Integration and Optimization of Hardware and Software for a Differential Flow Modulated GCxGC

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Basic Configuration

The configuration

Split/splitless inlet, hydrogen carrier gas

PCM module

Valve driver and timing board (7890A)

Three way modulation valve

Capillary Flow Technology modulator device

Two columns: 30m x 0.25mm non-polar, 5m x 0.25mm polar (typical)
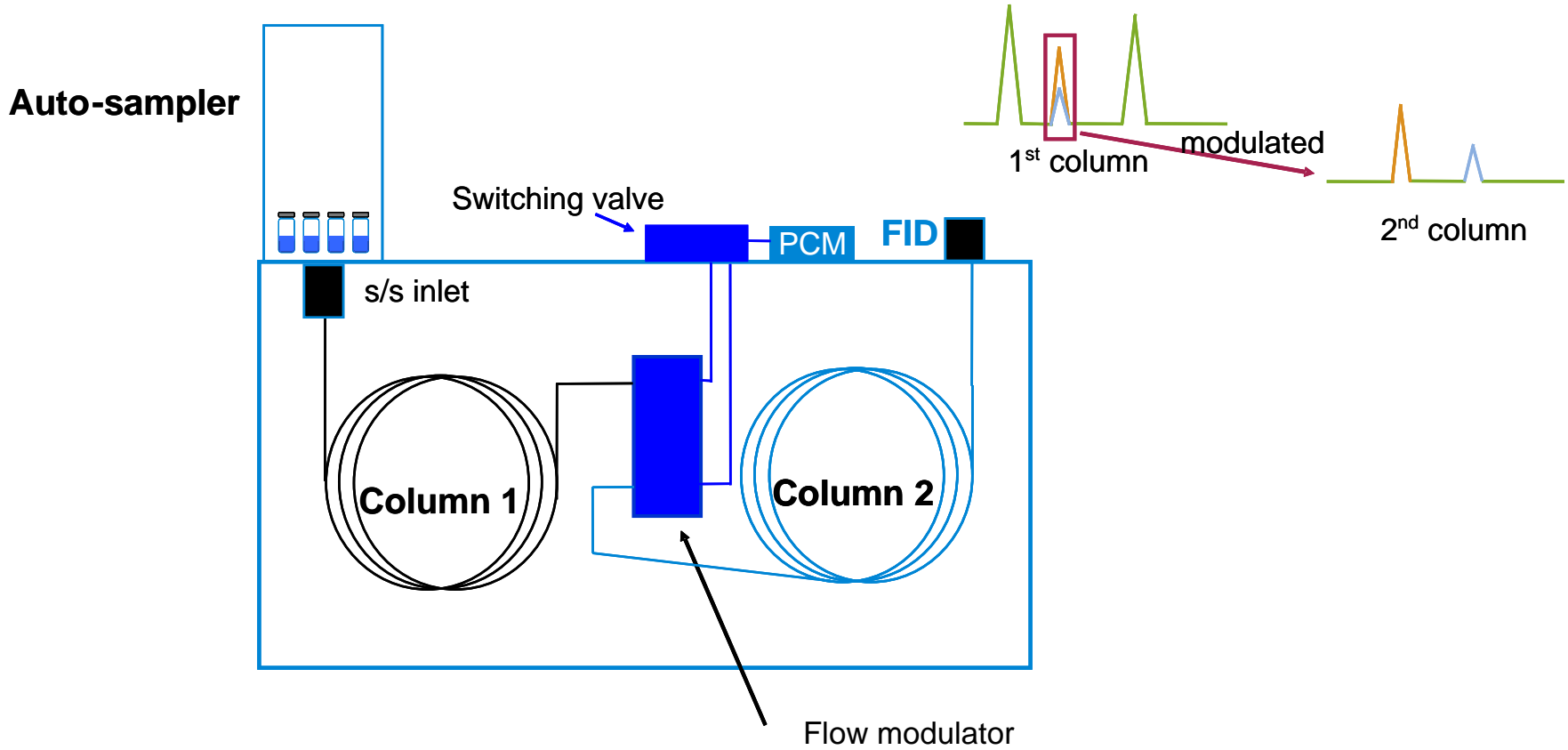
FID at 200 Hz

