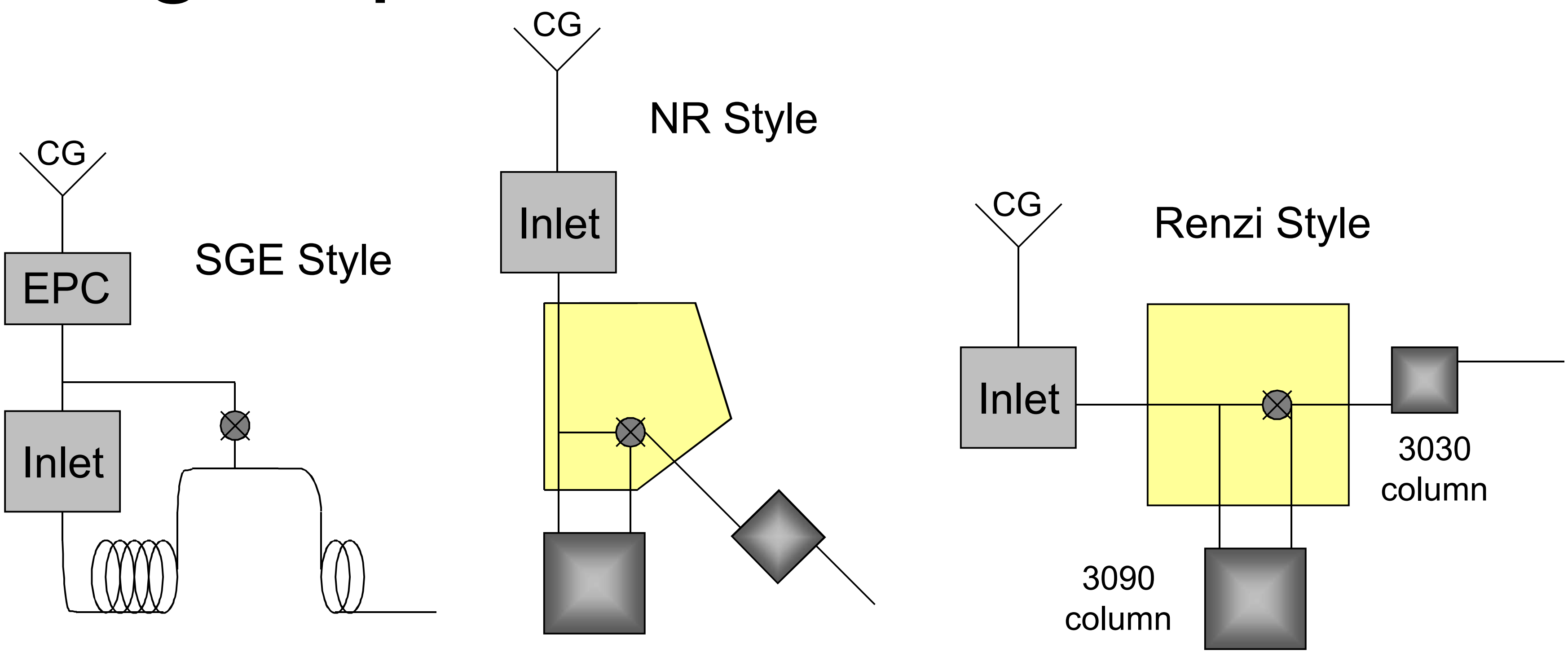
SAND2008-6502P

High-Speed Valve Modulation Studies

High-Speed Valve Modulators

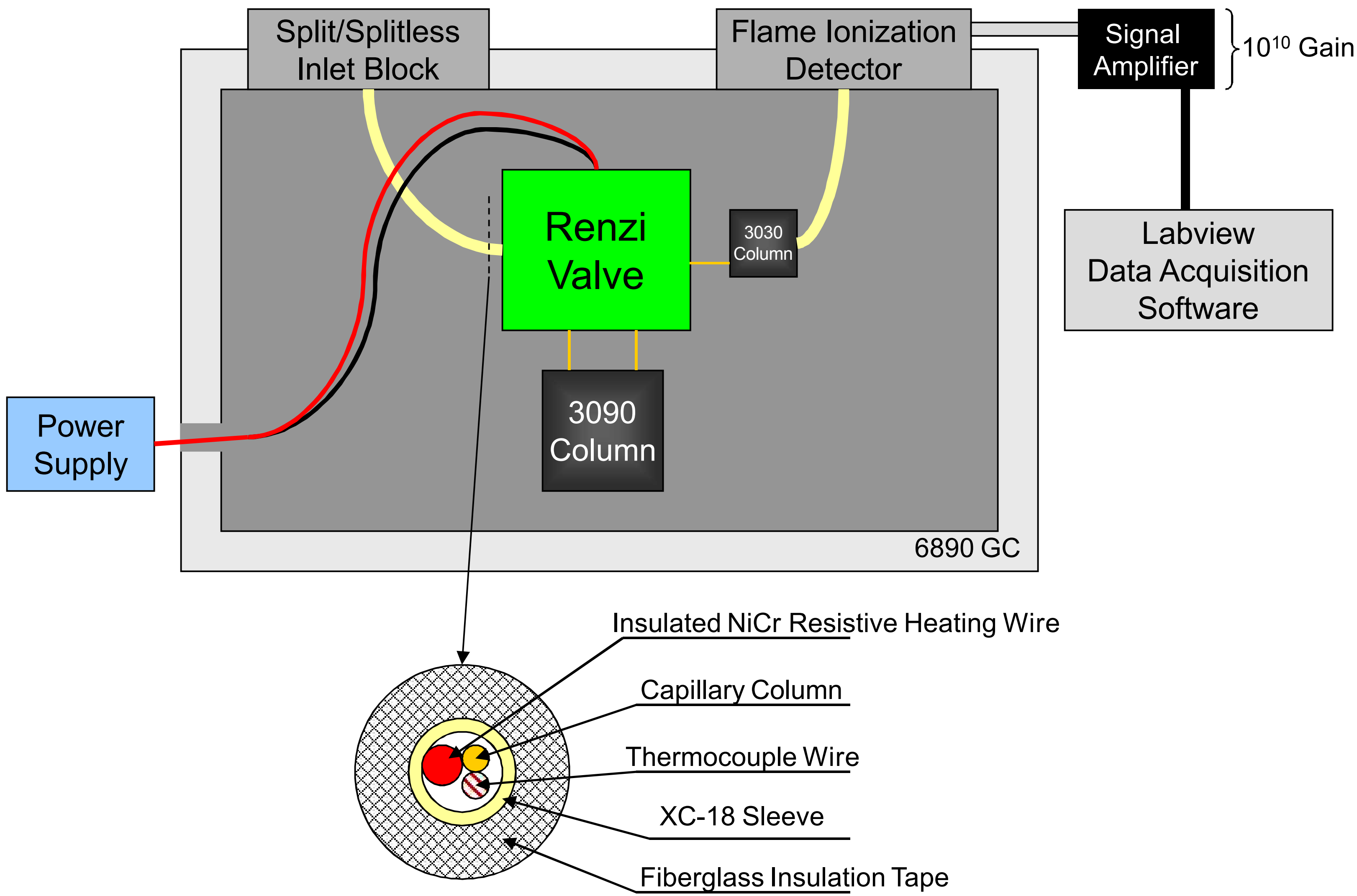
- For high-speed and portable applications, valve modulation is much more feasible than thermal modulation
- Focusing capability lost – modulation capability becomes analyte independent
- Less resource intensive – only electric power needed
- Aiming for 120 peak capacity in 4 seconds of analysis

