High-Speed Gas Chromatographic Analysis of Chlorinated Pesticides Using a Tandem Column Ensemble and Stop-Flow Modulation

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Stop-Flow GC: Improved Resolution with Fast Analysis Times

I. The Stop-Flow GC System

II. Advantages of Stop-Flow GC

III. Applications

   A. Chlorinated Pesticides

   B. Residual Solvents

Desires of GC Analysts

- Higher Sample Throughput
  - Lowers cost/sample
  - Increases sample capacity
  - Fewer instruments to accomplish same workload
- Better Resolution
  - Can allow for shorter run times
  - Improves quantitation
  - Can allow for analysis of very complex matrices

Methods to Improve Speed and/or Resolution

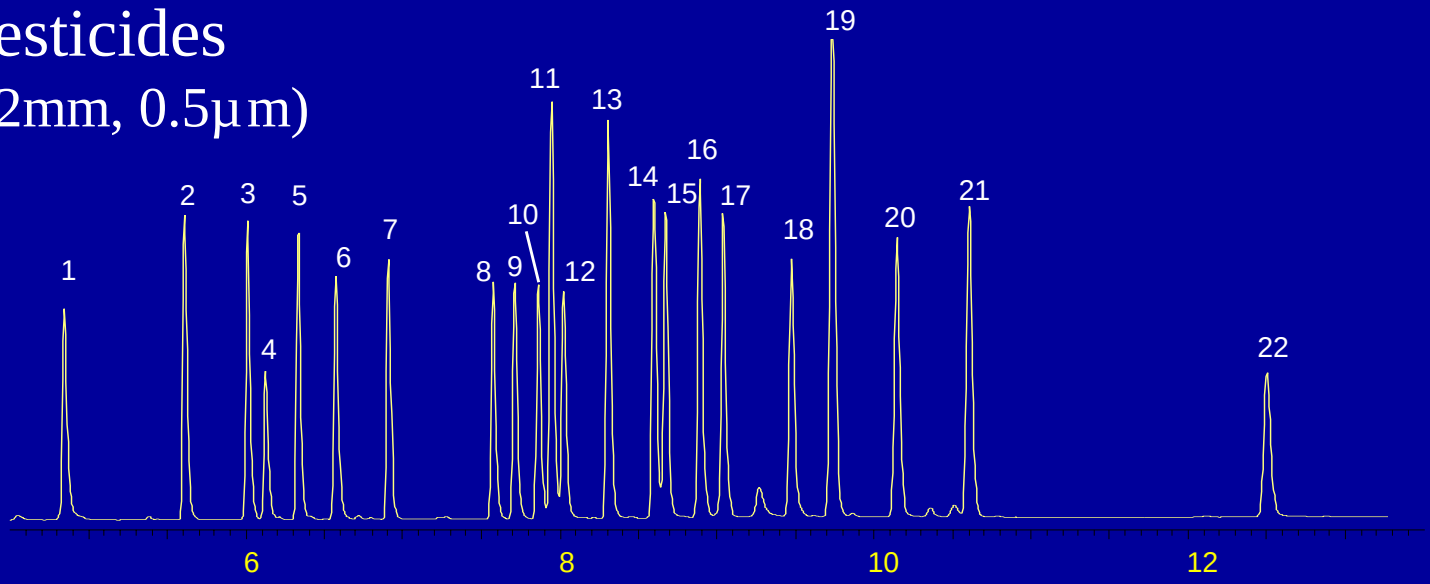
- Tuning Stationary Phase Selectivity
  - Design column to achieve specific separation
  - Users can send retention data for optimization
- Physical Parameter Optimization
  - Pro *ez*GC™ Software allows user optimization
- Hardware Modification
  - GC Racer allows increased temperature ramp rates with (common) existing instrumentation

Methods to Improve Speed and/or Resolution

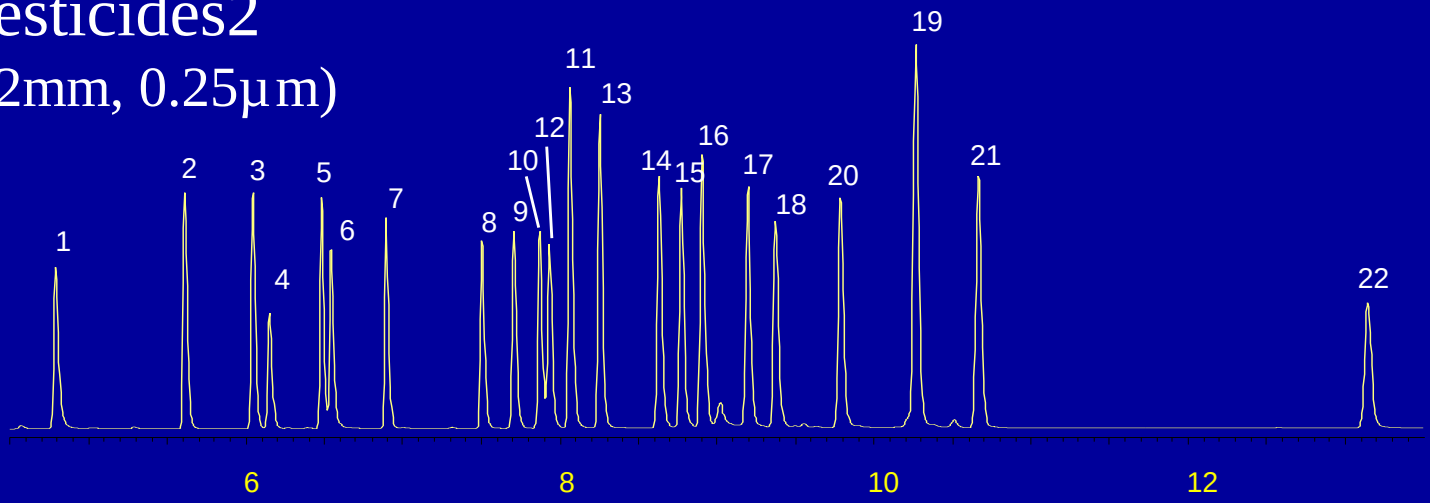
- Fast GC/Flash GC
  - Short, narrow i.d. columns
  - Ballistic heating (resistive, microwave)
- Multicolumn GC
  - Bertsch, Guichon, Giddings
- Comprehensive 2D-GC
  - Begun by John Phillips – Southern Illinois Univ.
- Stop-Flow GC
  - Richard Sacks – Univ. of Michigan

Chlorinated Pesticides Fast Runs

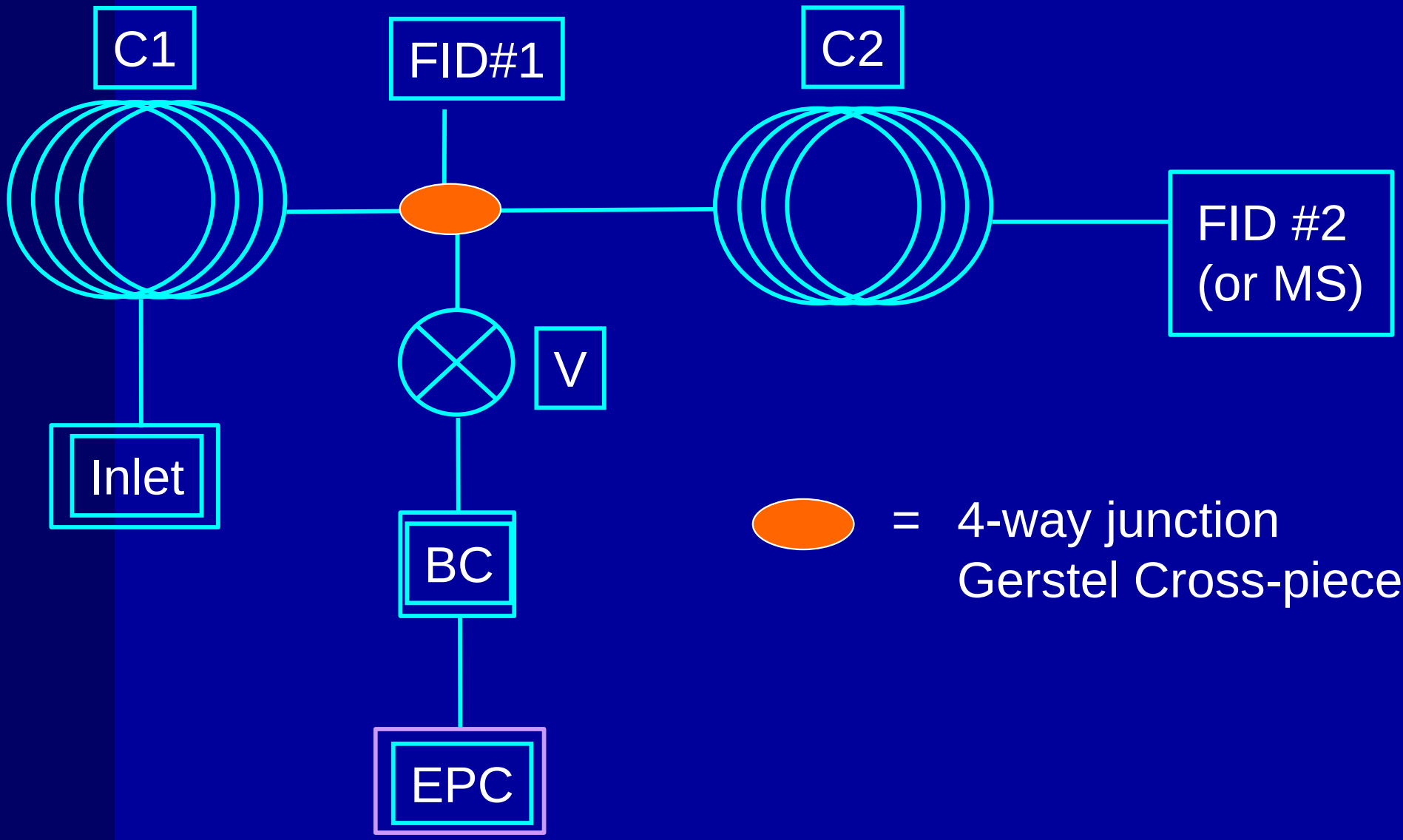
Rtx-CLPesticides
(30m x 0.32mm, 0.5µm)



Rtx-CLPesticides2
(30m x 0.32mm, 0.25µm)