7683 Auto Injector

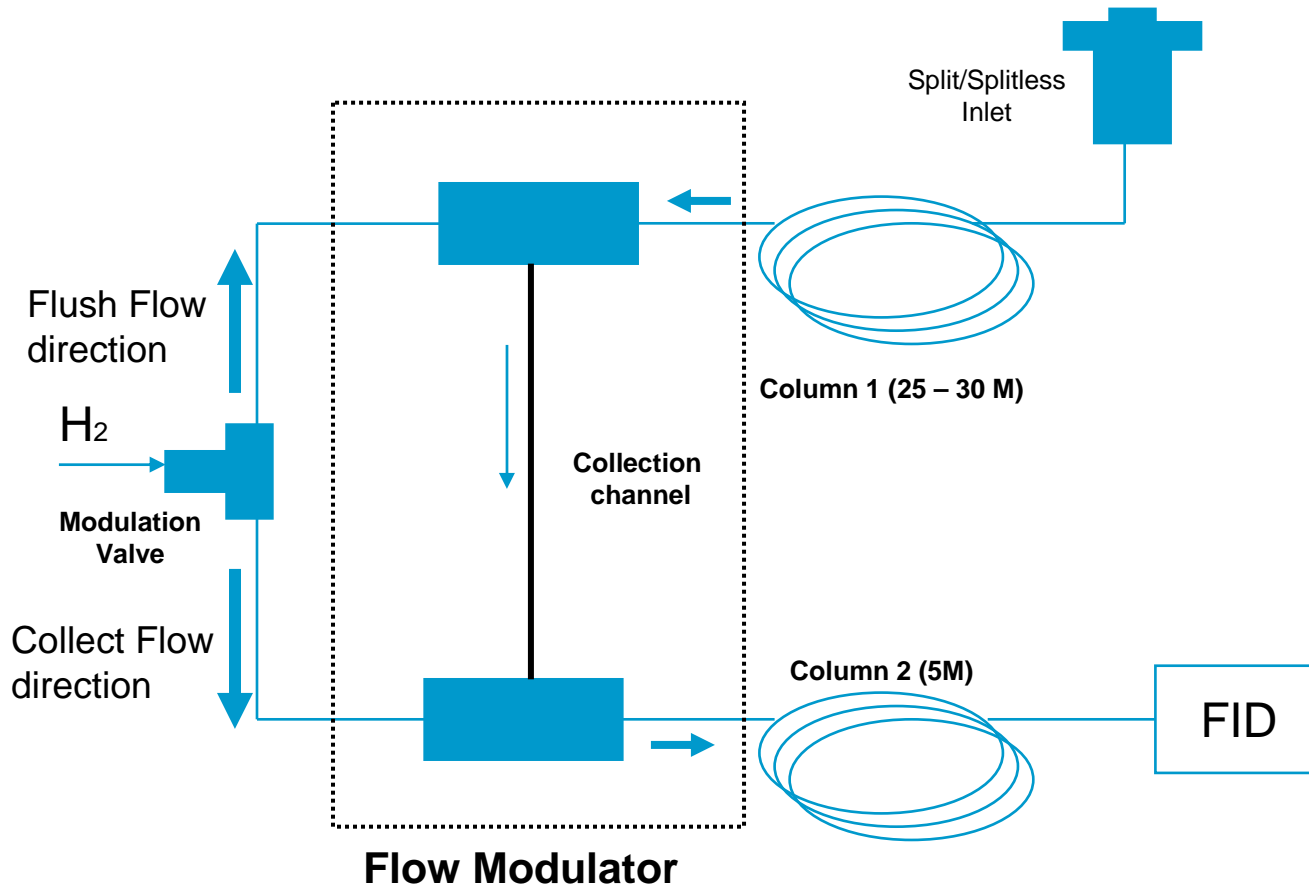## Data processing software

CG Image, LLC, Lincoln NE 68505
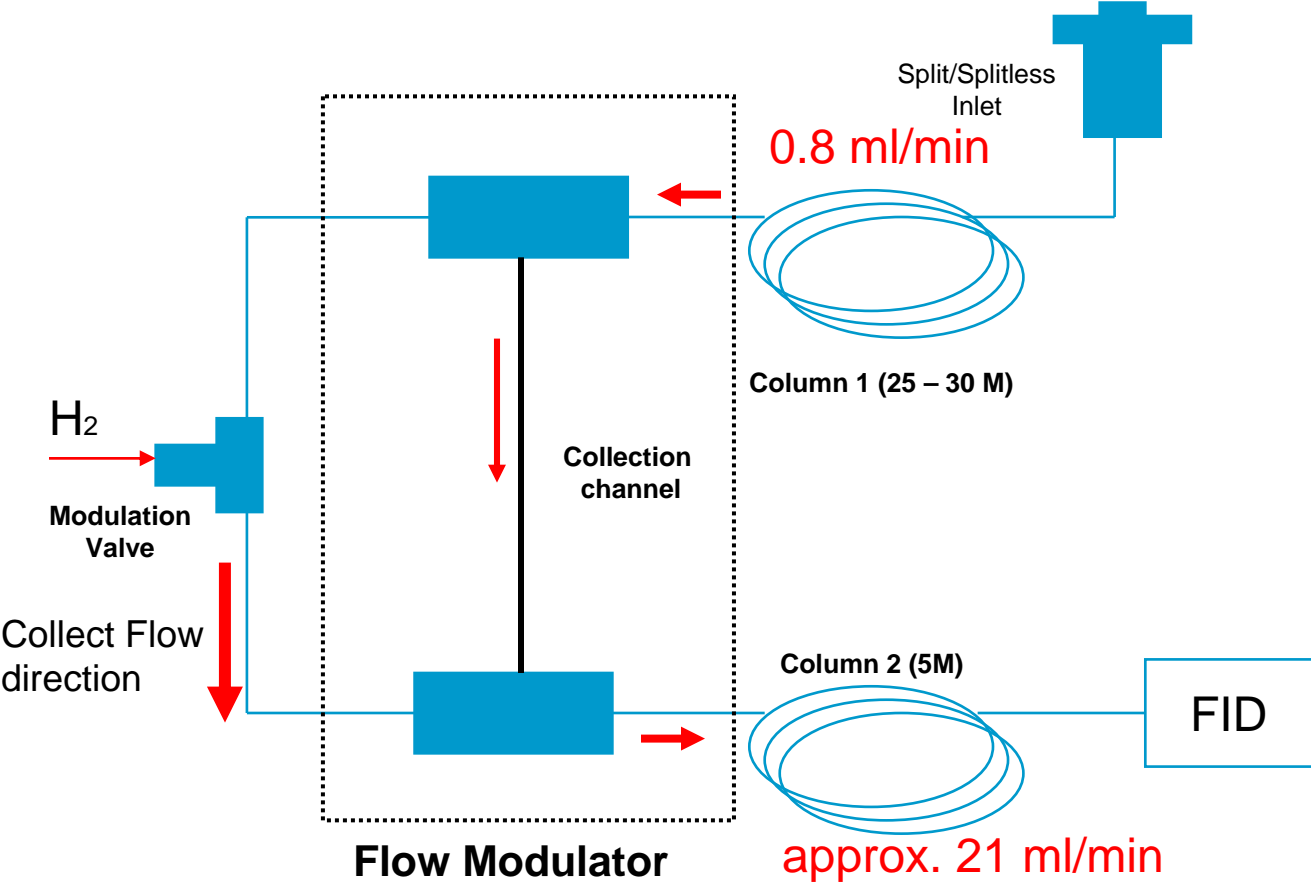
Zoex Corporation, Pasadena, TX 77505

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Basic System Layout

Auto-sampler

Switching valve

PCM

FID

s/s inlet

Column 1

Column 2

Flow modulator

1st column

modulated

2nd column

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Agilent's flow modulator : Differential Flow
Concept by John V. Seeley, Oakland University

Split/Splitless Inlet

Column 1 (25 – 30 M)

Flush Flow direction

H$_2$

Modulation Valve

Collection channel

Collect Flow direction

Column 2 (5M)

FID

Flow Modulator

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Load or Collect Step

Flow Modulator

- Split/Splitless Inlet
- 0.8 ml/min
- Column 1 (25 – 30 M)
- H₂
- Modulation Valve
- Collection channel
- Collect Flow direction
- Column 2 (5M)
- FID
- approx. 21 ml/min

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Inject Step

Split/Splitless
Inlet

0.8 ml/min

Inject Flow
direction

H₂

Modulation
Valve

Column 1 (25 – 30 M)

