SAND2009-0450P

Comprehensive Multidimensional Gas Chromatography and Modulator Development for Portable Instrumentation

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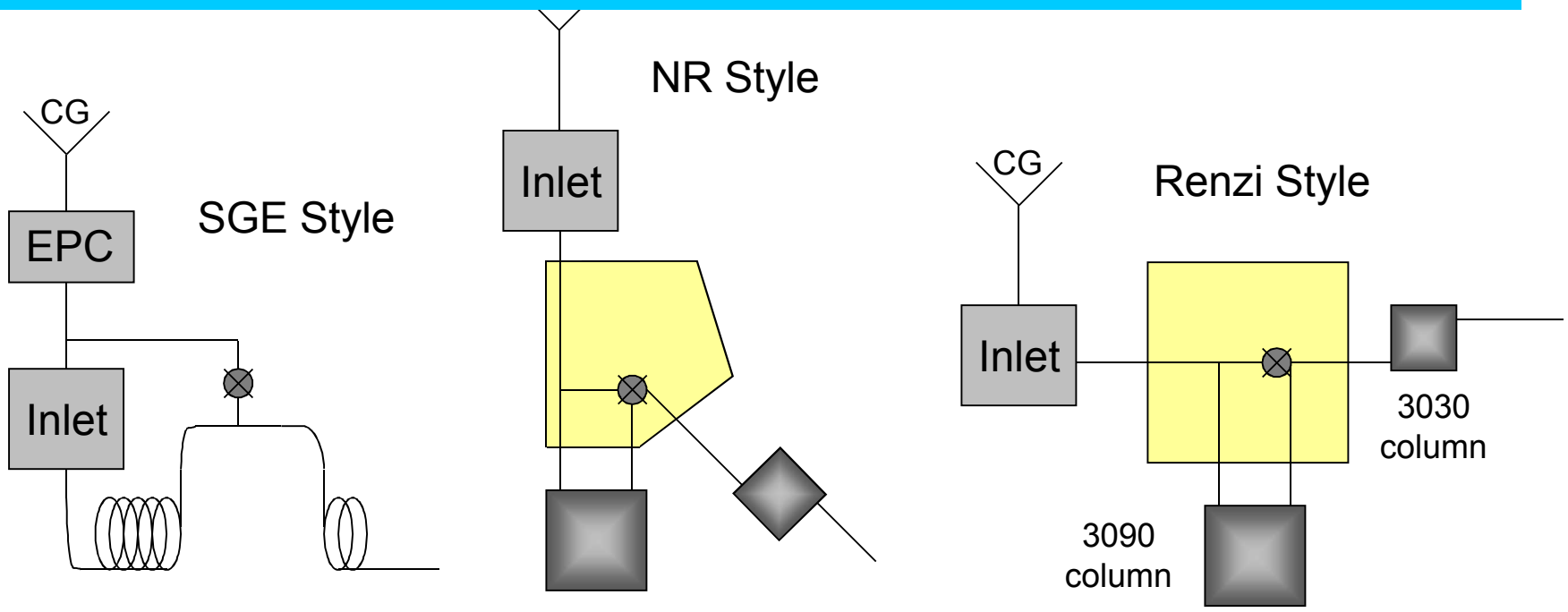
High-speed Valve Modulator