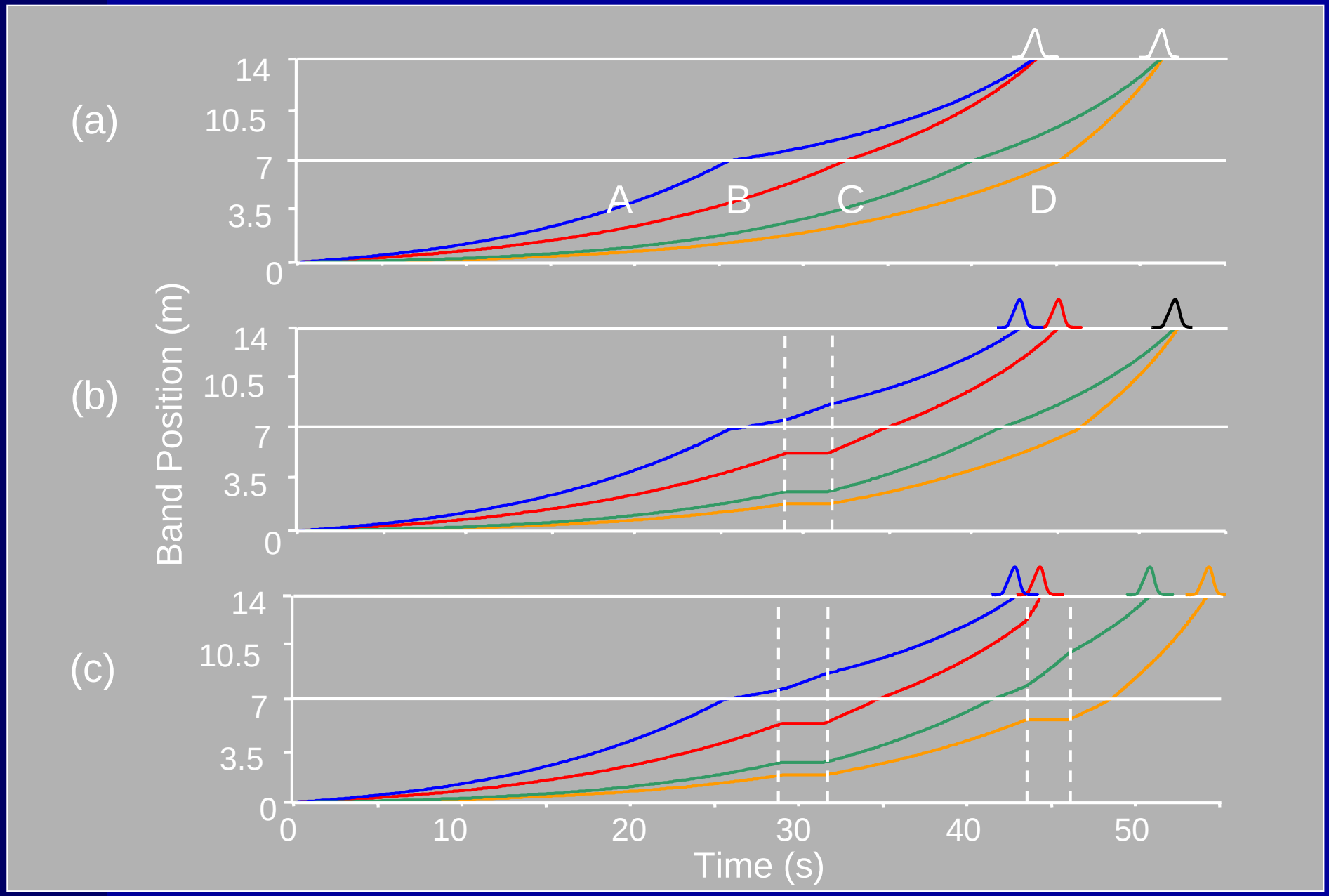


Stop Flow GC System: Sacks, et. al.*



*Richard Sacks, University of Michigan

Stop Flow System: Pressure Tunable Selectivity

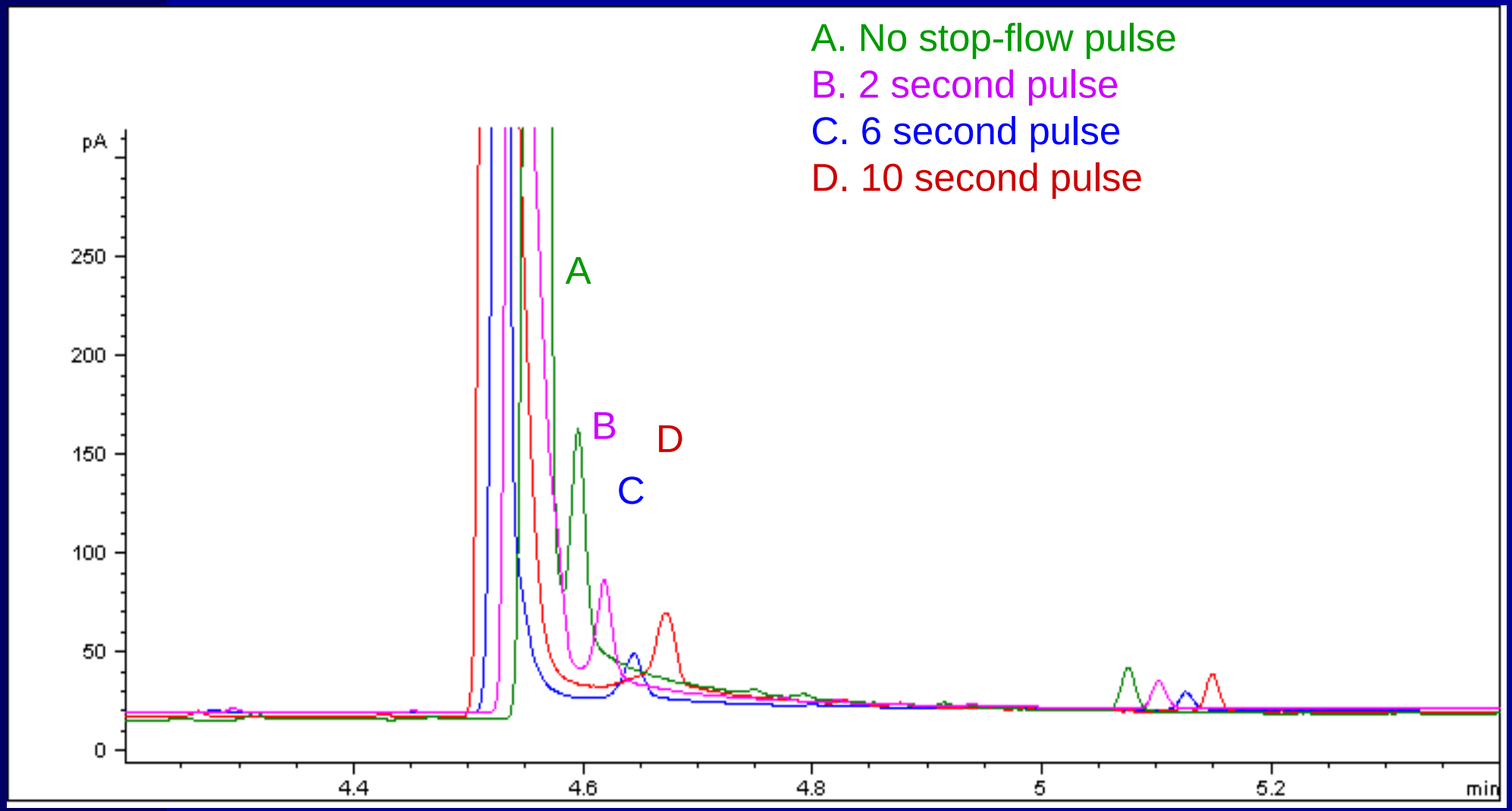


Advantages of Stop-Flow GC

- Minimal Hardware Modifications
- Dual-Column System
  - Standard dimension GC columns
- Flexibility
  - Ability to “tune” the selectivity of a separation
- Controlled by GC’s Current Software

Separation of Limonene and Eucalyptol

Increasing Stop-flow Pulse Lengths



Application: Chlorinated Pesticides

- Environmental testing industry
  - EPA methods 8081, 508, and 608
  - High volume tests
- Importance of rapid, accurate assays
  - Application-specific stationary phases
  - Best run times around 13 minutes

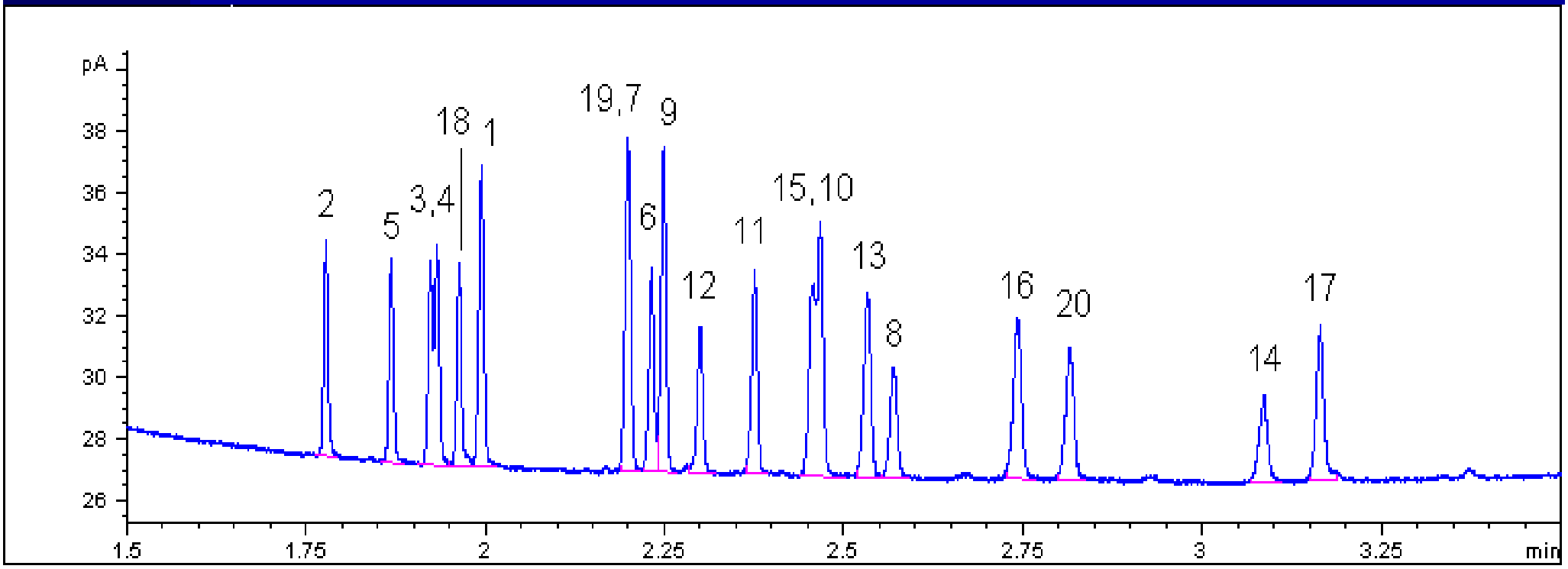
Chlorinated Pesticides

1	Aldrin
2	α-BHC
3	β-BHC
4	δ-BHC
5	γ-BHC (lindane)
6	α-Chlordane
7	γ-Chlordane
8	4,4’-DDD
9	4,4’-DDE
10	4,4’-DDT

11	Dieldrin
12	Endosulfan I
13	Endosulfan II
14	Endosulfan sulfate
15	Endrin
16	Endrin aldehyde
17	Endrin ketone
18	Heptachlor
19	Heptachlor epoxide
20	Methoxychlor

