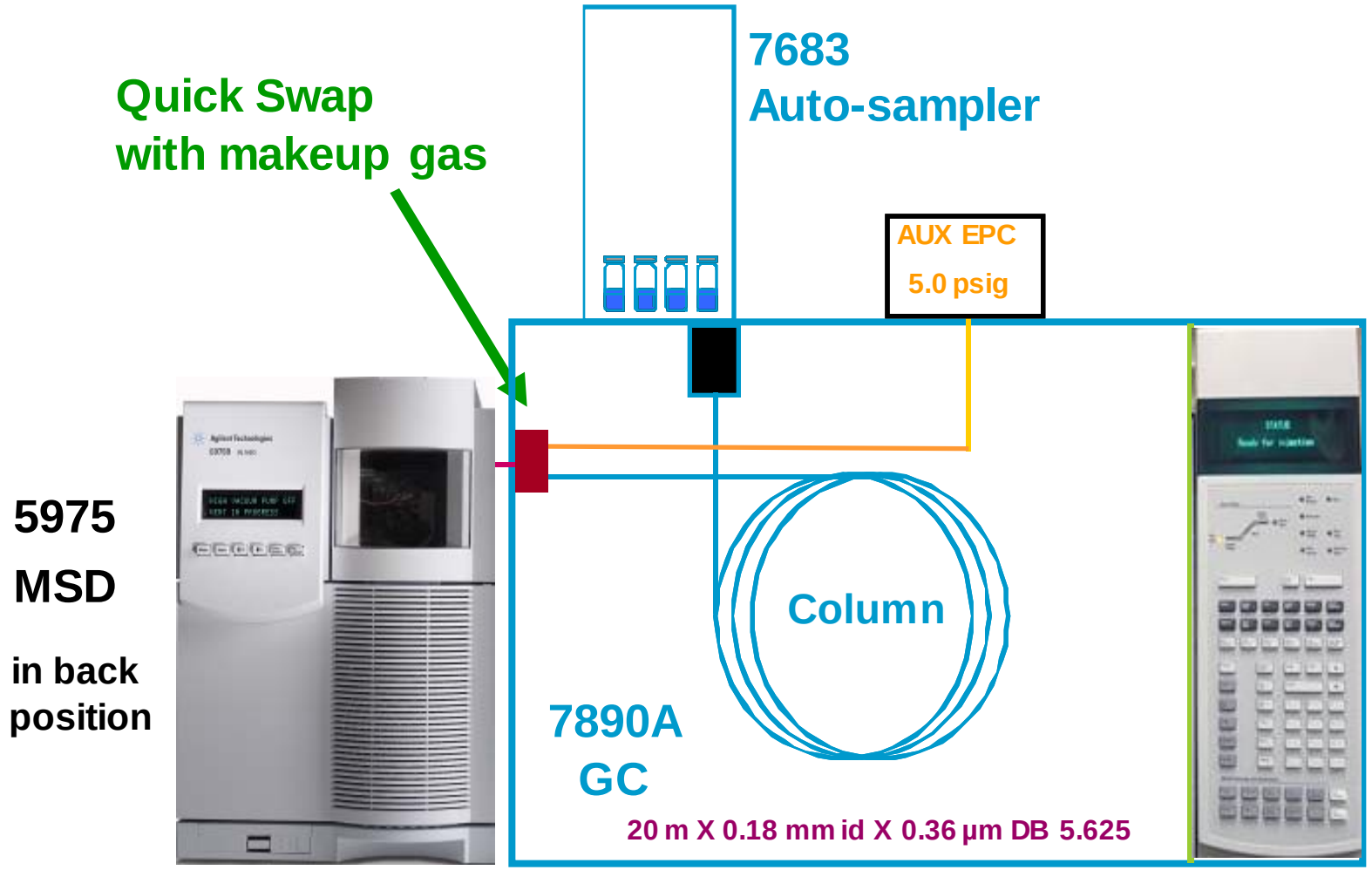
Semivolatiles Instrument



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