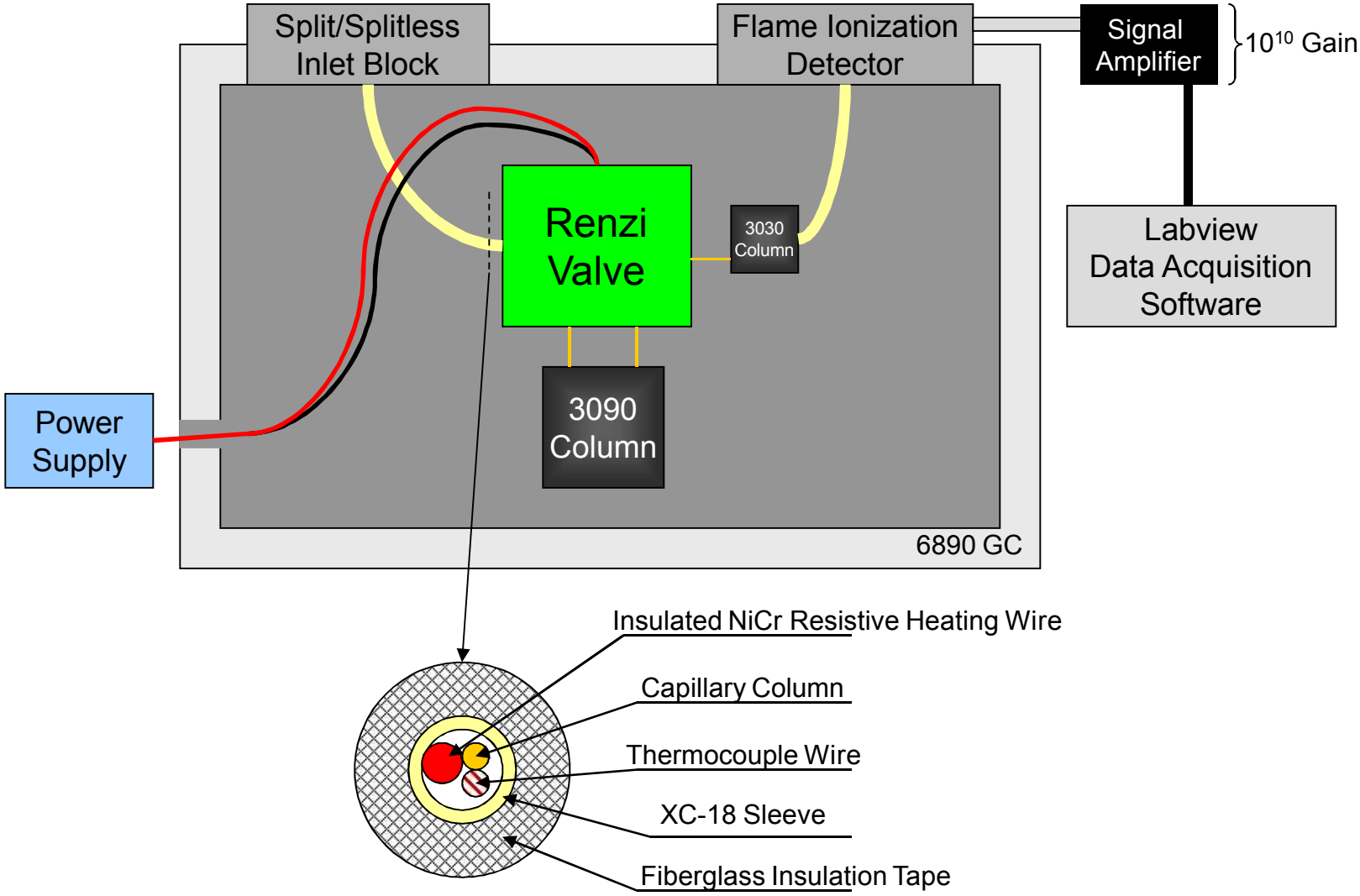
- For high-speed and portable applications, valve modulation is more feasible than thermal modulation
- Focusing capability lost – modulation capability becomes analyte independent
- Less resource intensive – only electric power needed
- Aiming for 120 peak capacity in 4 seconds of analysis

High-speed Valve Modulator



• Valve is outside sample path • Sample must travel through 1st column • Modulation capability = 100 ms period	• Valve is part of sample path • Sample can avoid 1st column • Modulation capability = 300 ms period	• Valve is usually outside sample path • Sample can avoid 1st column • Modulation capability = 240 ms period