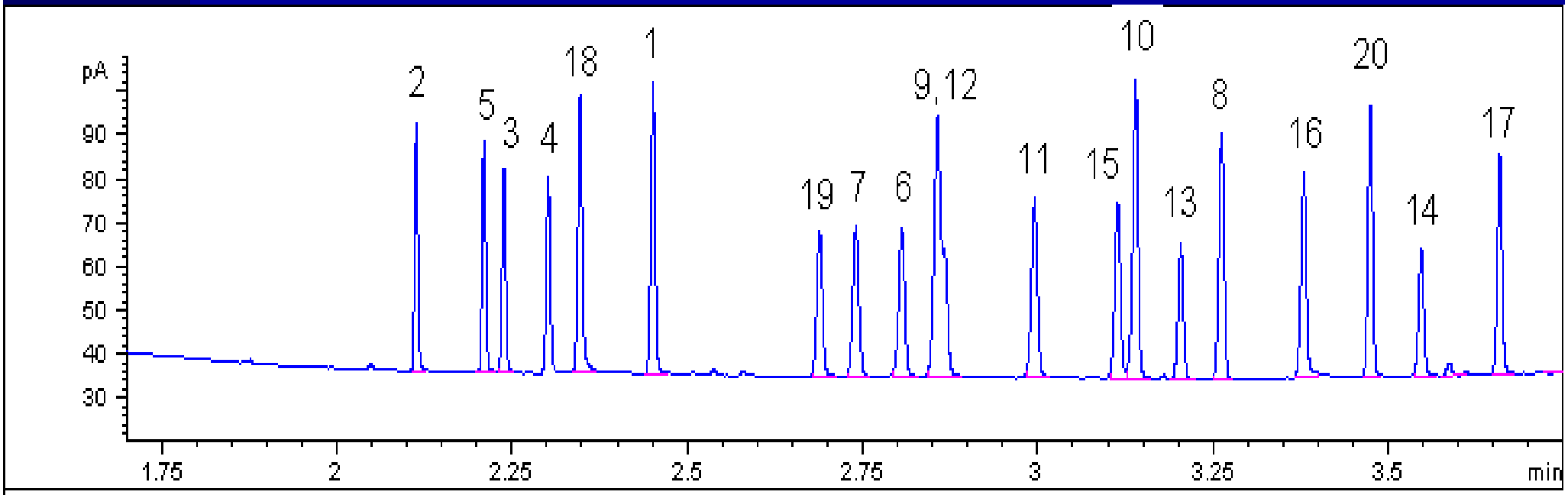
Chlorinated Pesticides

After column #1 (Rtx-200)



Chlorinated Pesticides

After column #2 (Rtx-5)

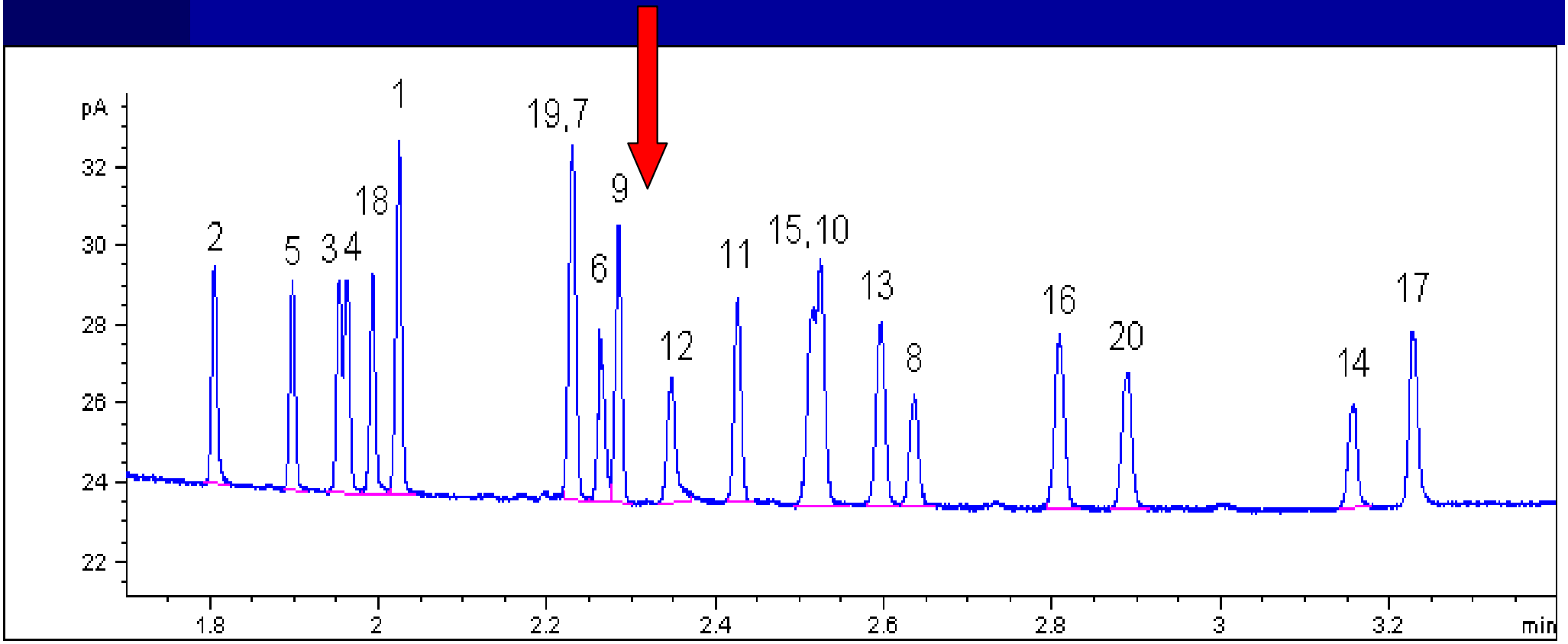


Chlorinated Pesticides: Run Conditions

	Fast Procedure
Analytical Columns	Rtx-200 10m x 0.18mm, 0.2µm Rtx-5 10m x 0.18mm, 0.18µm
Oven Program	60°C (0.4 min. hold) to 220°C at 100°C/min., to 235°C at 15°C/min., to 300°C at 120°C/min., 0.5 min. hold
Inlet Pressure	45 psig
Injector	300°C
Injection	0.2-0.5 µL splitless 0.25min hold time
Detectors	Dual FIDs @ 300°C