High-Speed Valve Flow Paths



• 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

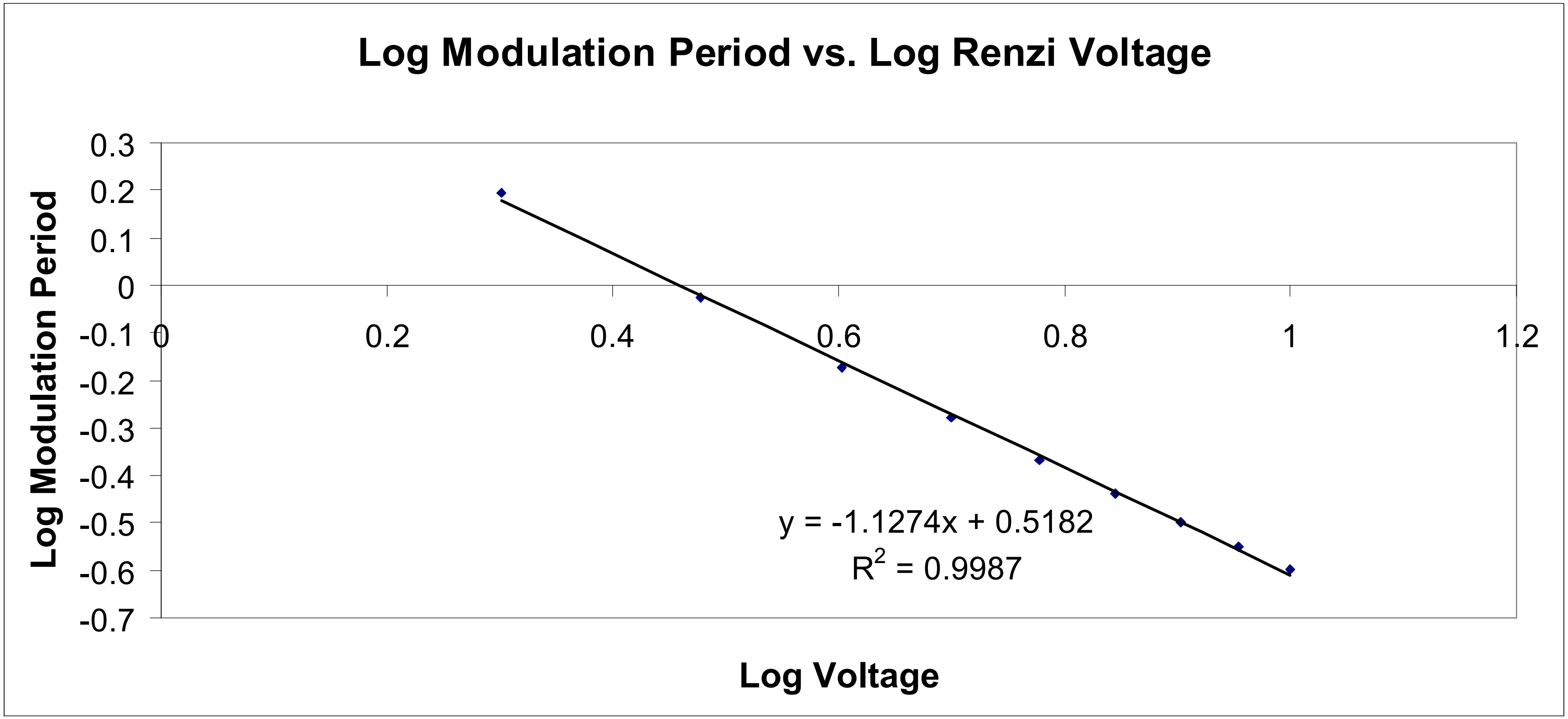
System Diagram



System Parameters

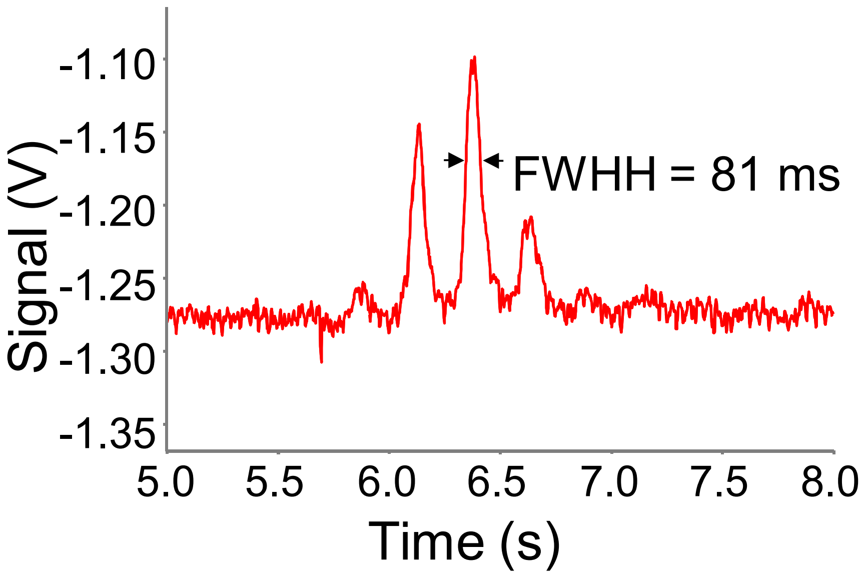
- Oven Setting = 25º C
- Microcolumns Temperature Ramp = 25º to 100º C in 10 s
- Inlet Pressures vary from 10 to 100 psig