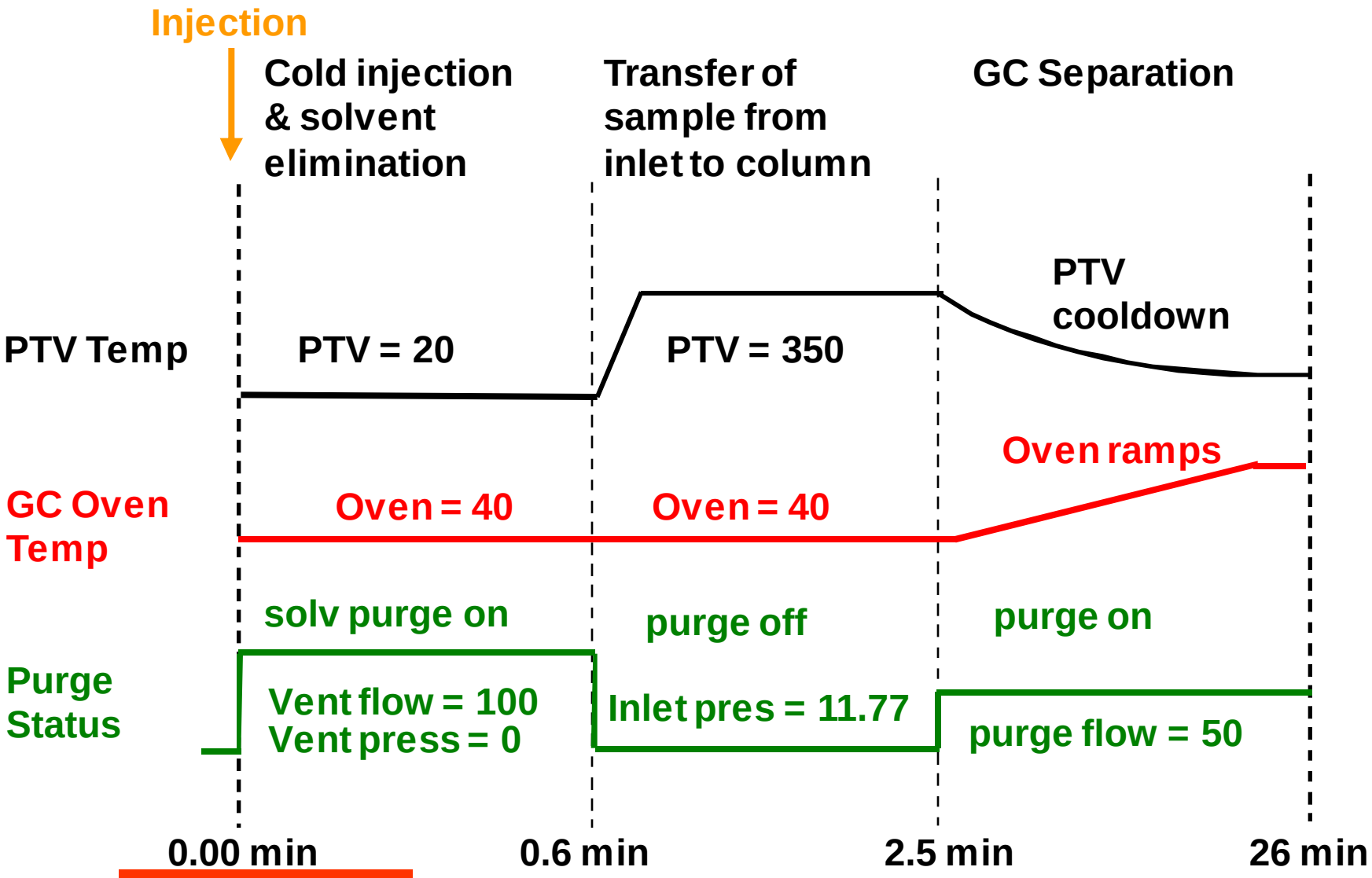
PTV Temperature and Flow Programs



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