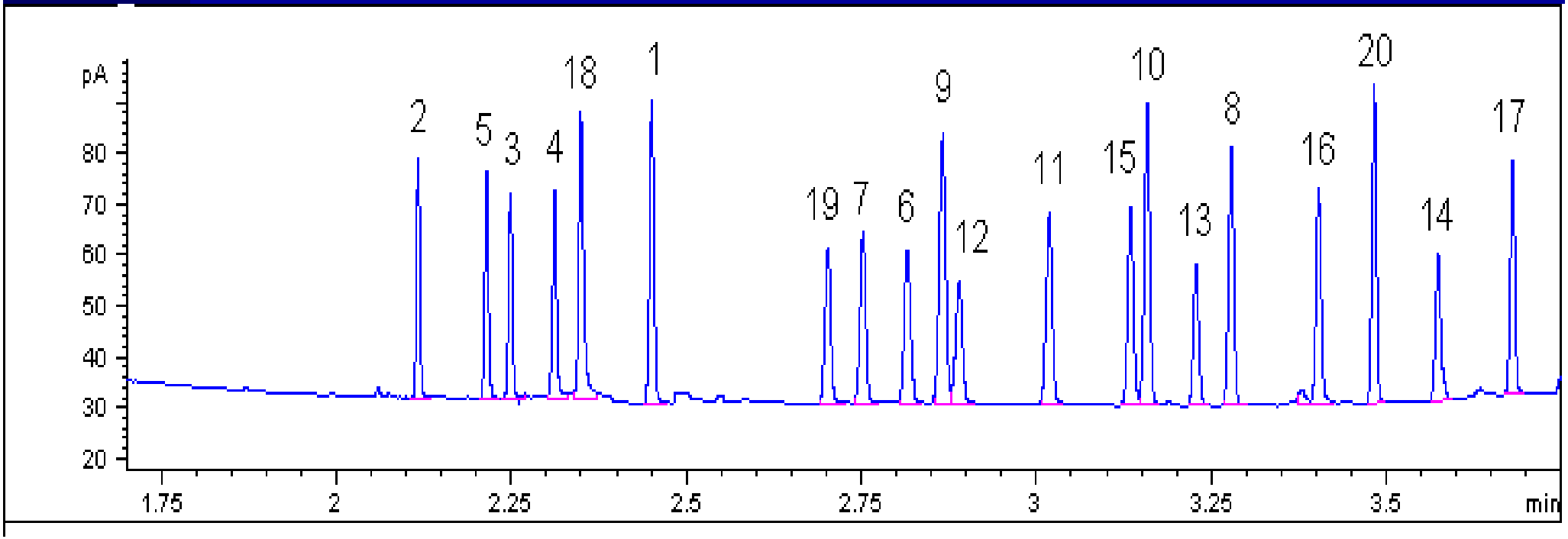
Chlorinated Pesticides

Showing location of the stop-flow pulse



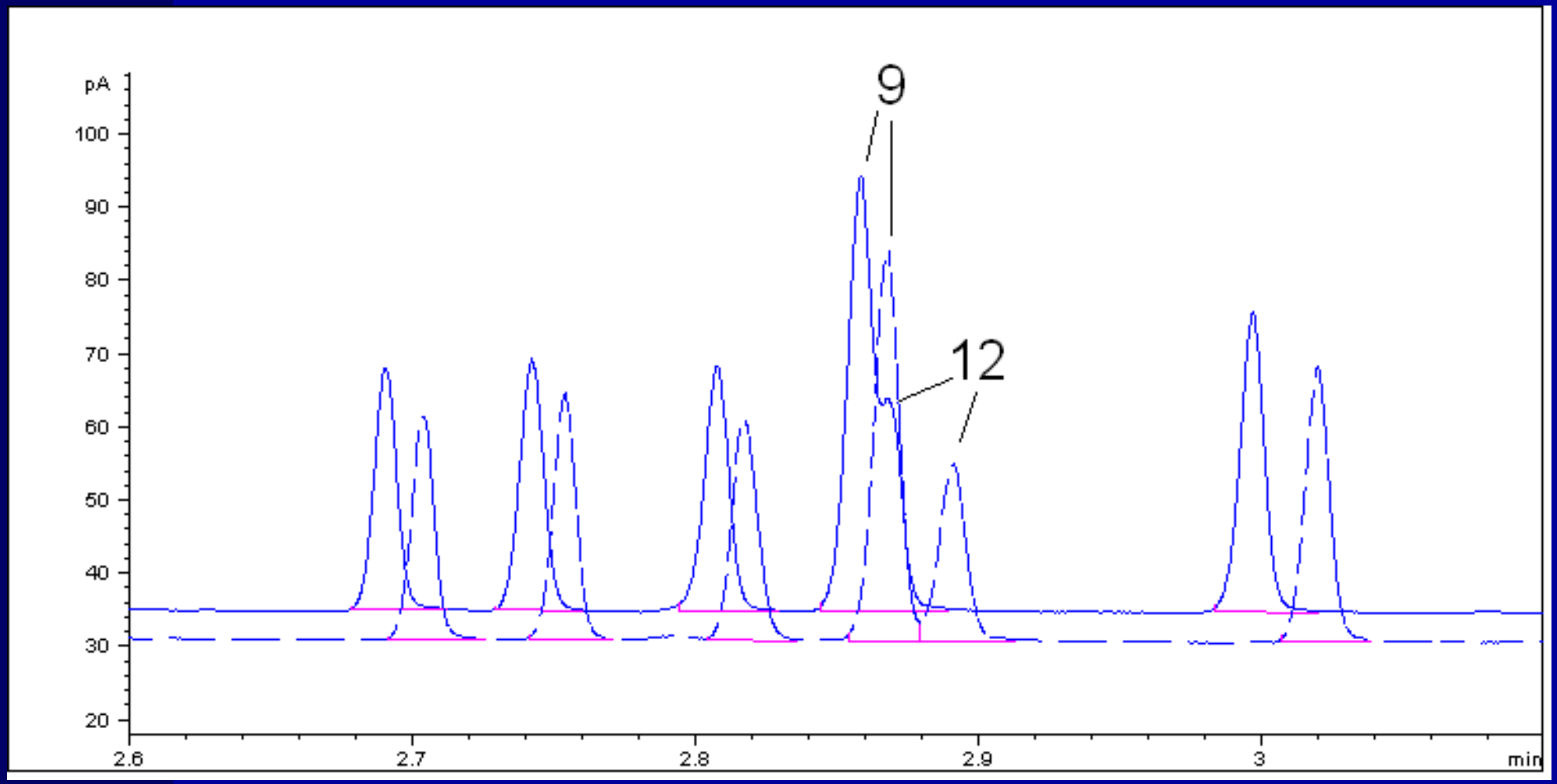
Chlorinated Pesticides

With 1 stop-flow pulse



Chlorinated Pesticides

With 1 stop-flow pulse



Stop-Flow GC

- Stop-Flow allows the analyst to add “space” between specific peaks
  - Improved use of chromatographic “real estate”
  - Permits time-compressed GC runs using faster oven temperature ramps

GC Racer

- Interfaces to existing GC's
- Operates using existing GC control
  - No software or firmware
- Allows for maximum ramp rates up to 440°C
- Can allow for 2-5 times speed enhancement for most methods

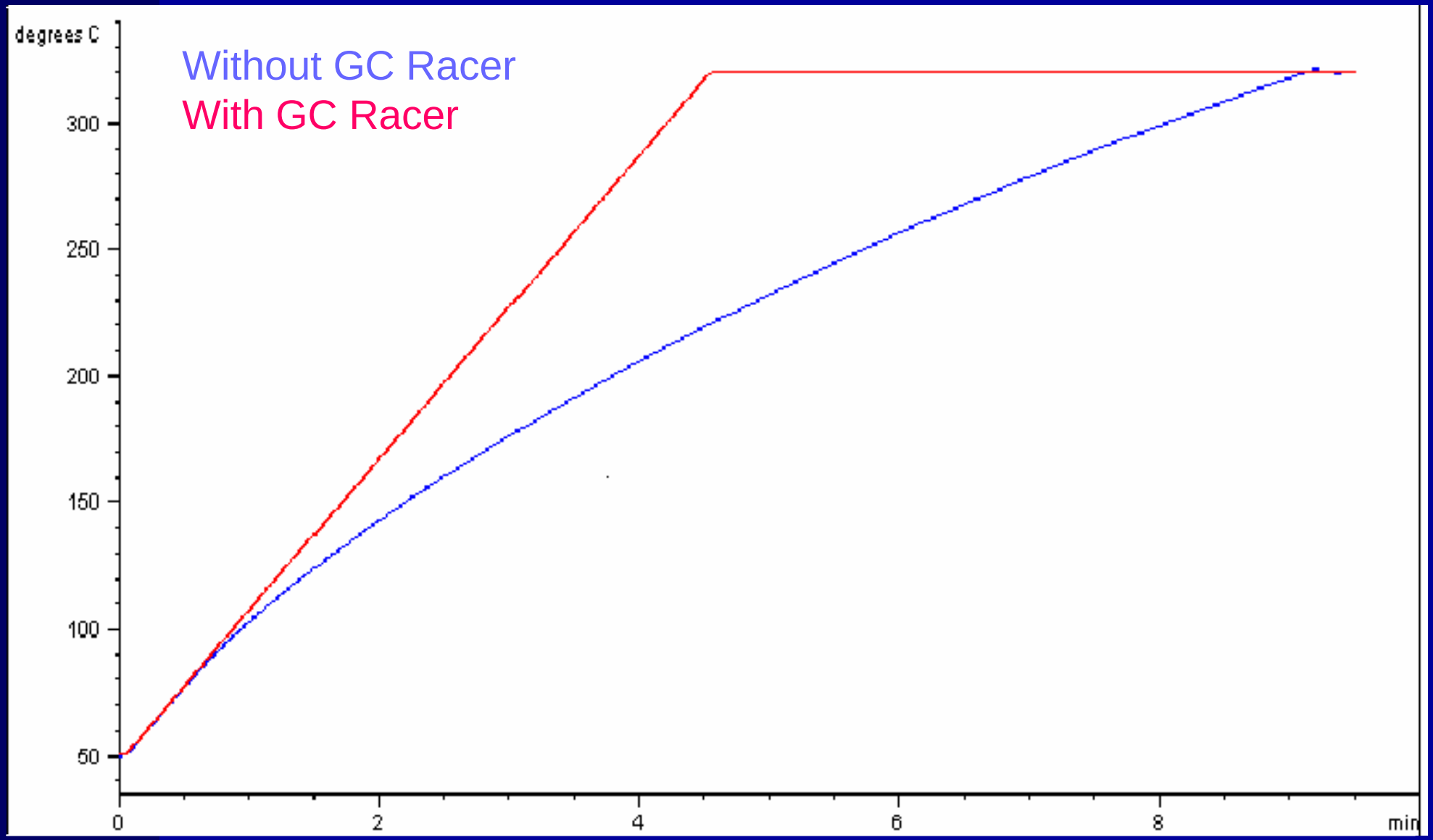
GC Racer

GC Racer Heater Installed in an Agilent 5890

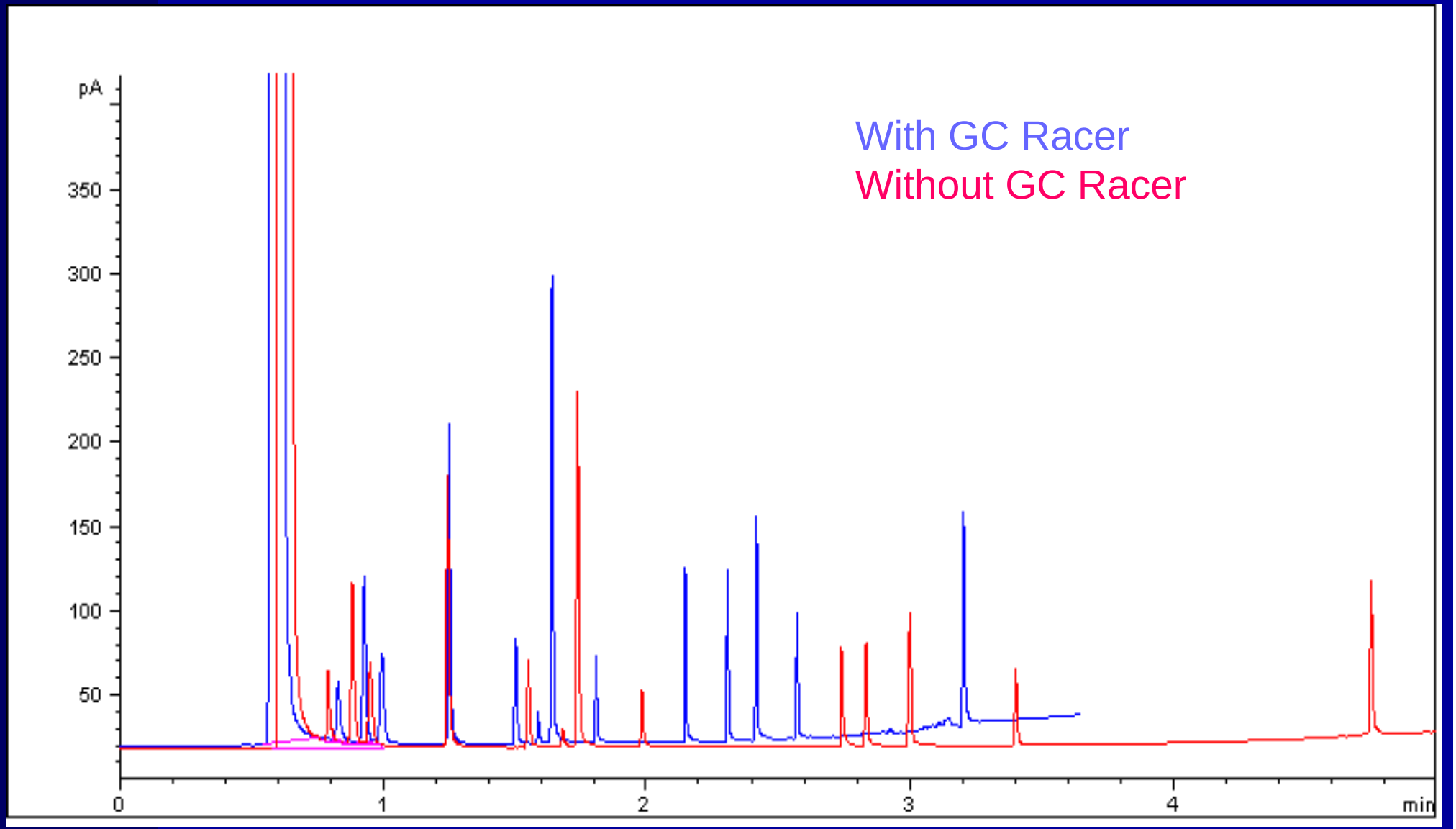
GC Racer

GC Racer Installed on an Agilent 5890

Agilent 6890 GC, temperature program of 60°C/min.