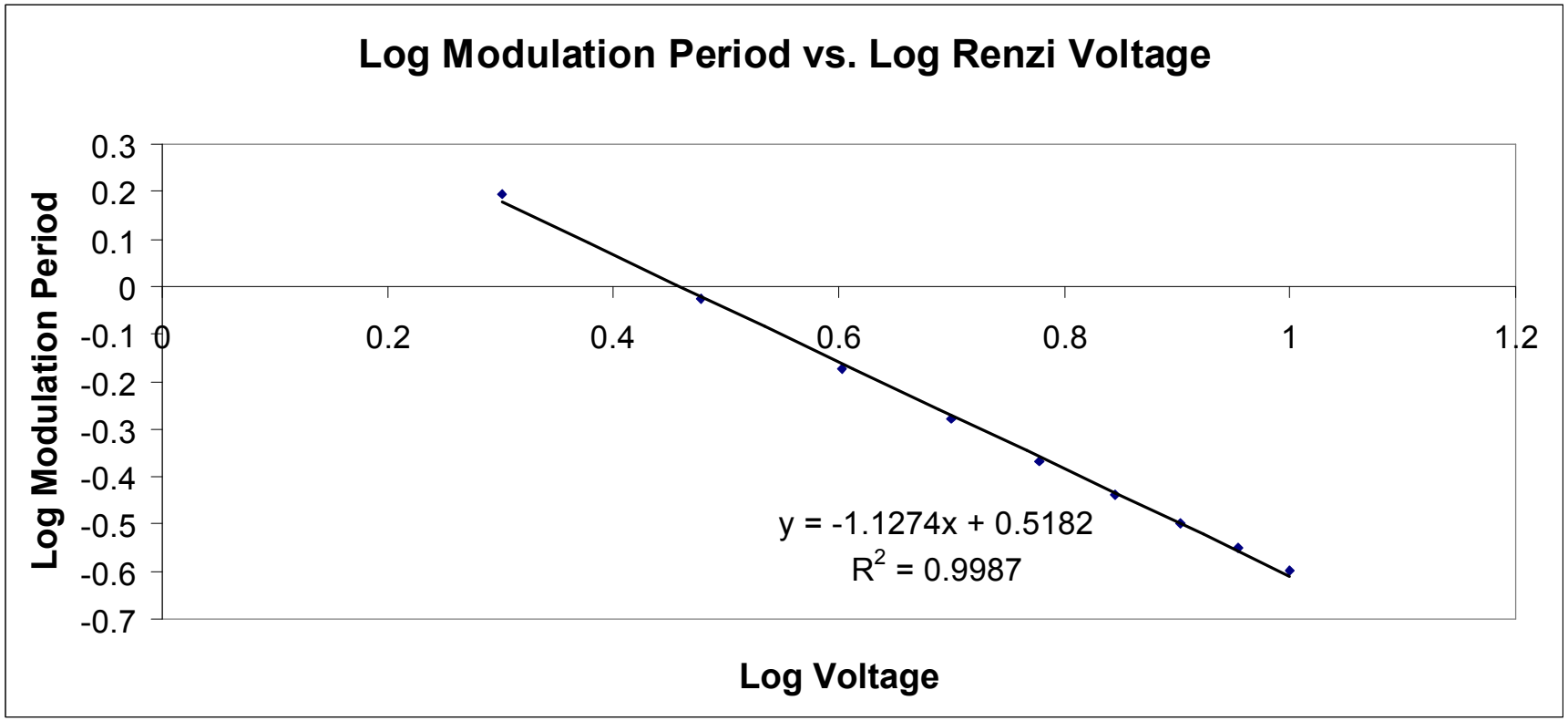
High-speed Valve Modulator



High-speed Valve Modulators

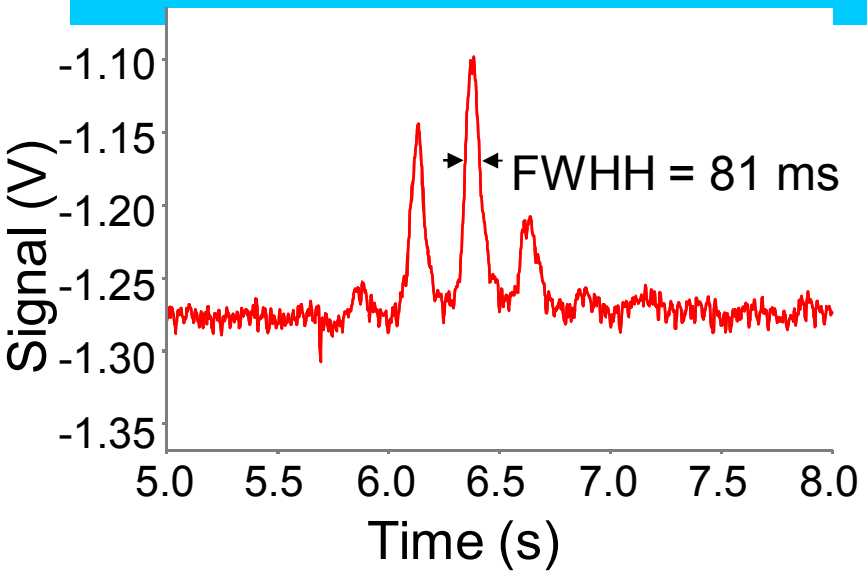
- Oven Setting = 25º C
- Microcolumns Temperature Ramp = 25º to 100º C in 10 s
- Inlet Pressures vary from 10 to 100 psig
- Applied Voltages from 0.5 to 10.0 V
- Gas injection sizes = 1 µL
- Liquid injection sizes = 0.2 µL