- Applied Voltages from 0.5 to 10.0 V
- Gas injection sizes = 1 µL
- Liquid injection sizes = 0.2 µL
- Test Samples
  - Renzi Valve Modulation Period Test: Air
  - Methane Modulation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

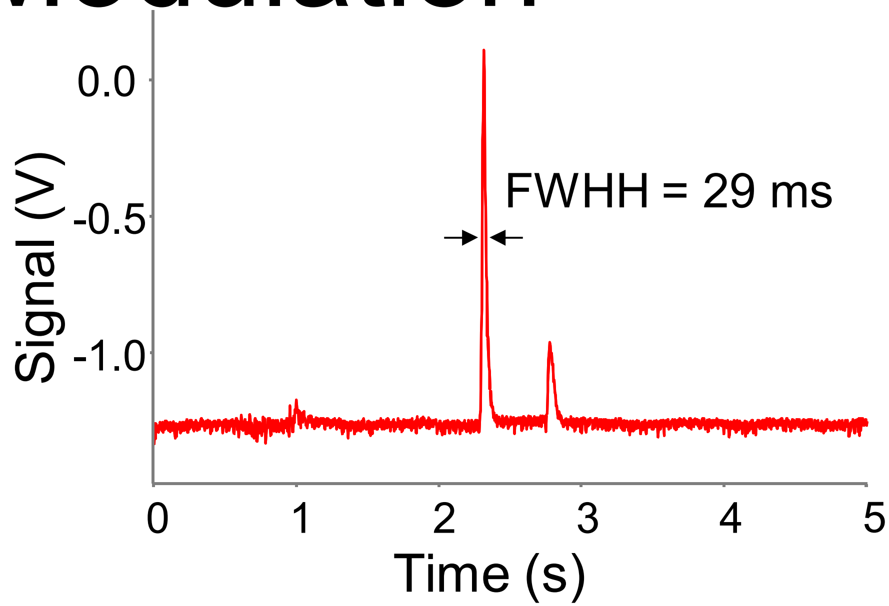
Modulation Period as a Function of Applied Valve Voltage Study