Volatile Compounds, with and without the GC Racer



Application: Residual Solvents

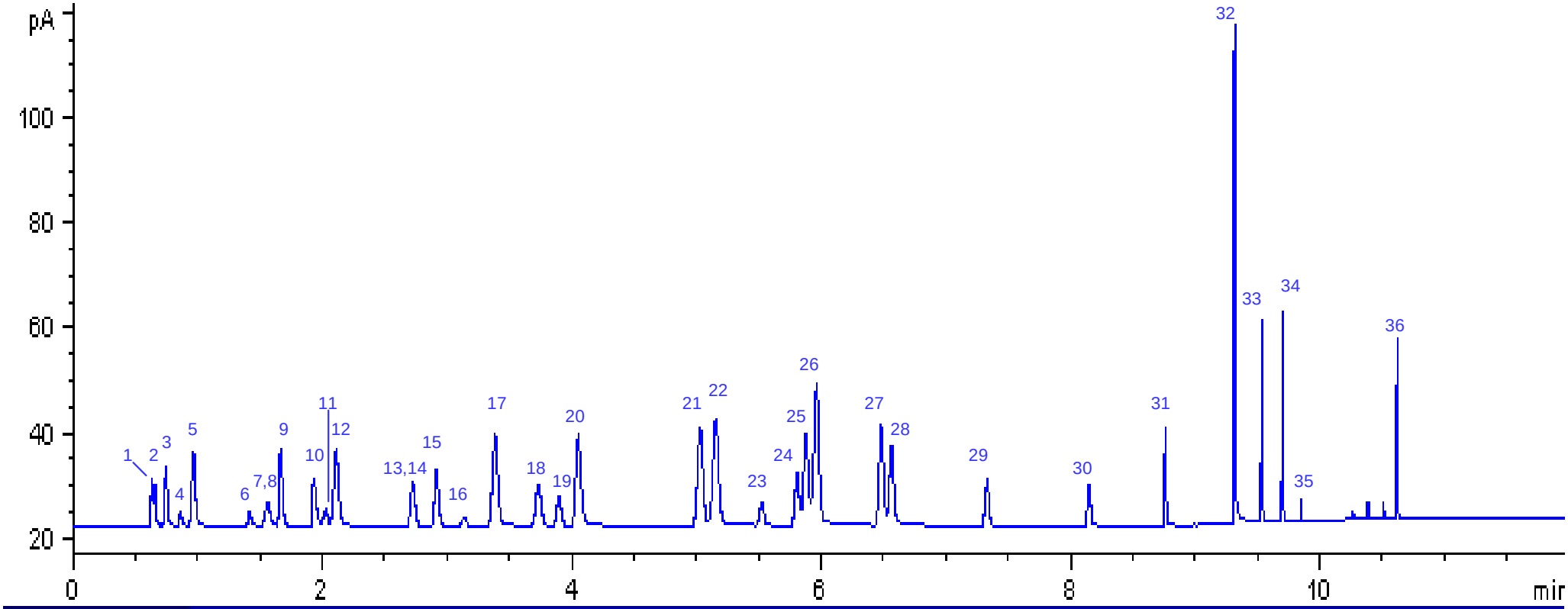
- Pharmaceutical Formulations
- Guidelines for Testing
  - International Conference on Harmonization
  - European Pharmacopoeia
- Compound Lists Vary
  - Over 60 compounds of regulatory interest
  - Classes based on toxicities
  - Resolution of large lists on a single stationary phase can be extremely difficult

Class I & II Residual Solvents

Peak #	Compound	Peak #	Compound
1	2-methylpentane	19	1,2-dichloroethane (1,2-DCA)
2	hexane	20	2-hexanone (MBK)
3	methyl cyclopentane	21	p-xylene
4	1,1-dichloroethene (1,1-DCE)	22	m-xylene
5	methyl cyclohexane	23	nitromethane
6	*trans*-1,2-dichloroethene	24	2-methoxyethanol
7	carbon tetrachloride (CCl4)	25	pyridine
8	1,1,1-trichloroethane (1,1,1-TCA)	26	o-xylene
9	methanol	27	chlorobenzene
10	1,2-dimethoxyethane	28	2-ethoxyethanol
11	methylene chloride (CH2Cl2)	29	1,1,2-trichloroethane (1,1,2-TCA)
12	benzene	30	dimethyl formamide (DMF)
13	*cis*-1,2-dichloroethene	31	N,N-dimethylacetamide (DMA)
14	trichloroethene (TCE)	32	1,2,3,4-tetrahydronaphthalene (THN)
15	acetonitrile (MeCN)	33	ethylene glycol (EG)
16	chloroform	34	1-methyl-2-pyrrolidinone (1-MP)
17	toluene	35	formamide
18	1,4-dioxane	36	sulfolone