- Test Samples
  - Renzi Valve Modulation Period Test: Air
  - Methane Modulation Test: Methane
  - Peak Area Conservation Test: *n*-decane in CS_2
  - 18-component Separation: See chart

High-speed Valve Modulators

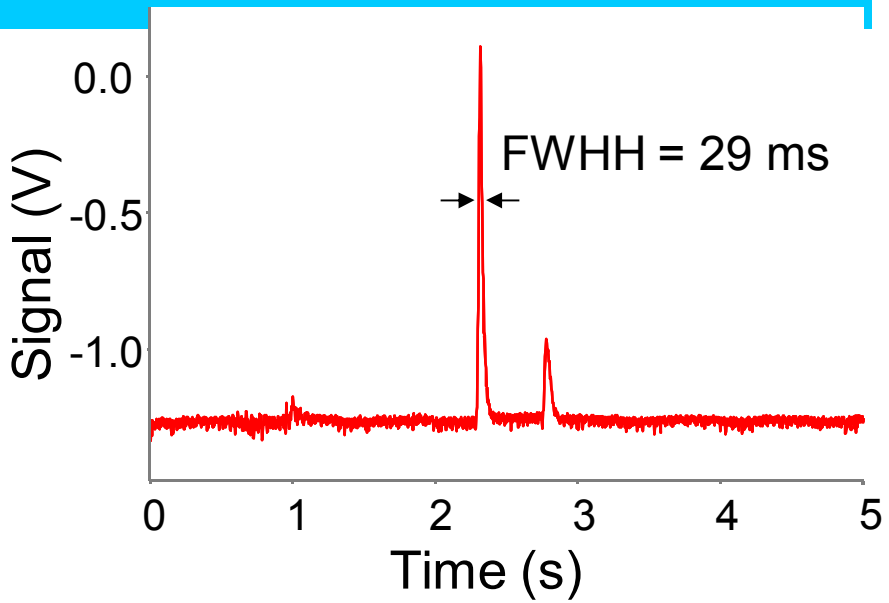


- Increasing applied voltage increases valve speed and summarily reduces the modulation period