Collection
channel

Column 2 (5M)
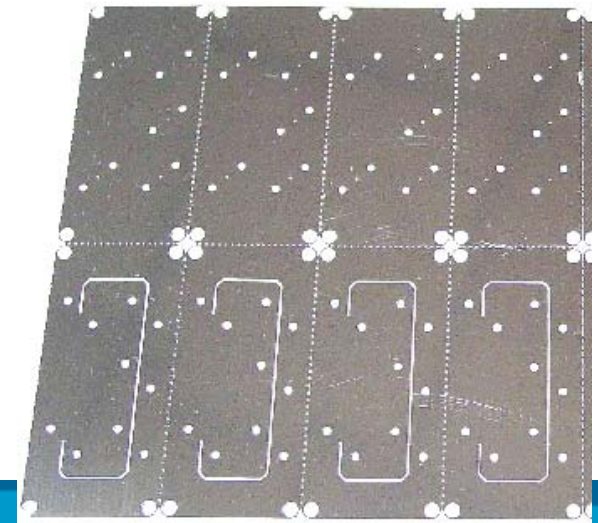
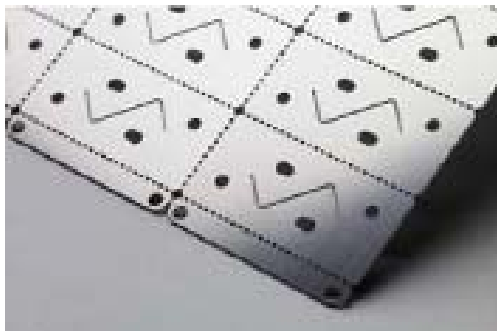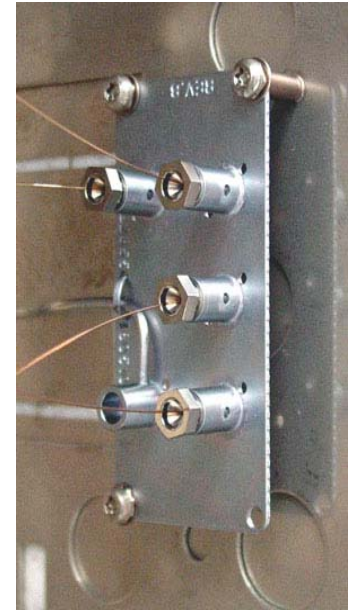FID

Approx. 21 ml/min

Flow Modulator

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Capillary Flow Technology- Design

… a proprietary Agilent Technology

- Photolithographic chemical milling for low dead volume

- Diffusion bond two halves to form a single flow plate

- Small, thin profile provides fast thermal response

- Projection welded connections for leak tight fittings

- Deactivation of all internal surfaces for inertness

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Flow Modulation Device

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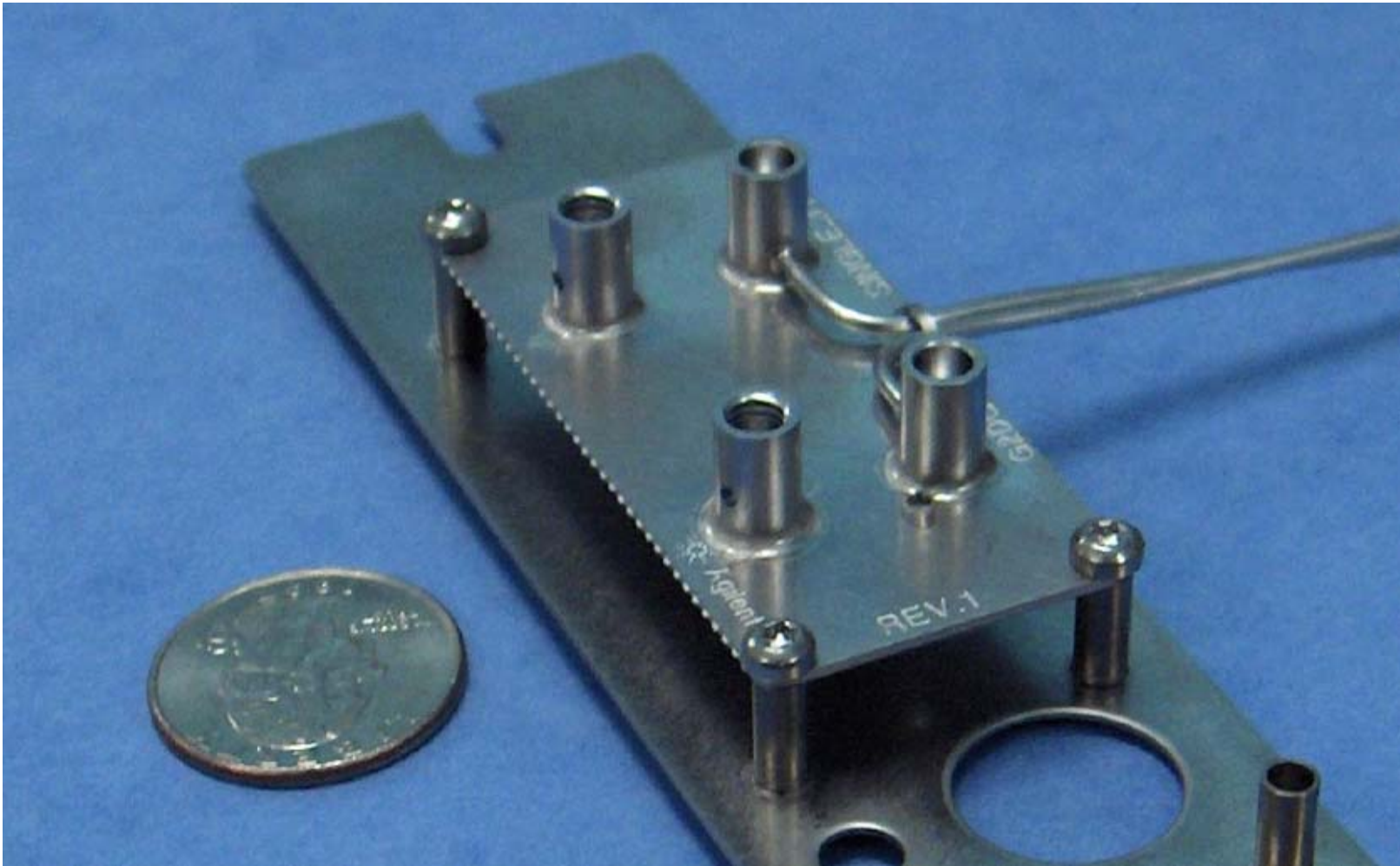
Modulation Device Installed