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

Methane Modulation

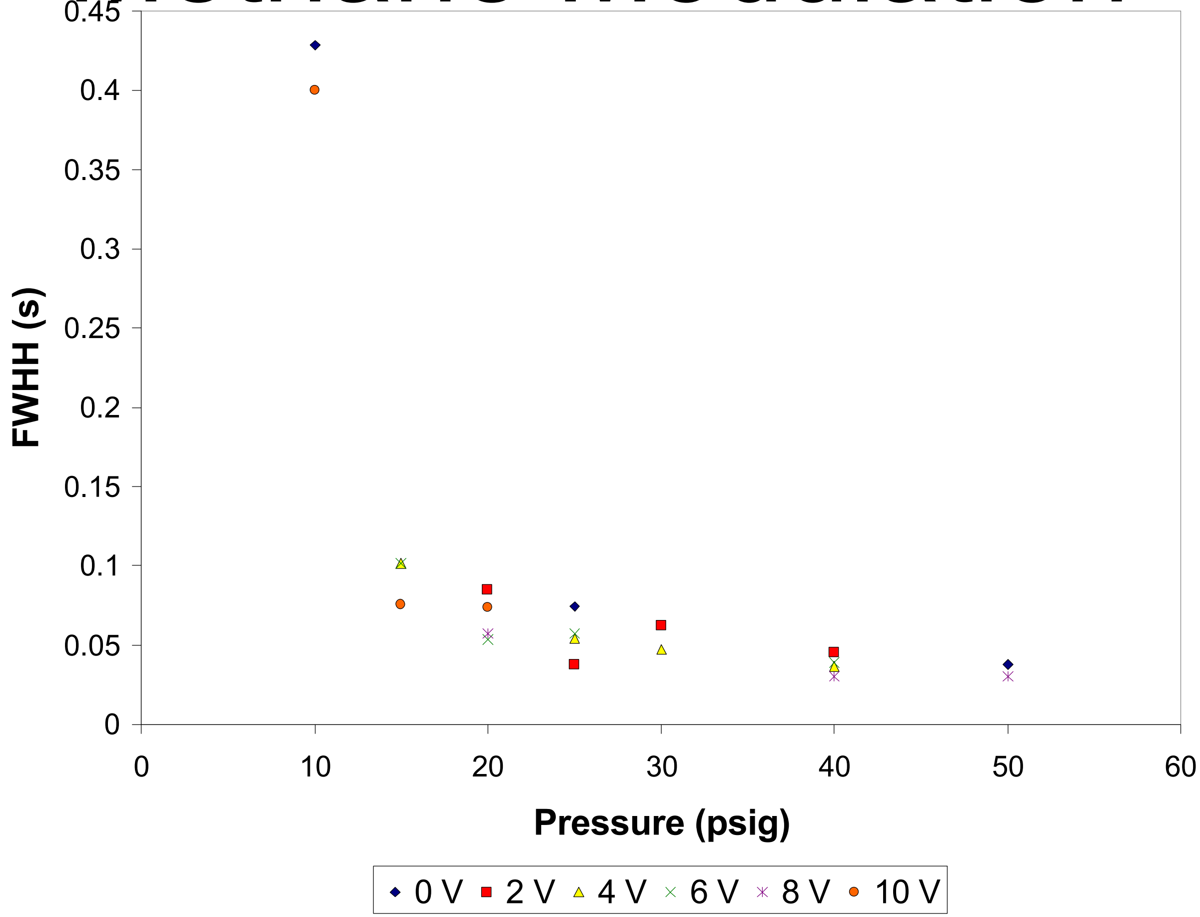




- 15 psig inlet pressure and 10.0 V applied voltage
- Good methane modulation peak profile

