EPA Method 8270D Analysis Using Narrow-bore GC Columns and Fast Data Acquisition with a Quadrupole GCMS System

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Introduction

Analytical support of environmental programs has been conducted for several decades using standard-bore capillary columns (0.25mmid) and quadrupole GCMS systems. Depending on method conditions and program requirements, the QC measures can consume a significant portion of a 12-hour shift, leaving less time for analysis of real-world samples. Typical cycle times (time from beginning of a run to the beginning of the following run) for EPA 8270D (and preceding semivolatile methods) have historically been on the order of 35-45 minutes, or longer.

The goal of this study was to demonstrate the capabilities of a new, sensitive, fast-scanning GCMS system to optimize productivity for EPA Method 8270D, while maintaining the strict QC measures of the method, optimizing sensitivity, and expanding the dynamic range.

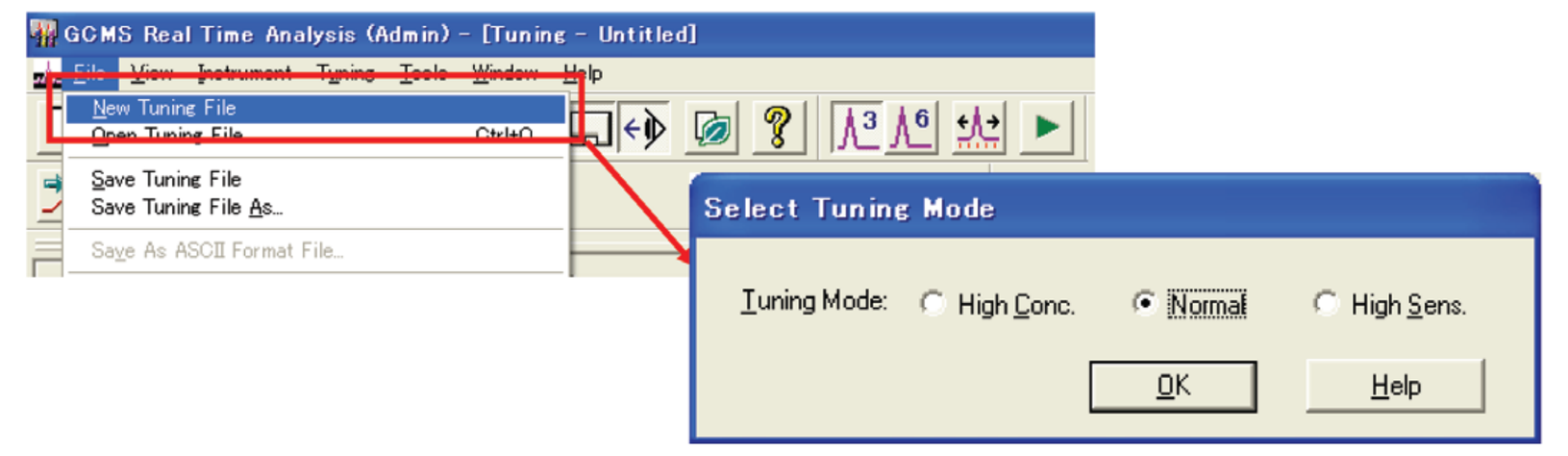
Significant reduction in the run time can be accomplished by applying the Fast GC technique to this method. This technique involves the use of narrow bore (0.15mm ID) columns, rapid oven heating and cooling, and rapid data acquisition. Several considerations are necessary for reliable analysis using narrow-bore columns. A sensitive quadrupole mass spectrometer is required for identification and quantitation of target compounds at sub-nanogram levels. In addition, fast mass spectral scanning and data acquisition are required, because very narrow chromatographic peaks are produced under these conditions.

A new, sensitive, fast-scanning quadrupole GCMS system was used to significantly reduce the run time for a mixture of 81 analytes. Excellent sensitivity and chromatographic resolution were demonstrated with a significantly reduced run/cycle time.

Conventional GCMS Conditions using a 0.25mm x 30M GC Column

- A highly sensitive mass spectrometer provides excellent sensitivity using the split injection mode.
- Newly-developed tuning modes provide a wide linear range for quantitation (0.2-160 µg/ml for many analytes).
- Split injection improves productivity – a higher starting temperature shortens run time and oven cooldown time.
- Limited material is introduced into the GC column and detector, minimizing instrument maintenance.
- Column overloading is minimized using split injection, maintaining optimum chromatographic performance.

Tuning modes expand linear range



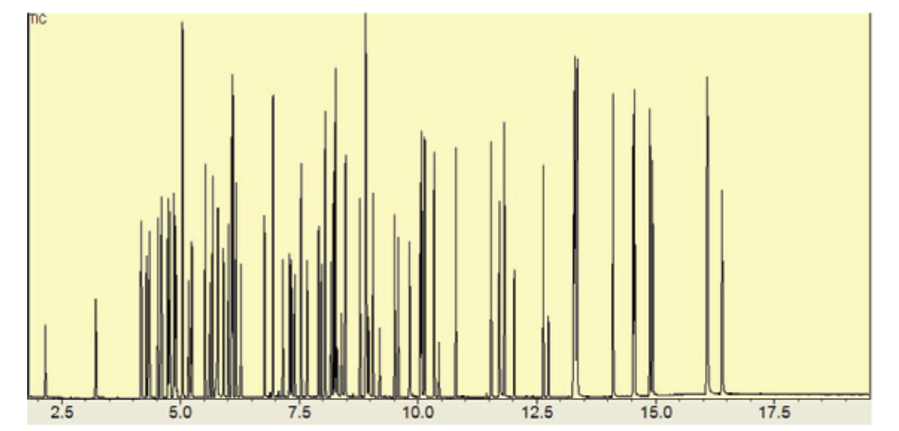
GCMS Conditions using a 0.25mm Column

Instrument conditions:

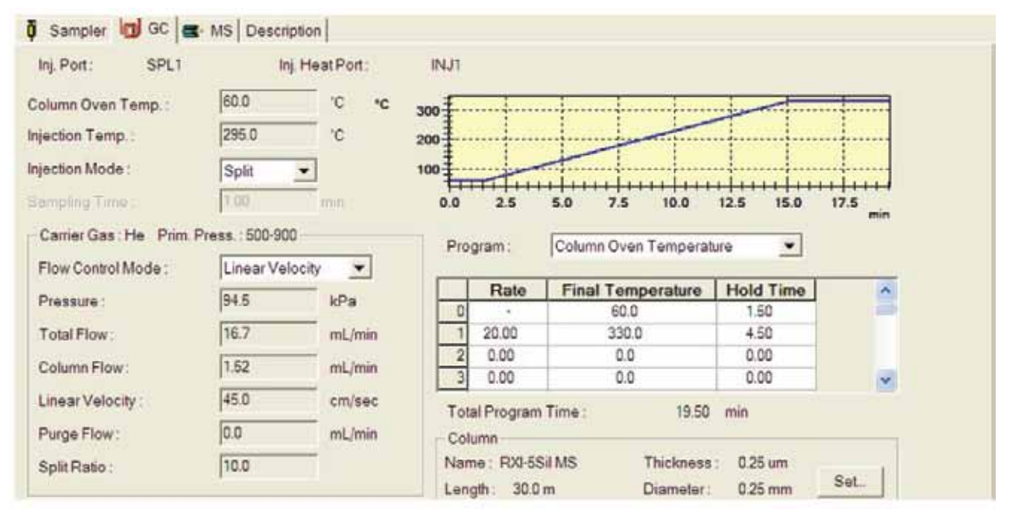
- Flow control using constant linear velocity (45cm/sec).
- Split injection (split ratio 10:1).
- GC temperature program 60-330°C (fast GC oven cooldown).
- Event time (scan interval) 0.15sec.