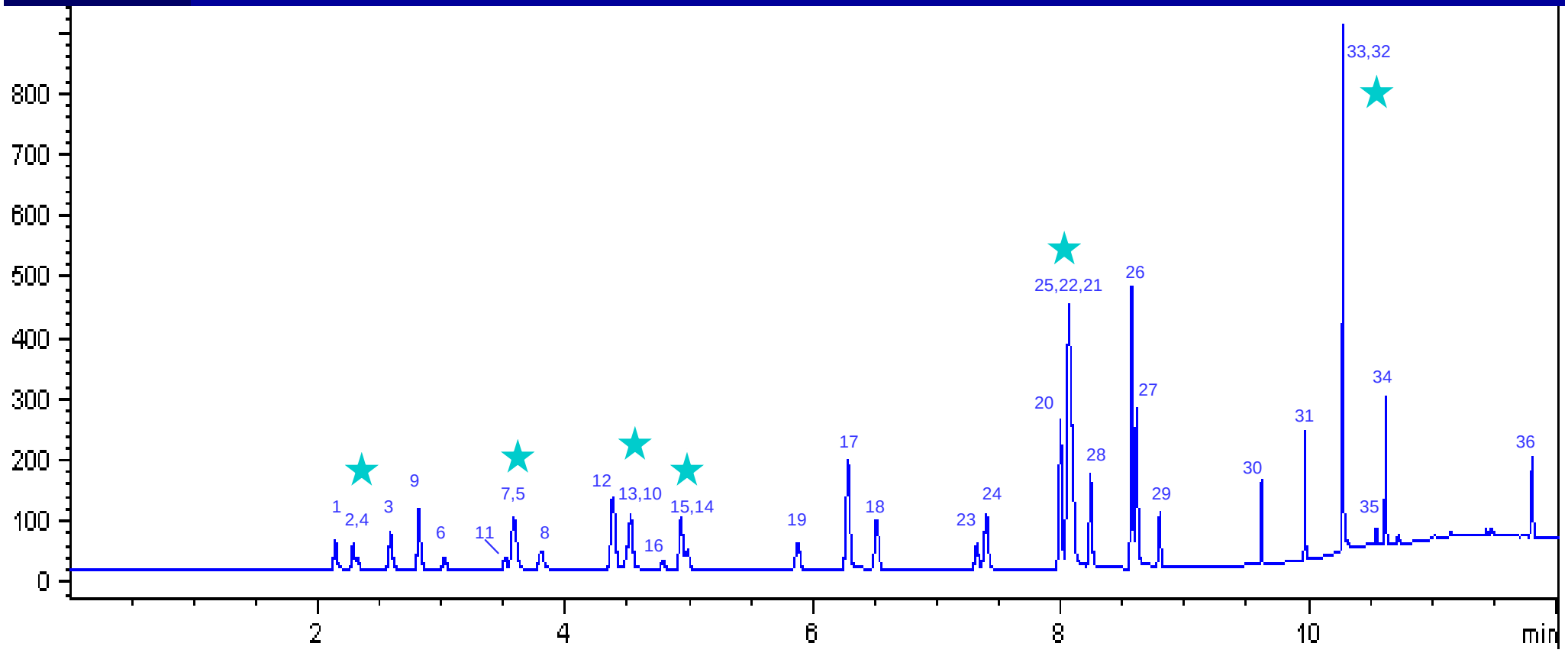
Fast Run Conditions: 1st FID

After Rtx-Stabilwax, 15m x 0.25mm x 0.5µm



Fast Run Conditions: 2nd FID

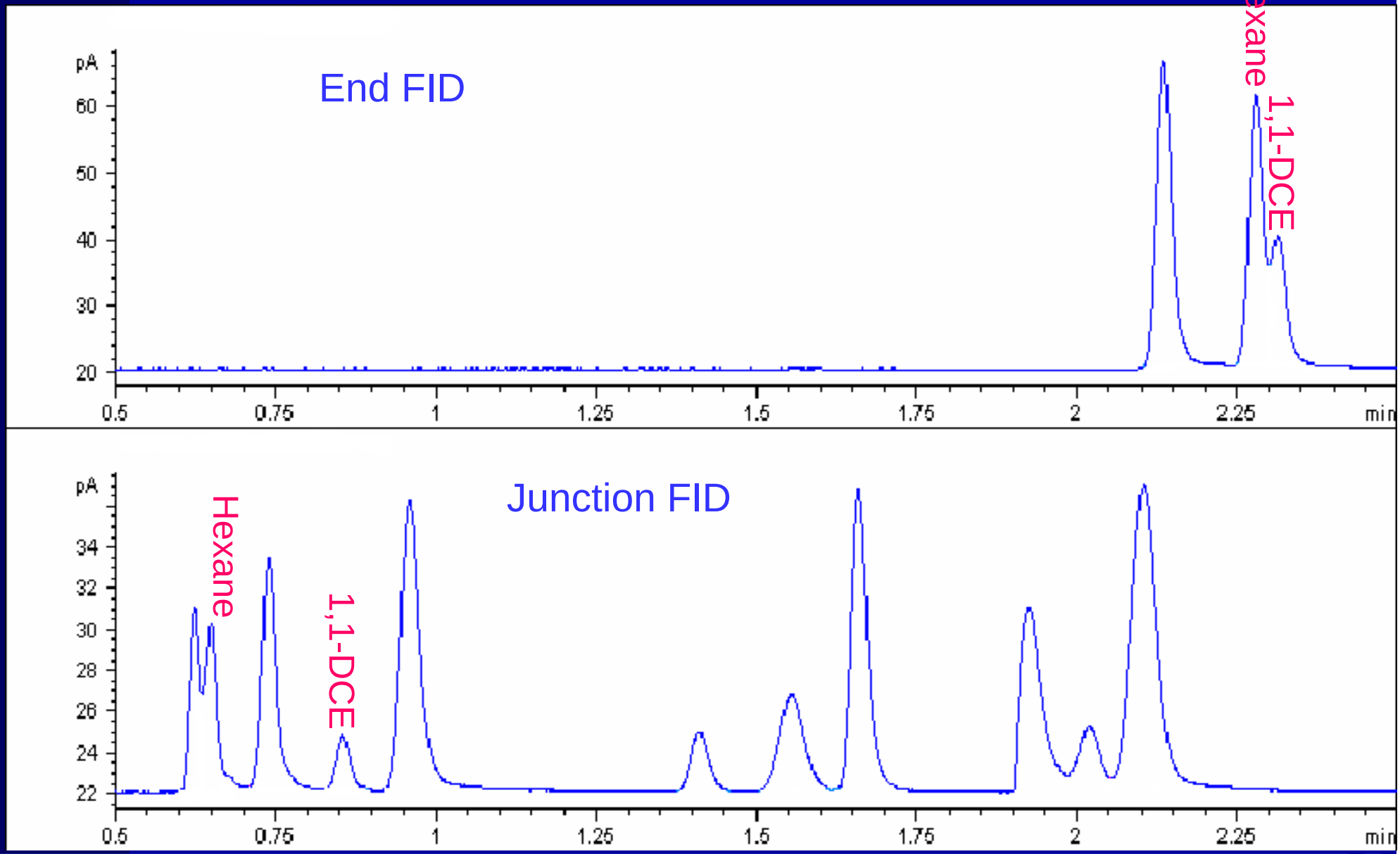
After Rtx-Stabilwax + Rtx-200 (30m x 0.25mm x 1.0µm)



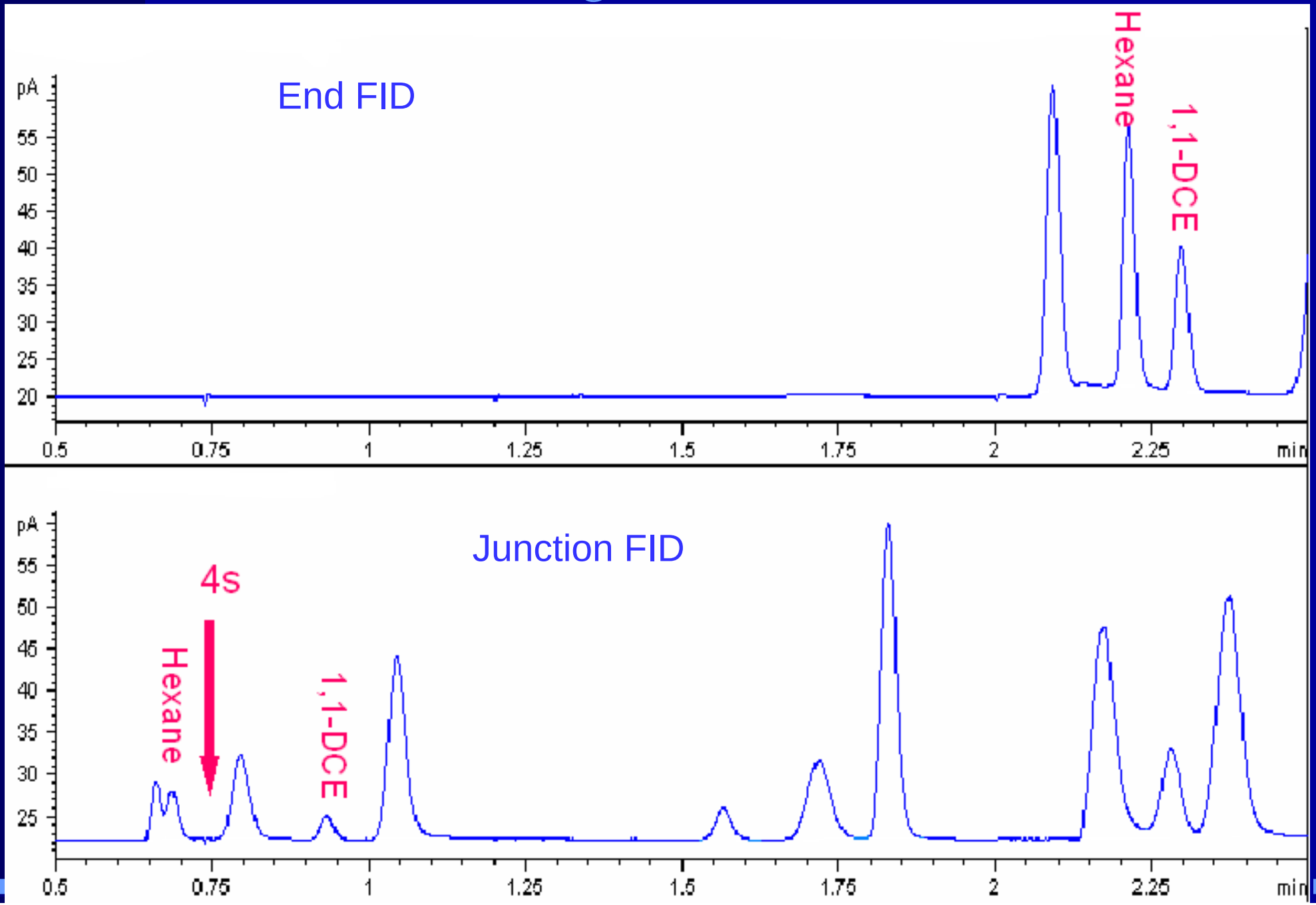
Residual Solvents: Run Conditions

	Standard Procedure	***Fast Procedure***
Analytical Columns	Stabilwax 15m x 0.25mm, 0.5µm Rtx-200 30m x 0.25mm, 1µm	Stabilwax 15m x 0.25mm, 0.5µm Rtx-200 30m x 0.25mm, 1µm
Oven Program	40°C (6 min. hold) to 100°C at 4°C/min., to 220°C at 15°C/min., 5 min. hold	40°C (1 min. hold) to 65°C at 6°C/min., to 100°C at 12°C/min., to 250°C at 70°C/min., 1.8 min. hold
Column Flow	1.5 mL/min. constant flow	2.5 mL/min. to 9.5 min. 3.5 mL/min. at 10 min.
Injector	230°C	230°C
Injection	0.2 µL HS, 200:1 split	0.2 µL HS, 200:1 split
Detectors	Dual FIDs @ 250°C	Dual FIDs @ 250°C

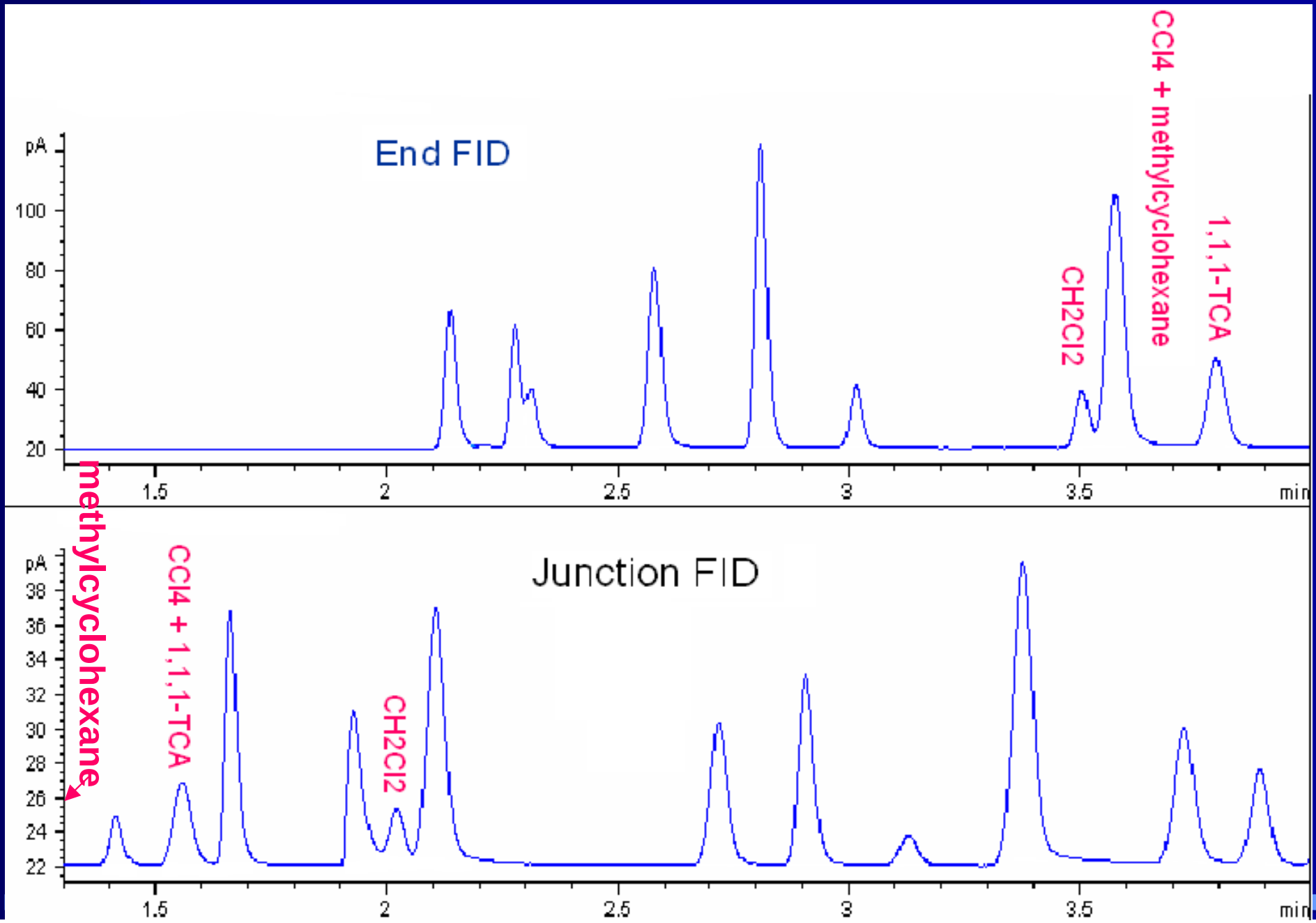
Class I & II Residual Solvents: No Pulses