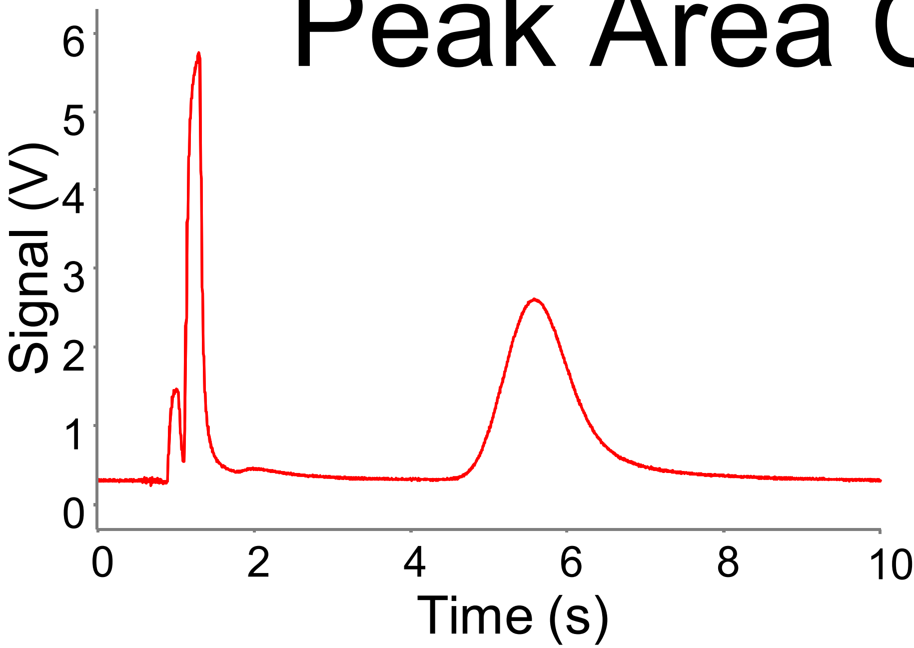
- 40 psig inlet pressure and 4.0 V applied voltage
- Fewer peak slices with reduced applied voltage
- Narrower peak width resulting from higher inlet pressure

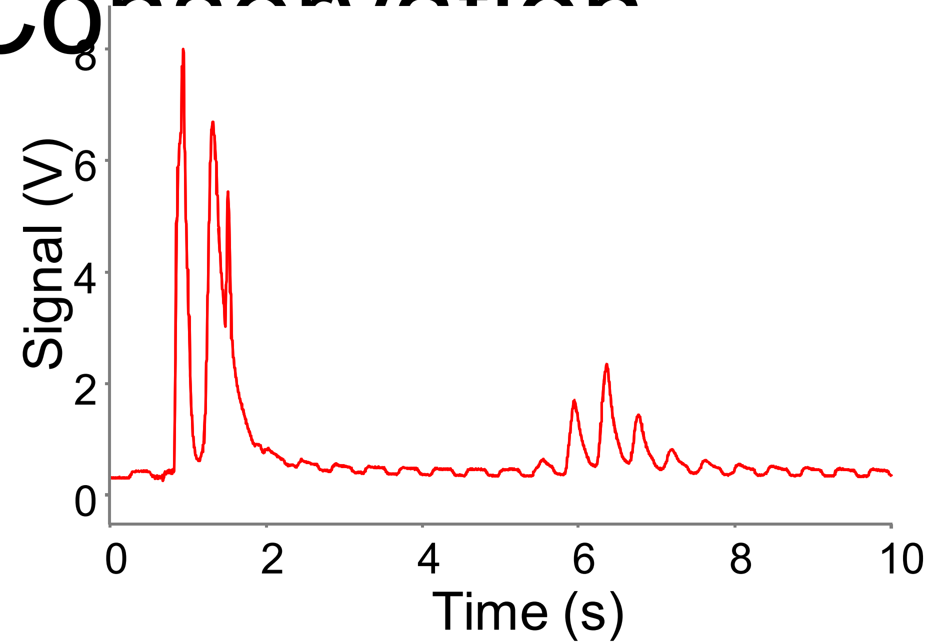
Methane Modulation



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

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
- Significant portion of dodecane passed through valve and eluted early (asymmetric peak around 1.2 s)
- That peak area added to modulated peak slice area

ANOVA Test

- Data1_A = Valve Off
- Data1_B = 6.0 V
- Data1_C= 8.0 V
- Data1_D= 10.0 V
- One-Way ANOVA

Summary Statistics

Dataset	N	Mean	SD	SE
Data1_A	3	2.2871	0.18463	0.10659
Data1_B	3	2.47701	0.20059	0.11581
Data1_C	3	2.22148	0.10496	0.0606
Data1_D	3	2.09279	0.24454	0.14118

Null Hypothesis: The means of all selected datasets are equal

Alternative Hypothesis: The means of one or more selected datasets are different

ANOVA

Source	DoF	Sum of Squares	Mean Square	F Value	P Value
Model	3	0.230711597	0.0769038658	2.11944	0.17601
Error	8	0.290279458	0.0362849322		