Under these conditions, all compounds elute in about 16.5 min. (first-eluting compound is N-nitrosodimethylamine at about 2min).

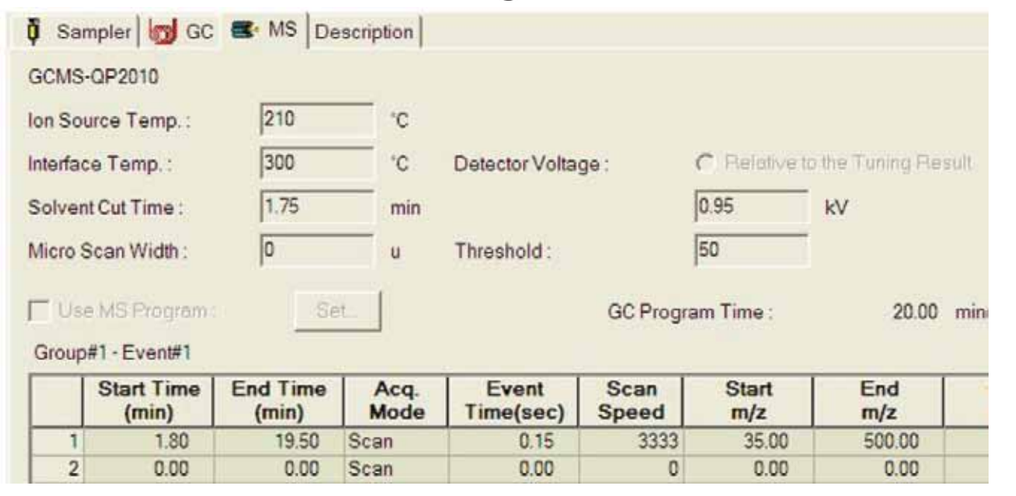
Chromatogram using a 0.25mm column



GC conditions using a 0.25mm column

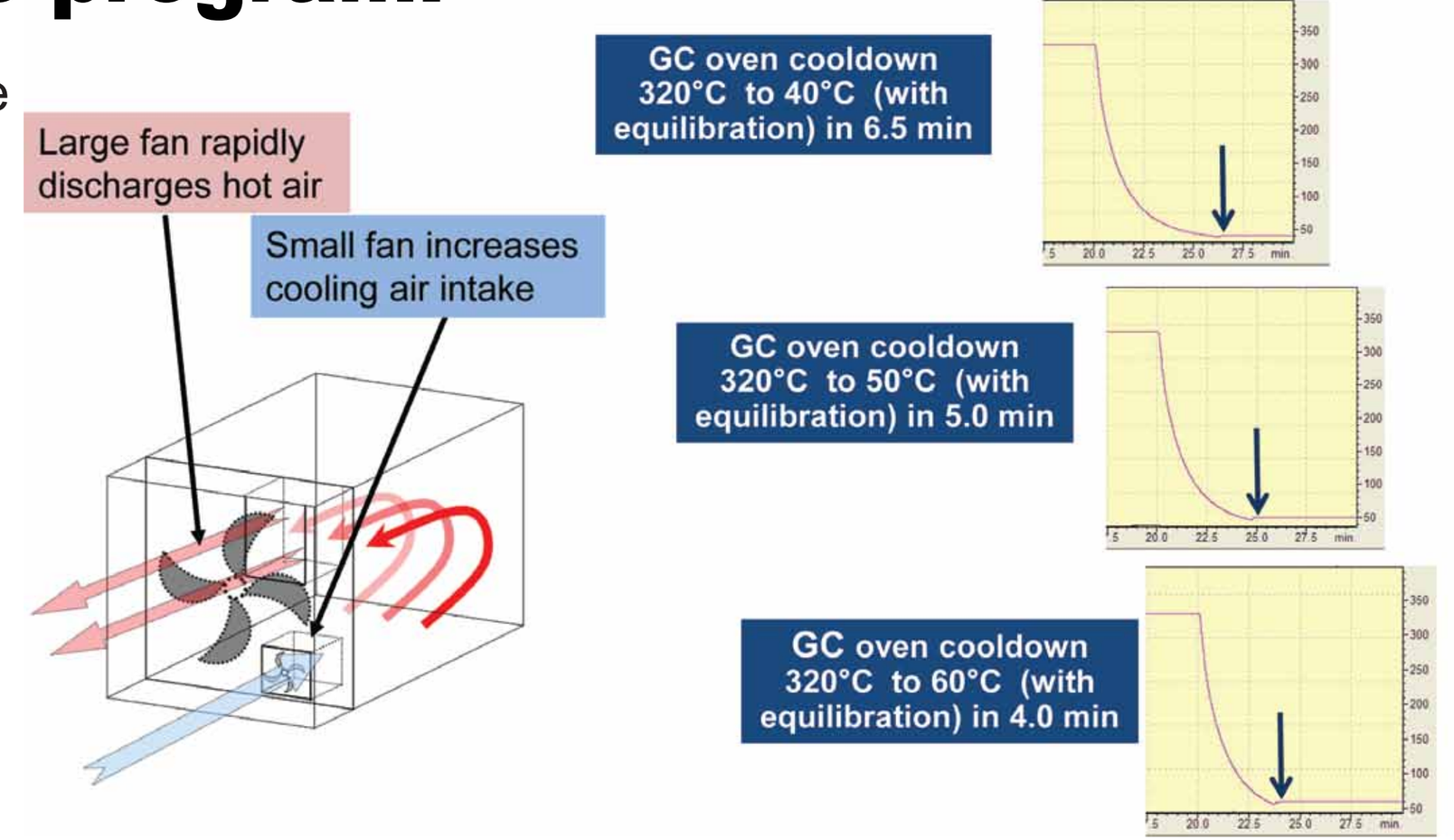


MS conditions using a 0.25mm column



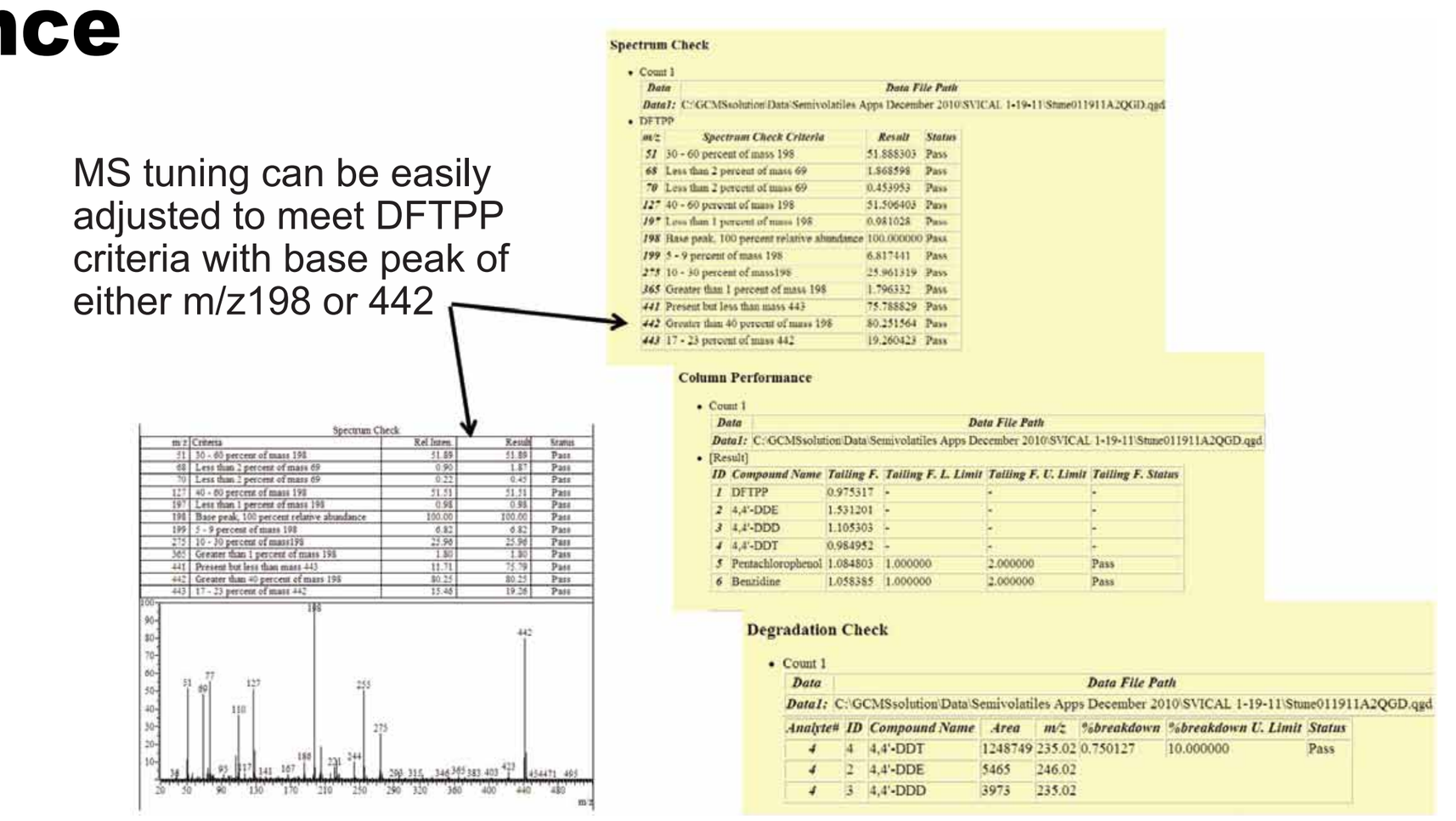
GCMS Conditions - split injection / oven temperature program:

- Split injection is chosen as the injection mode so that the GC program can be started at a higher temperature – re-condensation of the (low-boiling) methylene chloride solvent is not critical.
- Higher initial temperature shortens the run time slightly and GC oven cooldown time considerably (a rapid-cooling GC oven significantly shortens GC cooldown time).