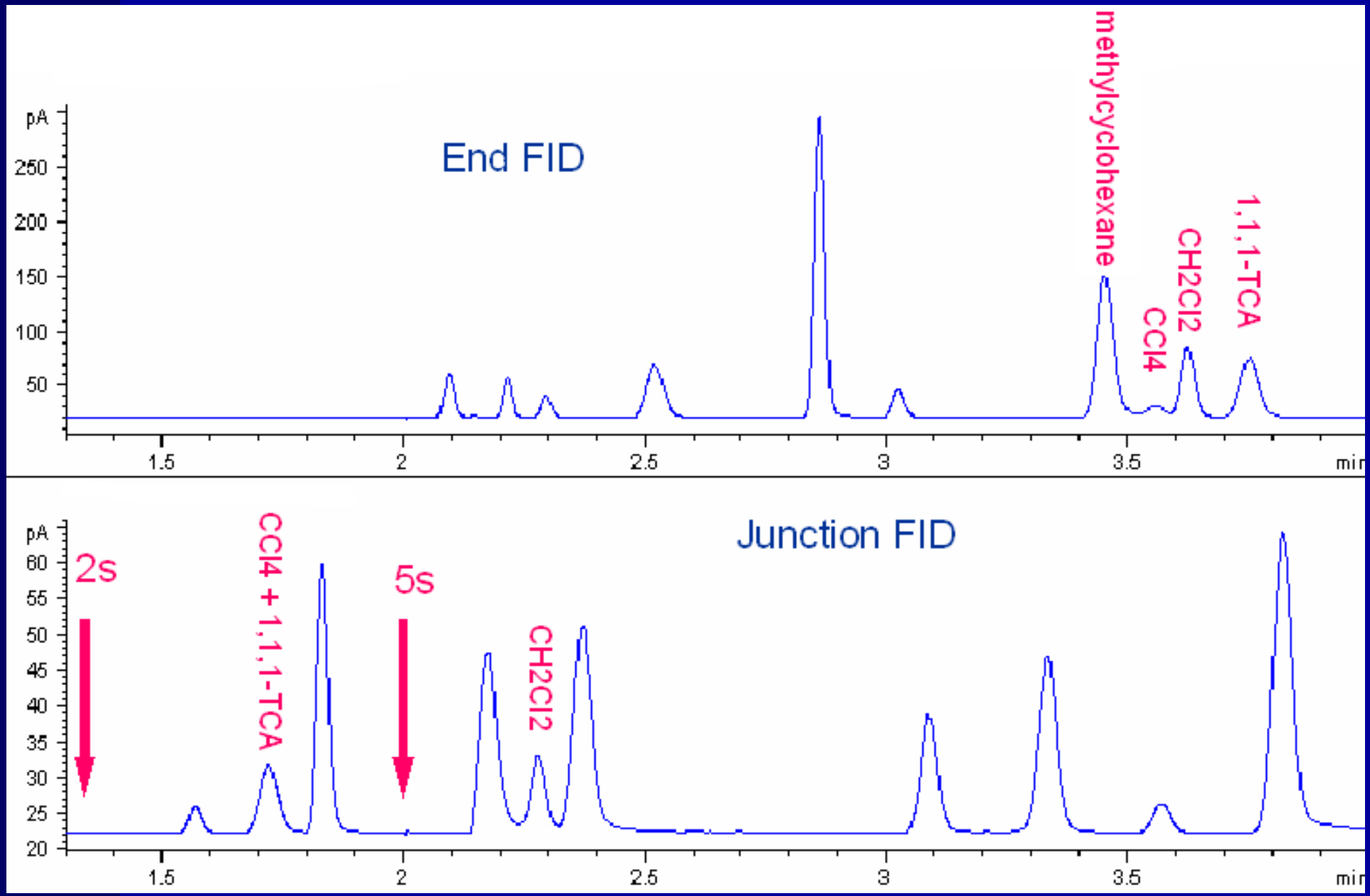
Residual Solvents: Pulse @ 44 sec.



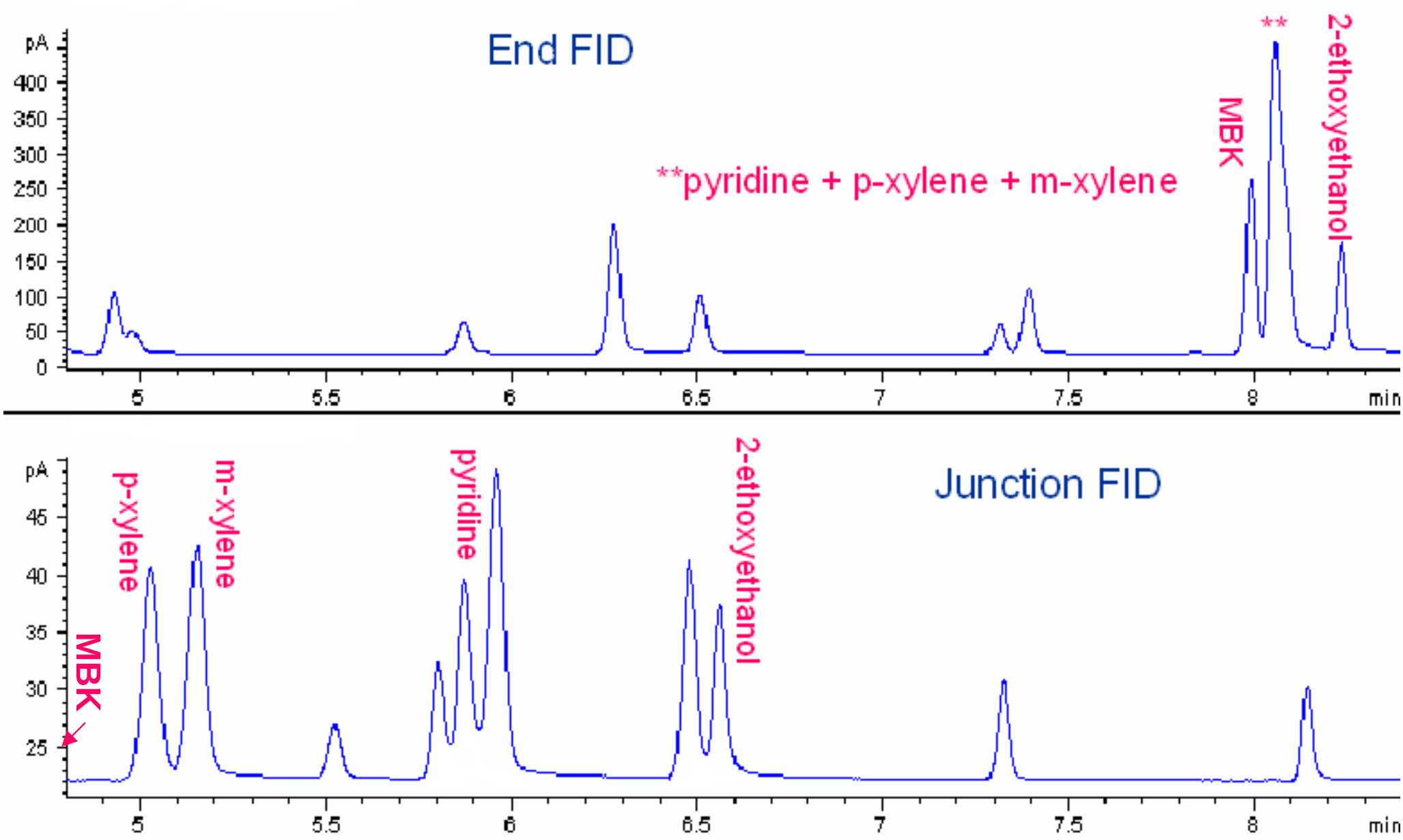
Residual Solvents: No Pulses



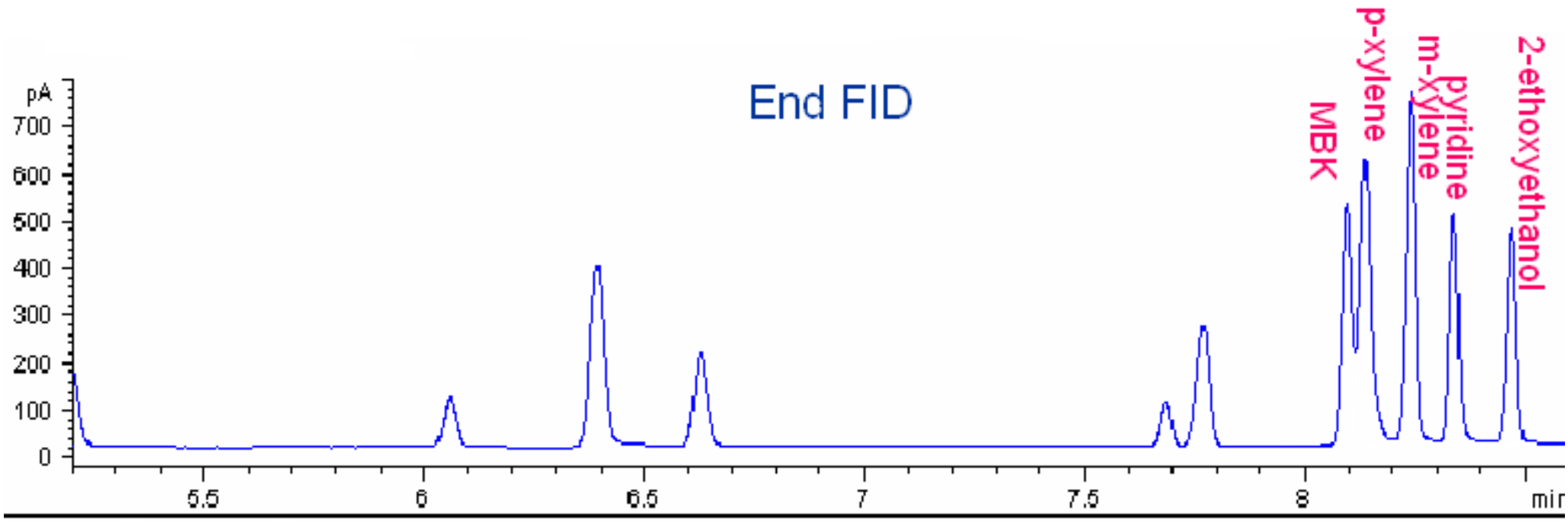
Residual Solvents: Pulses @ 72 & 120 sec.