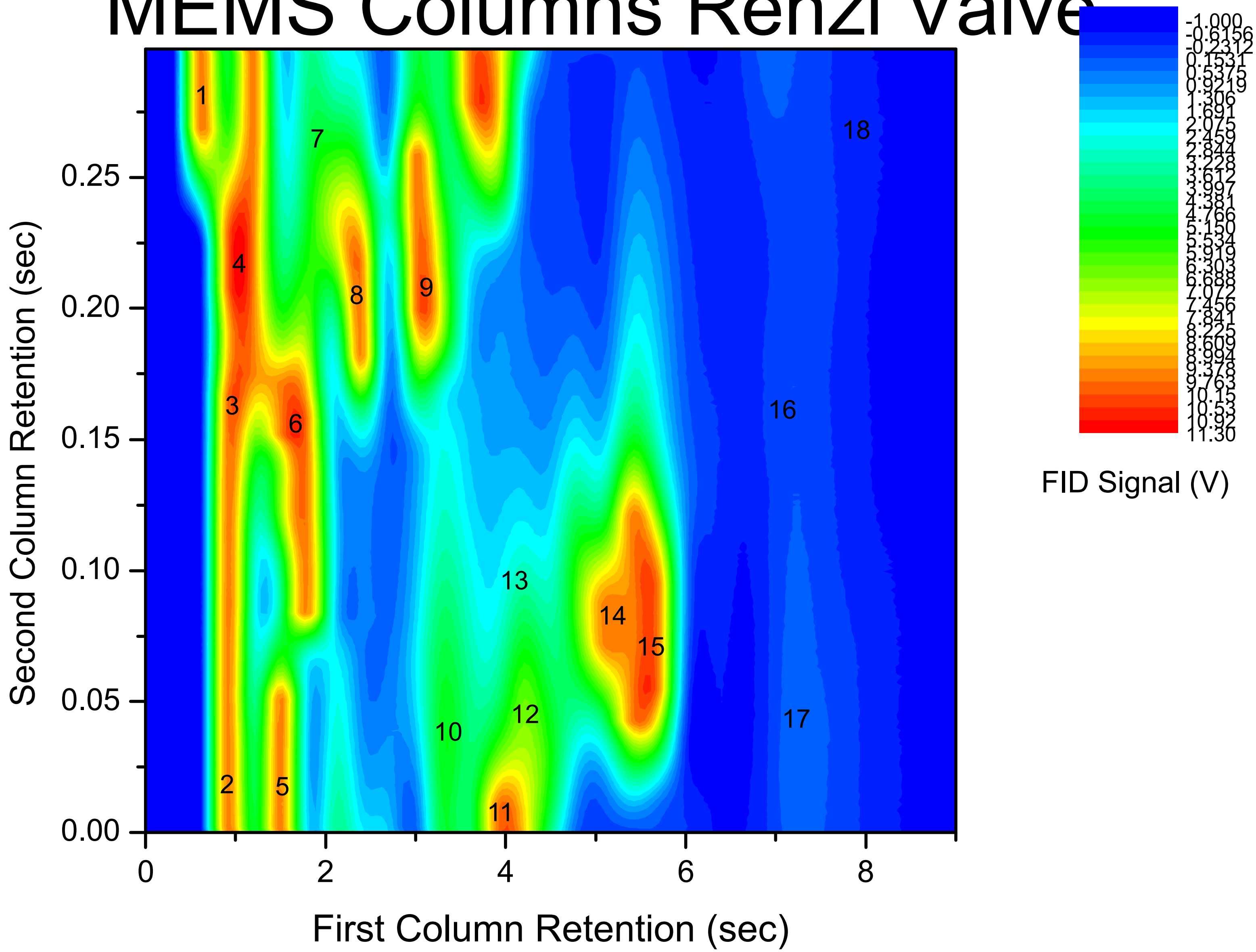
At the 0.0001 level,

the population means are not significantly different.