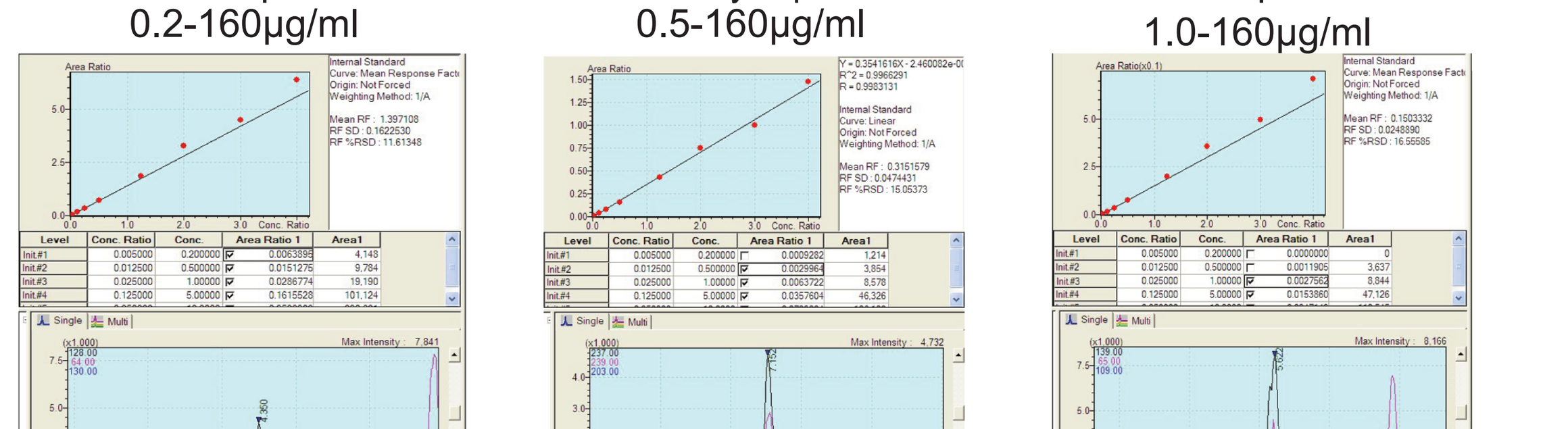
GCMS Performance

GC performance (tailing of pentachlorophenol and benzidine; DDT breakdown) and MS performance (tuning with DFTPP) are confirmed in a single 10-minute GCMS run. Performance criteria are verified with a single click.



Example calibration curves (0.25mm column) are shown below (chromatograms are lowest-level calibration point)

2-Chlorophenol	Hexachlorocyclopentadiene	2-Nitrophenol
0.2-160µg/ml	0.5-160µg/ml	1.0-160µg/ml



How many points are needed for quantification (spectra per GC peak)?

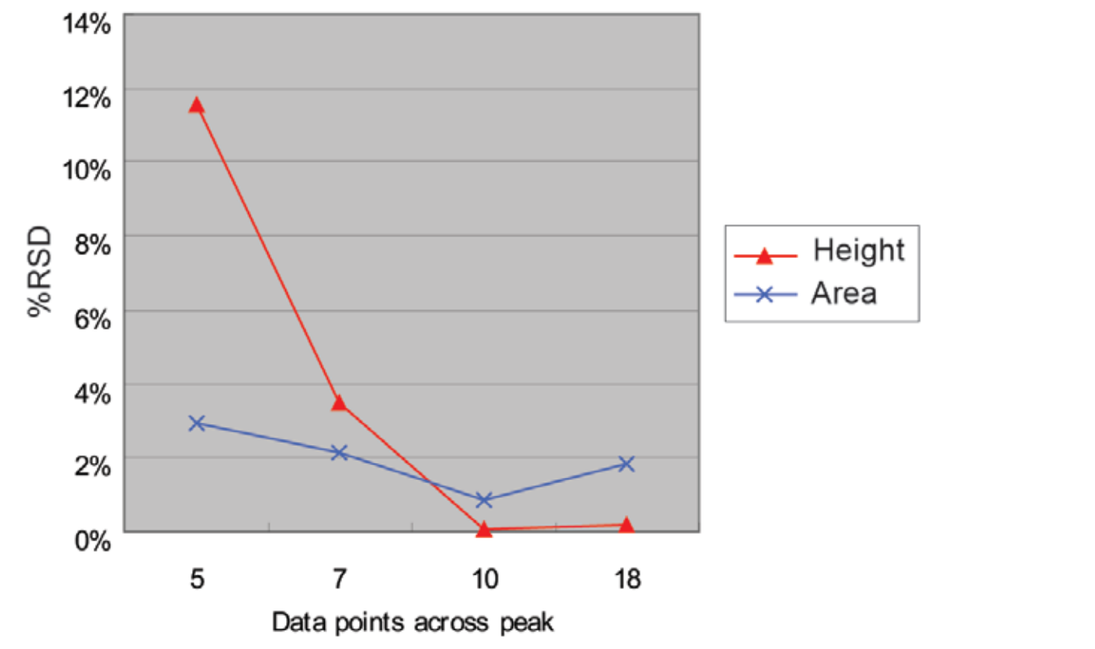
Dallüge, J. et al., J. Sep. Sci. 2002, 25, 608-614. → 5/6 points / peak

Poole, C.F., The Essence of Chromatography, Elsevier, Amsterdam, 2003, pp. 66-67 → 10 points / peak