High-speed Valve Modulators

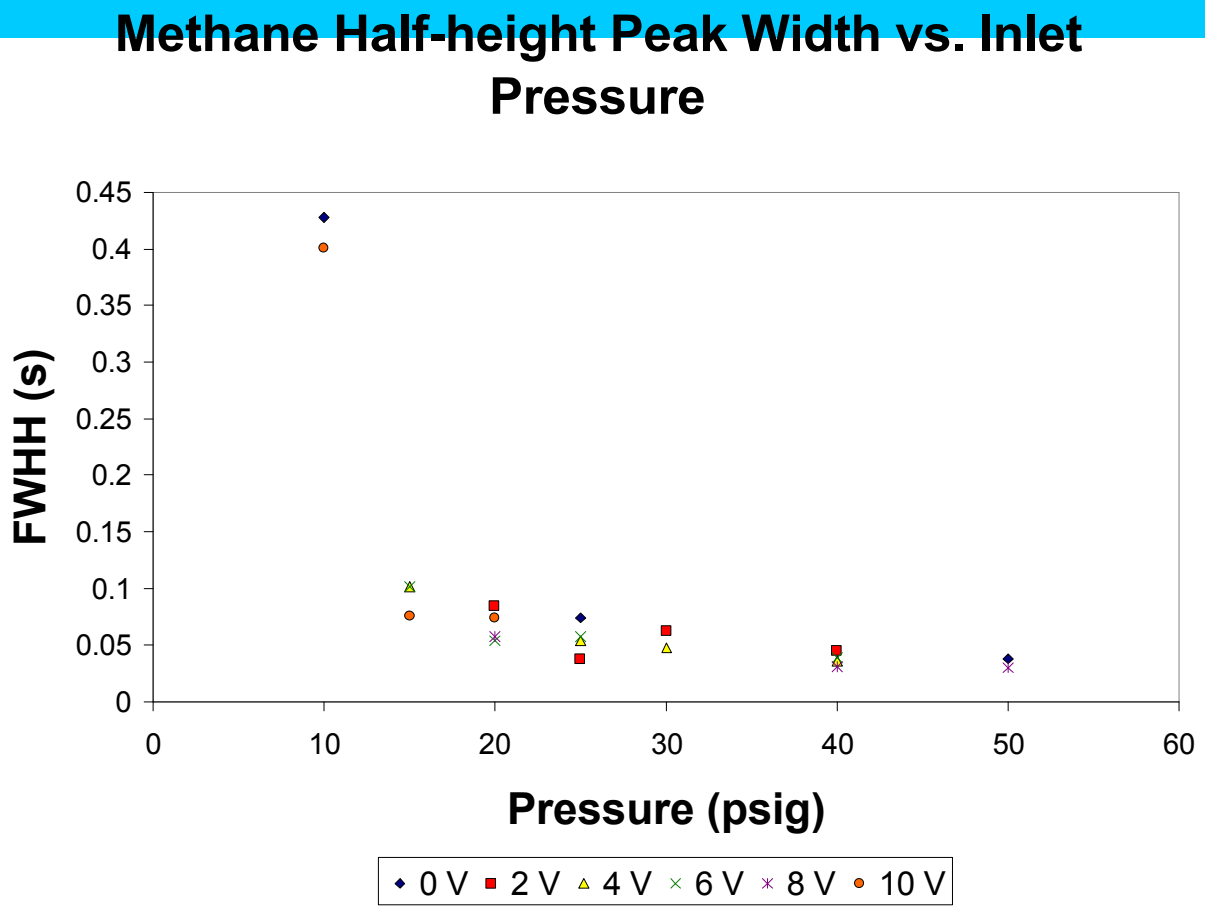


- 15 psig inlet pressure and 10.0 V applied voltage
- Good methane modulation peak profile



- 40 psig inlet pressure and 4.0 V applied voltage
- Fewer peak slices with reduced applied voltage
- Narrower peak width resulting from higher inlet pressure