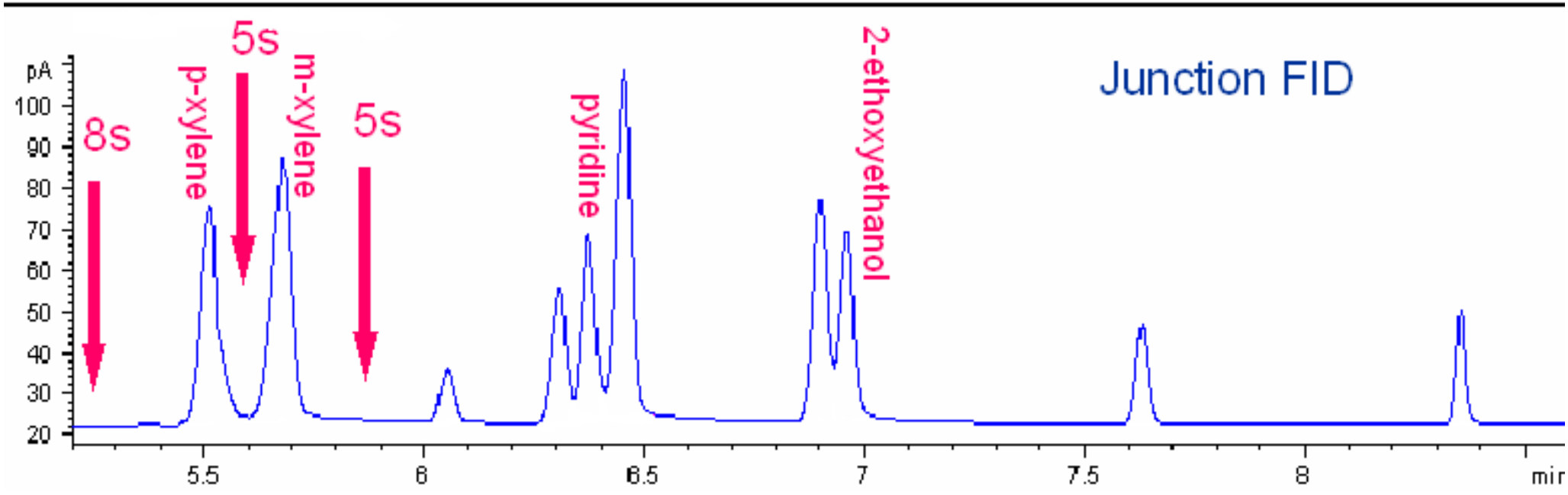


Residual Solvents: No Pulses



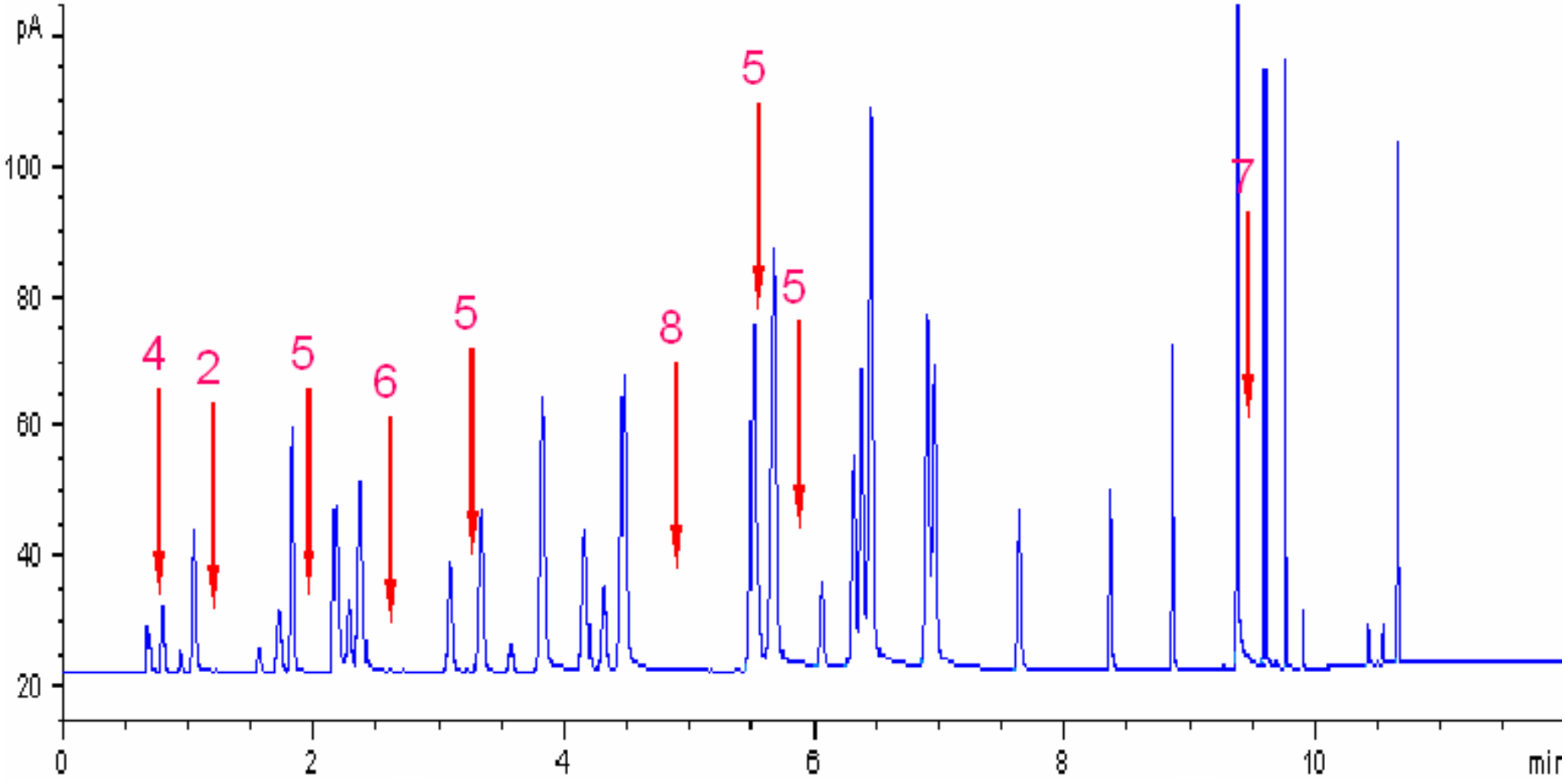
Residual Solvents: Pulses @ 290, 330, & 346 sec.





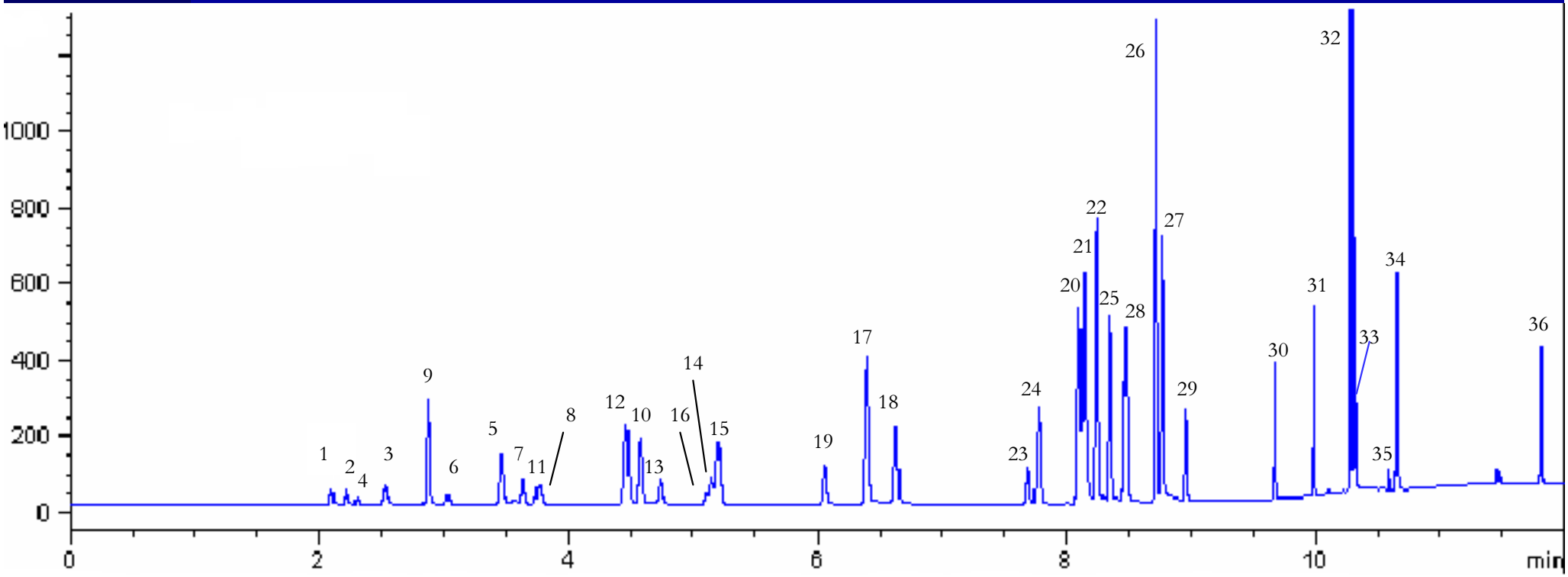
Class I & II OVIs: Total of 9 Pulses

At the Junction



Class I & II OVIs: Total of 9 Pulses

At the End Detector – all 36 resolved



Summary of Stop-Flow GC

- Ability to “Tune” the Selectivity
- Flexibility
  - Standard dimension columns
  - Can vary the pulse sequences
- Significant Improvements in Analysis Times Possible
  - Fast oven programs, high flow rates