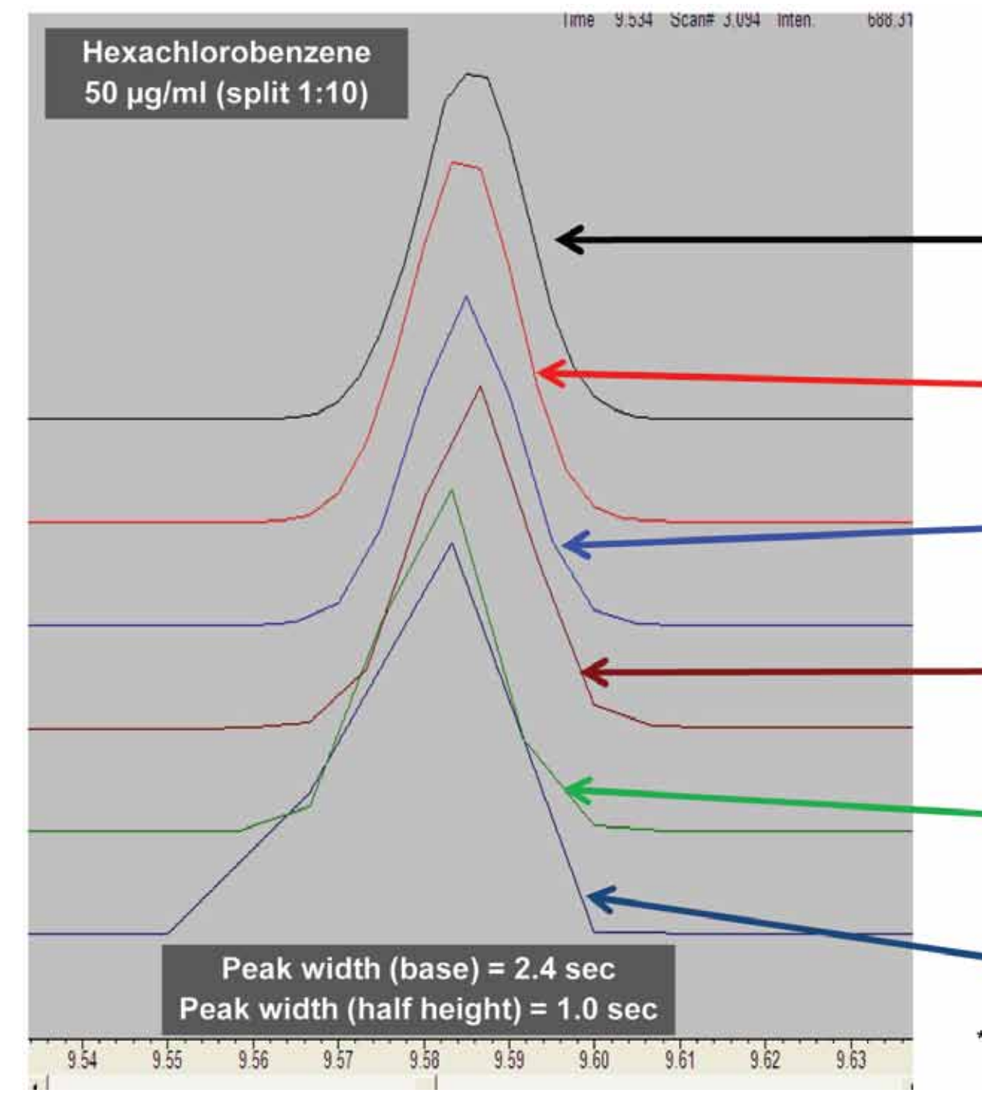
Hinshaw, J.V., LCGC North Am., 2003, 21, 268-272. → 10 points / peak (above half-height)

Statistics predict improved precision with more data points across a GC Peak; Improved precision is demonstrated by experimental results.

To optimize precision and accuracy, an event time (time required for acquisition of a single spectrum) was set at 0.15sec. for a 0.25mm GC column (EPA 8270D specifies a scan time of 1.0sec or less.)



Comparison of mass spectral scan rates (spectra per GC peak)



Event time (sec)	Scan Rate (amu/sec)	Total Spectra	Spectra > 1/2 height
0.15	3333	16	8
0.20	2500	11	6
0.30	1666	7	4
0.40	1250	6	3
0.50	1000	5	2
1.00*	476	2	2

* Minimum scan speed specified by EPA 8270D

Statistical Instrument Detection Limits (0.25mm column)

Compound	IDL µg/ml	Compound	IDL µg/ml	Compound	IDL µg/ml
2-Fluorophenol (SS)	0.11	Benzoic Acid	1.11	Fluorene	0.01
Phenol-d5 (SS)	0.05	Bis(2-chloroethoxy)methane	0.01	4-Nitroaniline	0.80
2-Chlorophenol-d4 (SS)	0.04	2,4-Dichlorophenol	0.08	2-Methyl-4,6-dinitrophenol	1.27
2,4,6-Tribromophenol (SS)	0.12	1,2,4-Trichlorobenzene	0.04	N-Nitrosodiphenylamine	0.02
1,2-Dichlorobenzene-d4 (SS)	0.09	Naphthalene	0.01	4-Bromophenyl phenyl ether	0.06
Nitrobenzene-d5 (SS)	0.08	4-Chloroaniline	0.03	Hexachlorobenzene	0.04
2-Fluorobiphenyl (SS)	0.07	Hexachlorobutadiene	0.06	Pentachlorophenol	0.01
Terphenyl-d14 (SS)	0.04	4-Chloro-3-methylphenol	0.06	Phenanthrene	0.04
N-Nitrosodimethylamine	0.04	2-Methlynaphthalene	0.02	Anthracene	0.01
Phenol	0.03	Hexachlorocyclopentadiene	0.13	Carbazole	0.03
Bis(2-chloroethyl) ether	0.02	2,4,6-Trichlorophenol,	0.09	Di-n-butyl phthalate	0.03
2-Chlorophenol	0.03	2,4,5-Trichlorophenol,	0.10	Fluoranthene	0.02
1,3-Dichlorobenzene	0.04	2-Chloronaphthalene	0.02	Pyrene	0.02
1,4-Dichlorobenzene	0.03	2-Nitroaniline	1.07	Butylbenzyl phthalate	0.03
1,2-Dichlorobenzene	0.03	Dimethyl phthalate	0.02	3,3'-Dichlorobenzidine	0.12
Benzyl Alcohol	0.10	2,6-Dinitrotoluene	0.06	Bis(2-ethylhexyl) phthalate	0.03
3&4-Methylphenol	0.06	Acenaphthylene	0.01	Benzo[a]anthracene	0.01
2-Methylphenol	0.03	3-Nitroaniline	1.94	Chrysene	0.02
Bis(2-Chloroisopropyl) ether	0.02	Acenaphthene	0.02	Di-n-octyl phthalate	0.02
N-Nitrosodi-n-propylamine	0.05	2,4-Dinitrophenol	1.94	Benzo[b]fluoranthene	0.03
Hexachloroethane	0.05	4-Nitrophenol	1.94	Benzo[kfluoranthene	0.05
Nitrobenzene	0.03	Dibenzofuran	0.02	Benzo[a]pyrene	0.03
Isophorone	0.02	2,4-Dinitrotoluene	0.11	Indeno[1,2,3-cd]pyrene	0.12
2-Nitrophenol	0.05	Diethyl phthalate	0.03	Dibenzo(a,h)anthracene	0.18
2,4-Dimethylphenol	0.02	4-Chlorophenyl phenyl ether	0.02	Benzo(g,h,i) perylene	0.28

GCMS Conditions using a 0.15mm Column

In an effort to shorten the run / cycle time for EPA 8270D analysis, a shorter, narrower-bore chromatographic column was employed (0.15mm x 0.15µ x 20M). The narrower column is more efficient, so faster run times are possible with equivalent chromatographic performance.