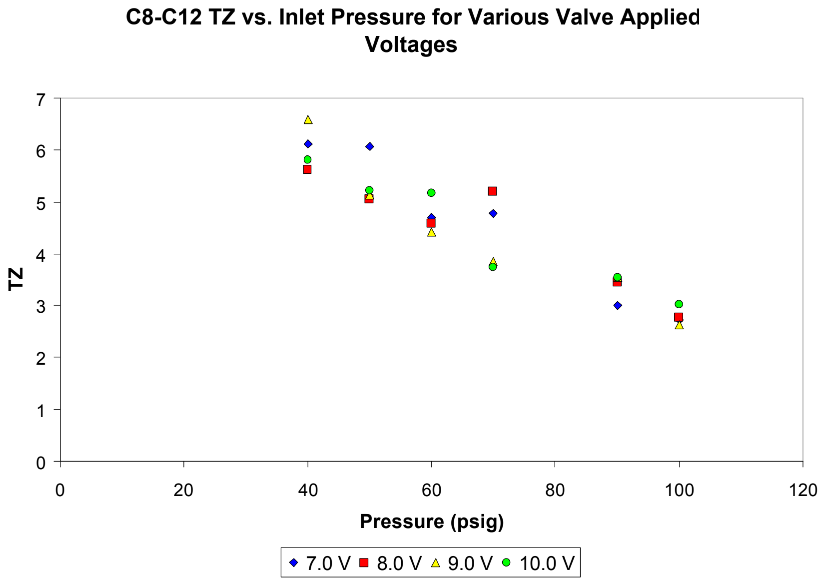
18 Compound GCxGC Separation Chemicals

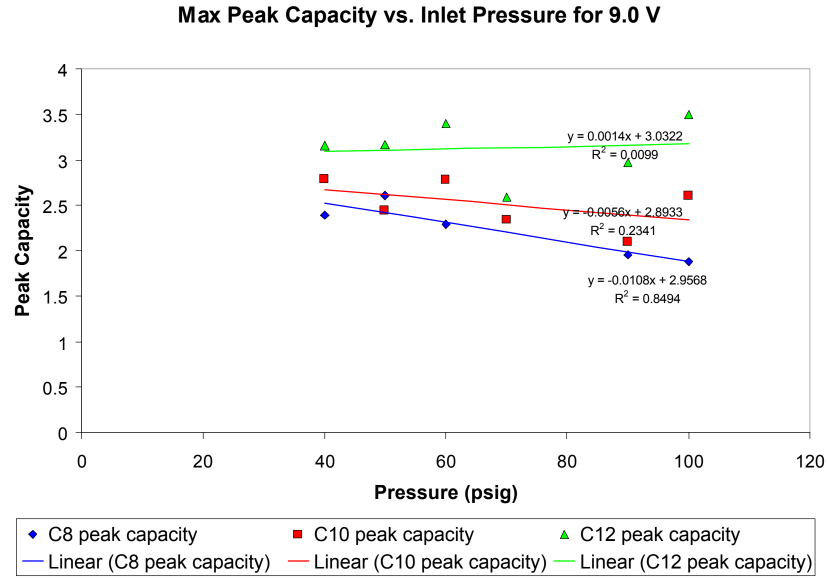
Sample #	Chemical Name	Boiling Point (º C)
1	carbon disulfide	45.9
2	toluene	111
3	*n*-octane	126
4	iso-octane	99
5	1,3-dichloropropane	121
6	dimethyl methylphosphonate	187
7	1-octanol	195
8	1,4-dichlorobutane	154
9	*n*-decane	174
10	diisopropyl methylphosphonate	219
11	di-*n*-butyl sulfide	189
12	2-chloroethyl 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 MEMS Columns Renzi Valve



Peak Capacity Plots





- 1st dimension peak capacity calculated using Trenzall (TZ) numbers
- Strong correlation with inlet pressure, little correlation with modulation period

- 2nd dimension peak capacity calculated using peak capacity equation
- Little correlation with inlet pressure though some correlation to analyte

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