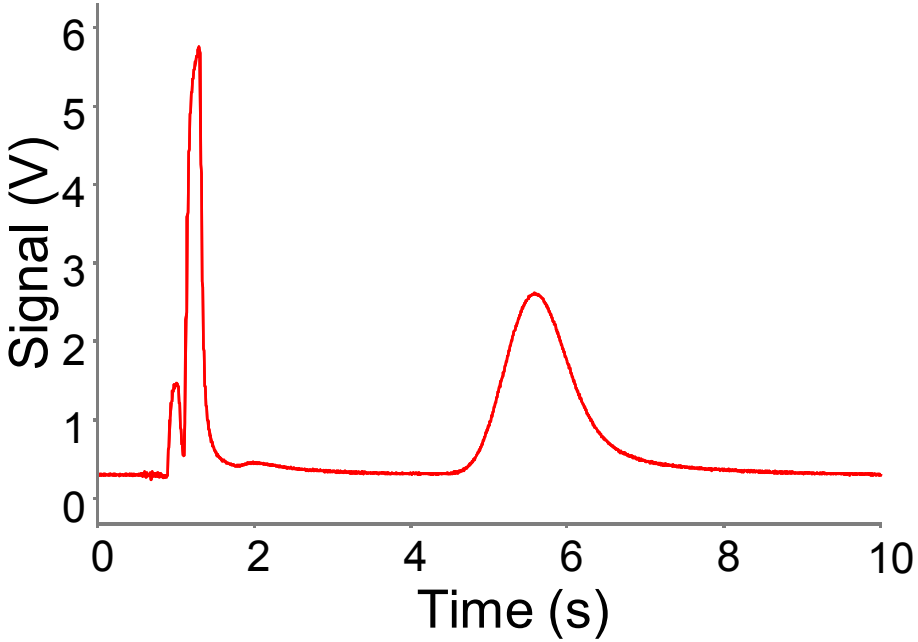
High-speed Valve Modulators

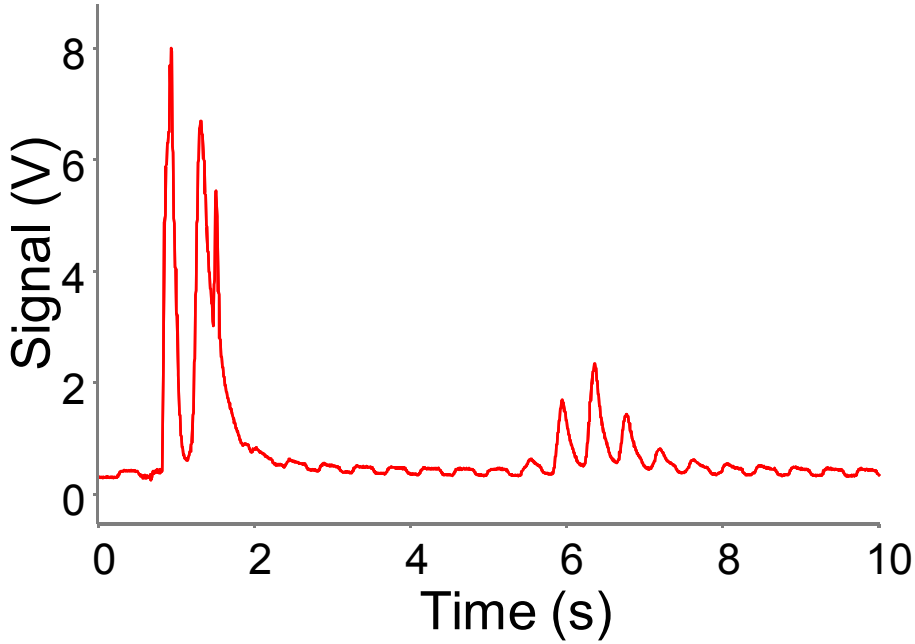


- Peak width appears to depend on inlet pressure strongly and is independent of applied voltage