Conditions for a 0.15mm GC column (relative to those used with a 0.25mm GC column):

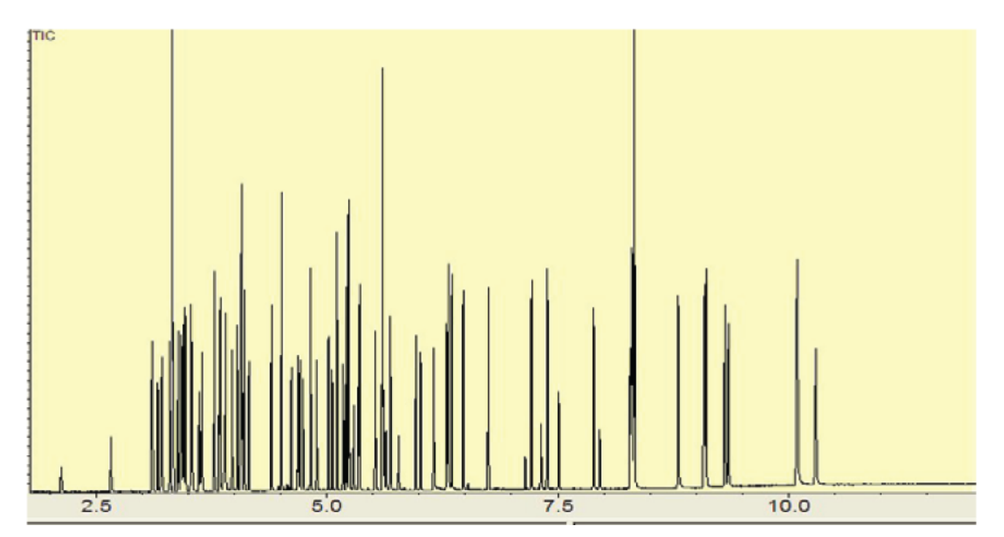
- Column dimensions: 0.15mm x 0.15µ x 20M
- Split injection with a split ratio of 10:1 (unchanged)
- Carrier gas constant linear velocity maintained at 45cm/sec (unchanged)
- MS scan (event) time set to 0.10 sec to accommodate narrower chromatographic peaks
- GC oven temperature program increased to 30°C, utilizing a more efficient GC column

Instrument conditions:

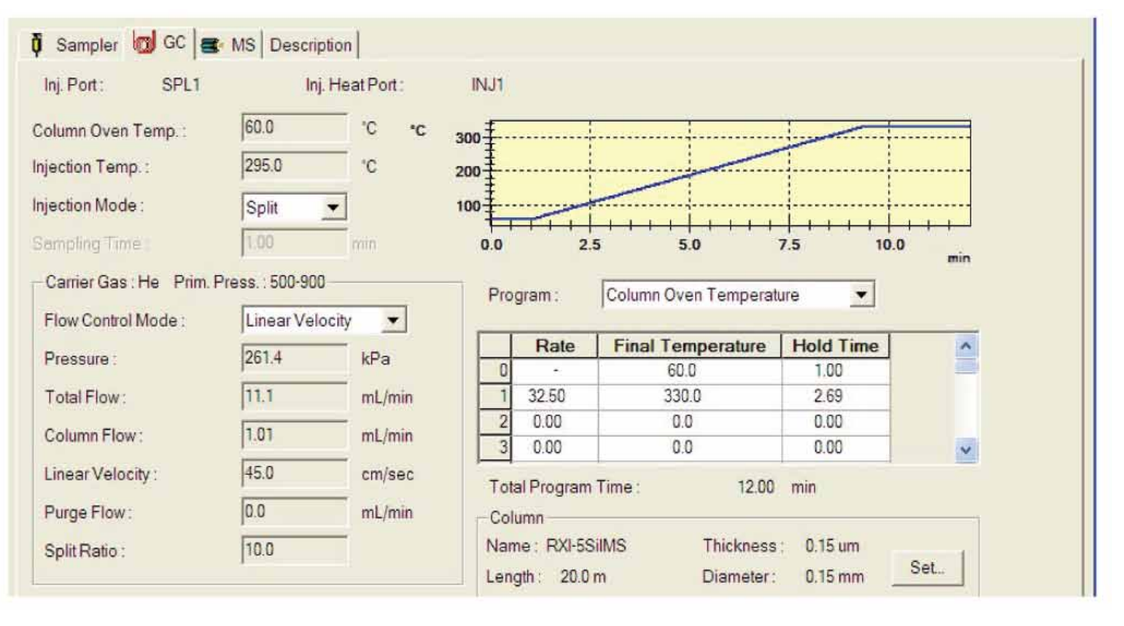
- Flow control using constant linear velocity (45cm/sec).
- Split injection (split ratio 10:1).
- GC temperature program 60-330°C with faster temperature program and fast GC oven cooldown.
- Event time (scan interval) 0.10sec.

Under these conditions, all compounds elute in about 10.5 min. (first-eluting compound is N-nitrosodimethylamine at about 2 min).

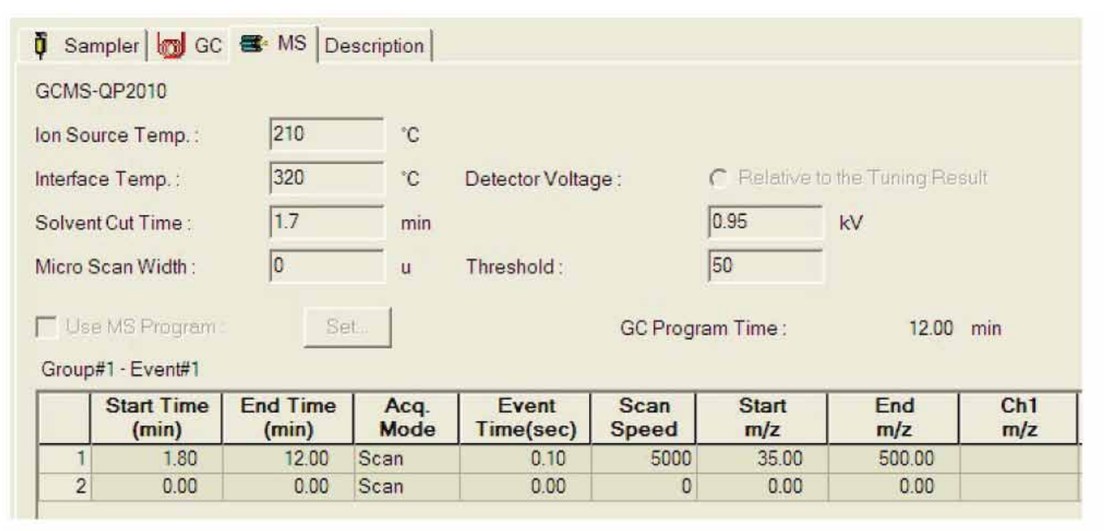
Chromatogram using a 0.15mm column



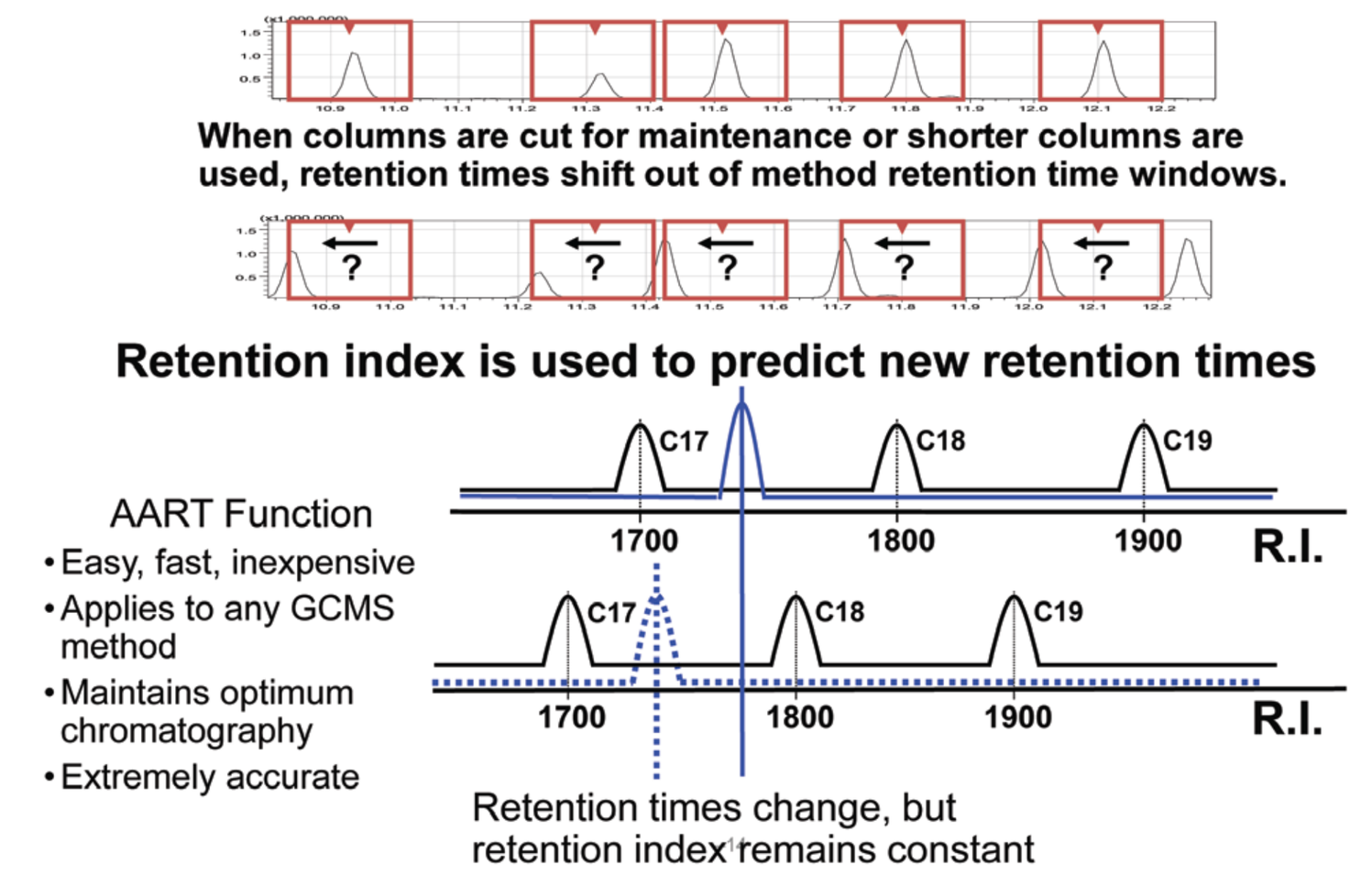
GC conditions using a 0.15mm column

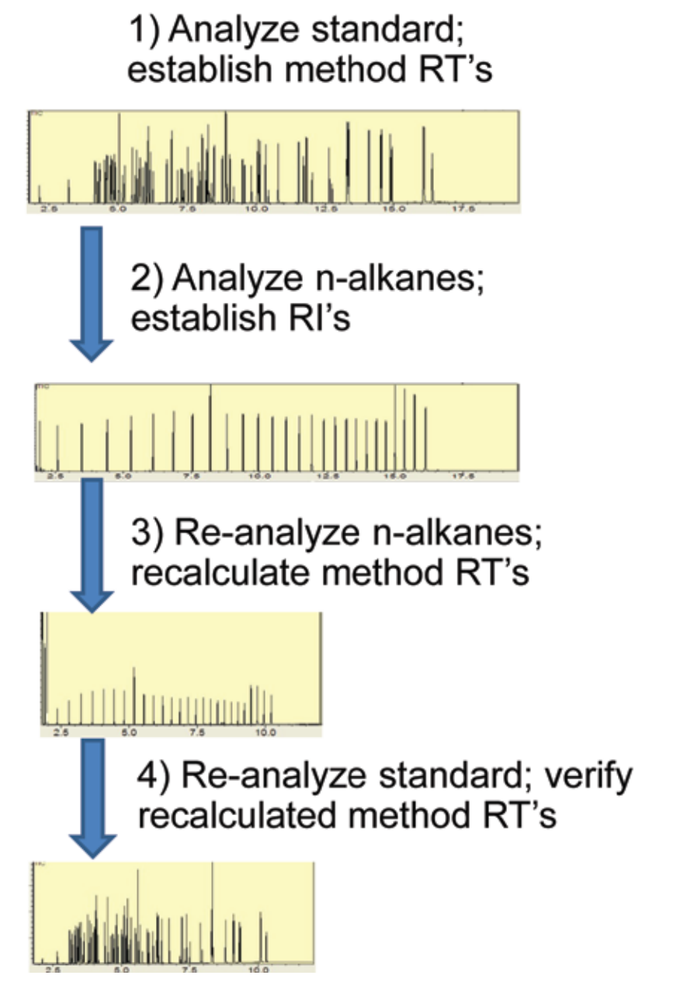


MS conditions using a 0.15mm column



Automatic Adjustment of Retention Times (AART)



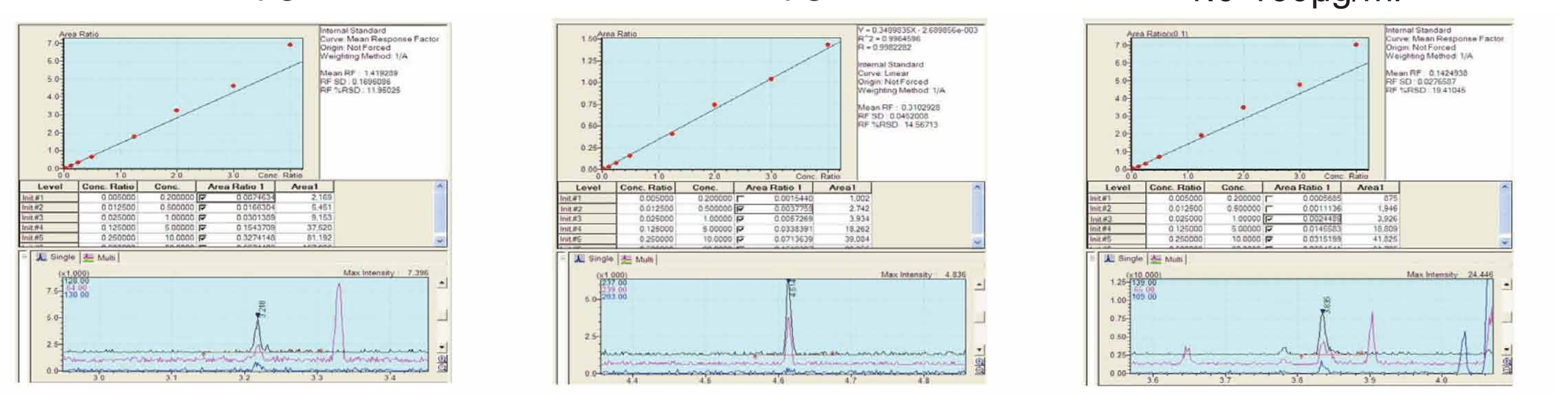


AART function is used to update method RT's; the predicted RT's are very accurate (examples below)