High-speed Valve Modulators

Peak Area Conservation





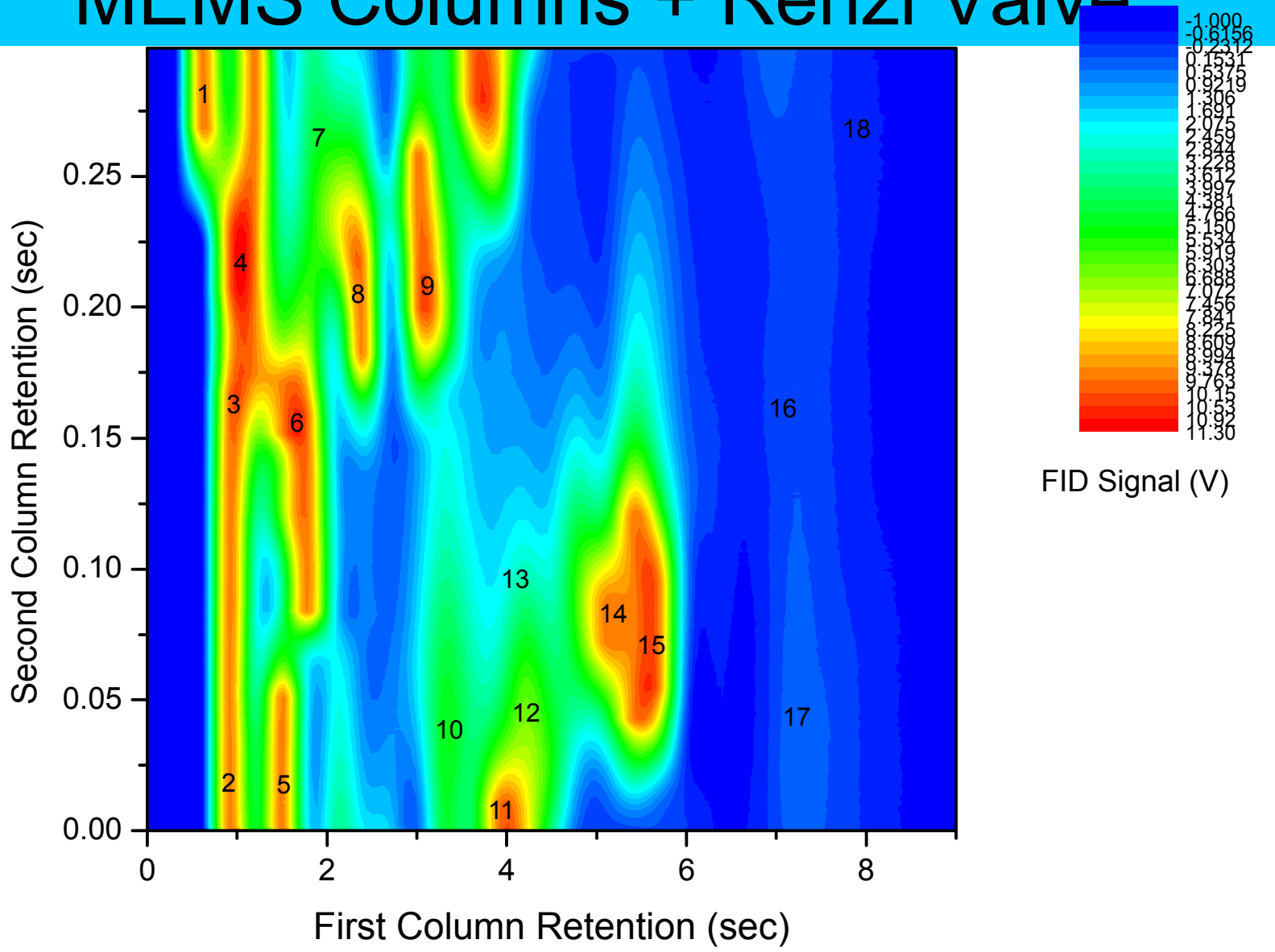
- 100 psig inlet pressure and no voltage applied
- Dodecane peak shape is as expected
- Slight amount of dodecane passed through valve and eluted early

- 100 psig inlet pressure and 6.0 voltage applied
- Dodecane modulated peak shape exhibits classic profile

High-Speed Valve Modulators

Sample #	Chemical Name	Boiling Point (º C)
1	carbon disulfide	45.9
2	toluene	111
3	*n*-octane	126
4	iso-octane	99
5	1,3-dichloropropane	121
6	dimethyl methylphosphonate	187
7	1-octanol	195
8	1,4-dichlorobutane	154
9	*n*-decane	174
10	diisopropyl methylphosphonate	219
11	di-*n*-butyl sulfide	189
12	2-chloroethyl ethyl sulfide	156
13	1,6-dichlorohexane	204
14	*n*-dodecane	216
15	O,S-diethyl methylphosphonothioate	78*
16	diisobutyl methylphosphonate	254
17	2-chloroethyl phenyl sulfide	245
18	O,S-diisobutyl methylphosphonothioate	139*
		*= 12 mm Hg

18 Compounds GCxGC Separation on MEMS Columns + Renzi Valve



Conclusions

- Renzi valve can successfully be used for fast GCxGC analysis with complex mixtures
- Further improvements can be made
  - Reduce dead volume to improve peak capacity through narrower second-column band-widths.
  - Phase control necessary for reproducibility, wrap-around detection, and prevention of analyte passing through valve
- Compounds of very low boiling point such as methane susceptible to modulation

Conclusions

- GCxGC is a powerful technique that is receiving more and more attention for improving the separation capabilities of a GC system
- Advances in the field are moving GC and GCxGC systems towards portability with the goal of getting immediate separations on site
- Modulator development is key for achieving portability with these instruments