Compound	Method RT	Actual RT	Difference
1,4-Dichlorobenzene-d4 (IS)	3.314	3.327	-0.013
Naphthalene-d8 (IS)	4.048	4.066	-0.018
Acenaphthene-d10 (IS)	5.196	5.210	-0.014
Phenanthrene-d10 (IS)	6.290	6.298	-0.008
Chrysene-d12 (IS)	8.322	8.310	0.012
Perylene-d12 (IS)	9.418	9.350	0.068
2-Fluorophenol (SS)	2.664	2.662	0.002
Phenol-d5 (SS)	3.113	3.103	0.010
2-Chlorophenol-d4 (SS)	3.193	3.205	-0.012
2,4,6-Tribromophenol (SS)	5.768	5.778	-0.010
1,2-Dichlorobenzene-d4 (SS)	3.401	3.417	-0.016
Nitrobenzene-d5 (SS)	3.620	3.635	-0.015
2-Fluorobiphenyl (SS)	4.738	4.744	-0.006
Terphenyl-d14 (SS)	7.510	7.510	0.000
N-Nitrosodimethylamine	2.112	2.123	-0.011
Phenol	3.120	3.110	0.010
Bis(2-chloroethyl) ether	3.170	3.168	0.002
2-Chlorophenol	3.201	3.214	-0.013
1,3-Dichlorobenzene	3.285	3.300	-0.015
1,4-Dichlorobenzene	3.324	3.337	-0.013
1,2-Dichlorobenzene	3.408	3.425	-0.017
Benzyl Alcohol	3.386	3.389	-0.003
3&4-Methylphenol	3.450	3.444	0.006
2-Methylphenol	3.536	3.529	0.007
Bis(2-Chloroisopropyl) ether	3.467	3.465	0.002
N-Nitrosodi-n-propylamine	3.538	3.540	-0.002

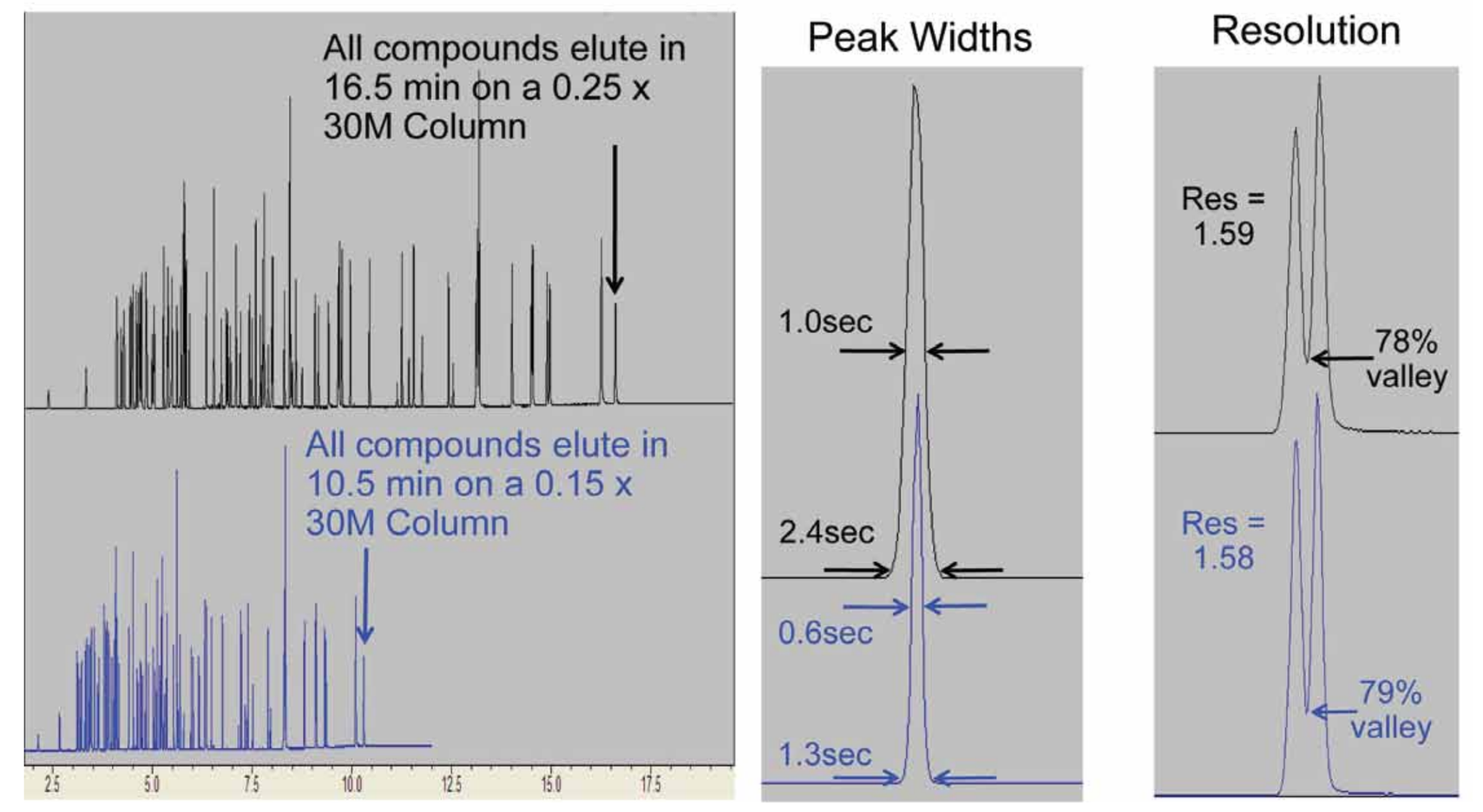
Example calibration curves (0.15mm column) are shown below (chromatograms are lowest-level calibration point)

2-Chlorophenol	Hexachlorocyclopentadiene	2-Nitrophenol
0.2-160µg/ml	0.5-160µg/ml	1.0-160µg/ml



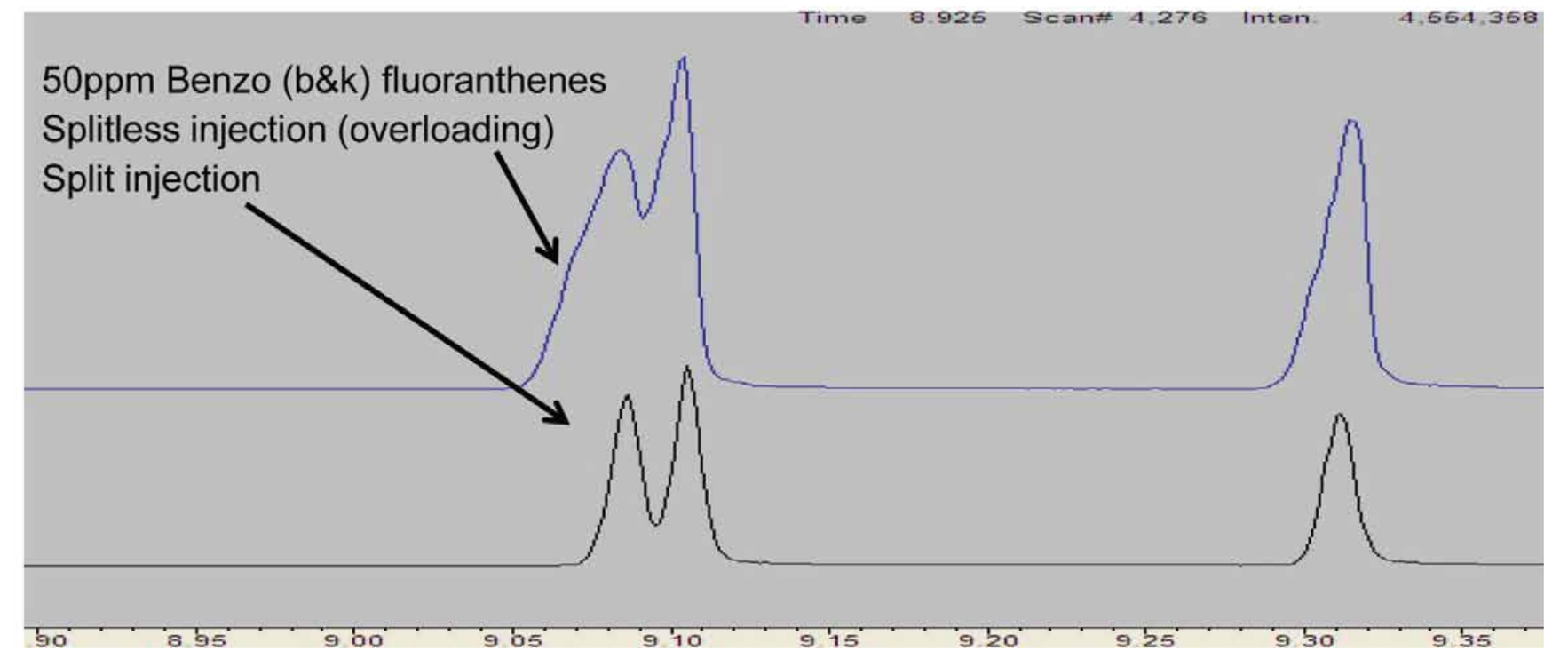
Calibration results using a 0.15mm column are very similar to those using a 0.25mm column; method sensitivity is also similar.

Comparison of Chromatographic Results 0.25mm Column vs 0.15mm Column

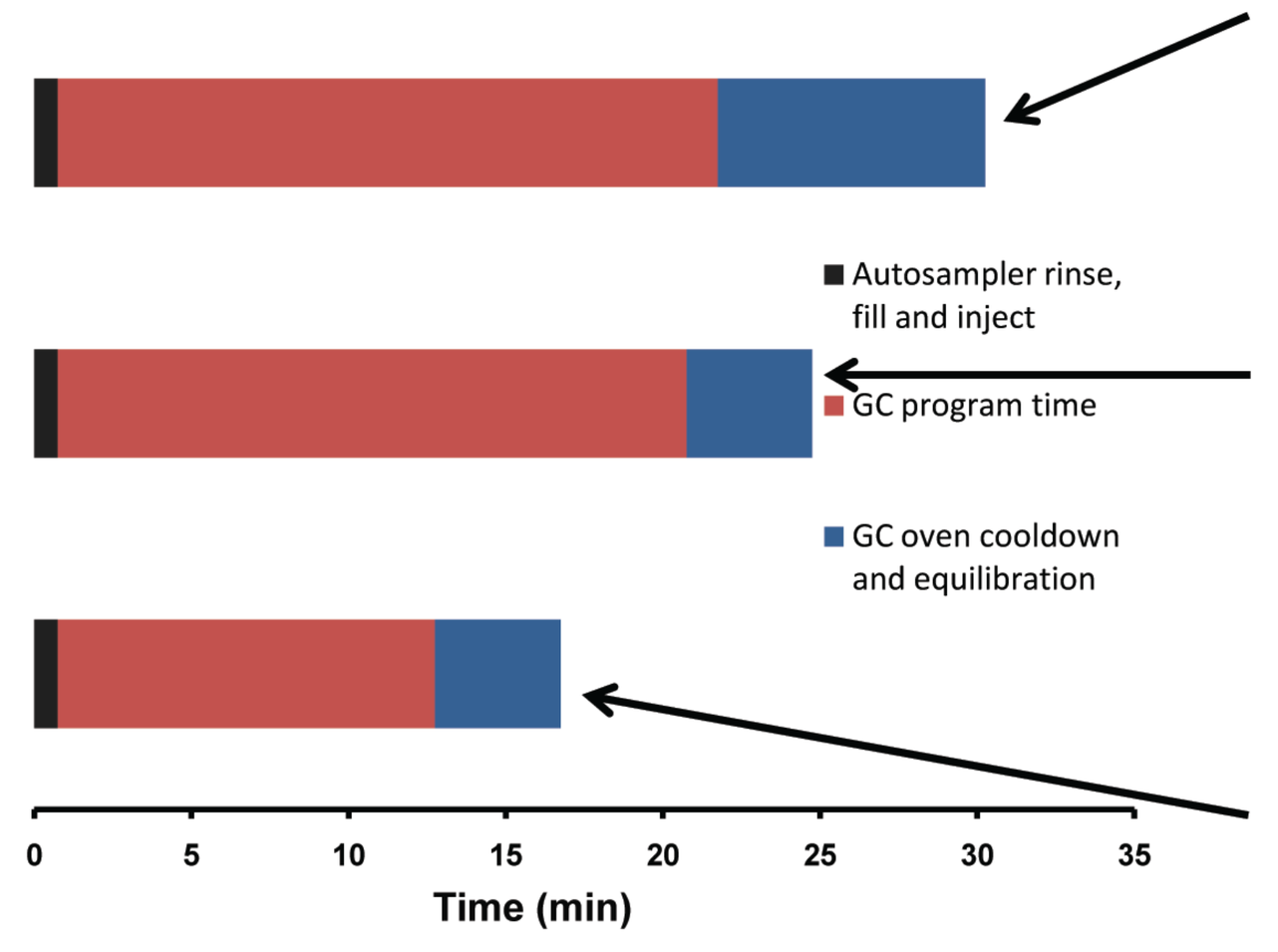


Column overloading is minimized using the split injection mode

Column overloading can be a significant problem, particularly with narrow-bore columns. The problem of overloading is minimized by using the split injection technique. The example below shows chromatograms of a 50ppm standard run on a 0.15mm column in the split mode and in the splitless mode.



Saving run/cycle times



Conventional (splitless) analysis – low starting temperature (40°C) requires longer run time and longer cooldown time.
Cycle time = 30min
24 runs per 12 hr shift

Modified analysis with split injection and 0.25mm GC column. Higher starting temperature (60°C) shortens run time. Cooldown time to 60°C is shortened considerably with new rapid cooling GC oven.
Cycle time = 25min
29 runs per 12 hr shift

Fast analysis with split injection and 0.15mm GC column. Run time is shortened dramatically while maintaining sensitivity and chromatographic resolution.
Cycle time = 17min
42 runs per 12 hr shift

Summary

- Goals of study to optimize instrument performance for EPA Method 8270D:
  - Maintain strict method QC
  - Optimize sensitivity and dynamic range
  - Maximize productivity
- The split injection mode was used; this mode provides:
  - Excellent sensitivity
  - Slightly shorter run times (higher initial temperature) than splitless injection
  - Wide dynamic range
  - Excellent chromatography without column overloading
- Run times are improved slightly using conventional conditions (30M x 0.25mm column):
  - Higher initial temperature shortens run time slightly and cooldown time considerably
  - Newly enhanced GC oven cools much more quickly than previous models
- Cycle time is shortened by 30% using a narrow-bore GC column (20M x 0.15mm column):
  - Chromatographic resolution is nearly identical to that achieved using a standard GC column
  - Sensitivity and dynamic range are maintained
  - A rapid-scanning quadrupole MS is used to collect at least 10 data points (spectra) per GC peak for optimum precision and accuracy
- Changes in method retention times are easily accommodated with AART function using retention index.
- Scan rate experiments indicate optimum scan speed for 0.25mm id columns is about 0.2sec/scan; optimum for 0.15mm id columns is about 0.1sec/scan

Acknowledgement

- The authors wish to thank Gary Stidsen, Restek Corporation for supplying columns for this investigation and to Michelle Misselwitz, Restek Corporation for fruitful discussions.