Lines from modulation valve

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Micro Modulation Valve

10/26/2007 2:58 pm

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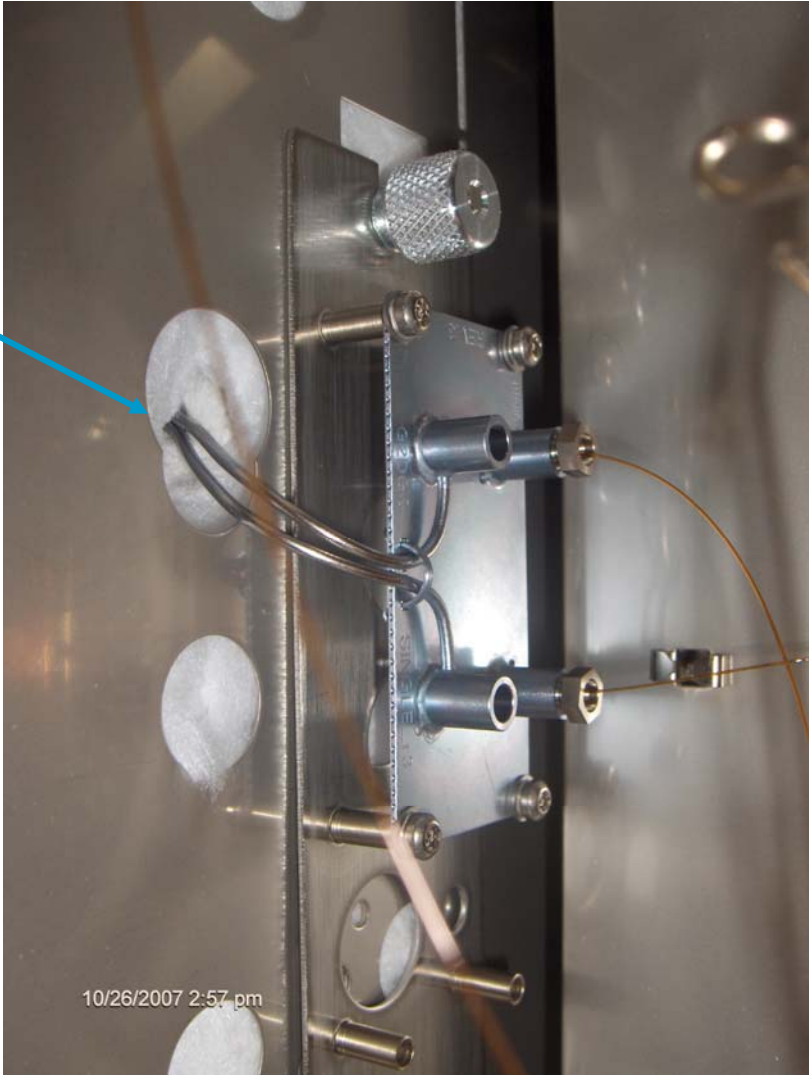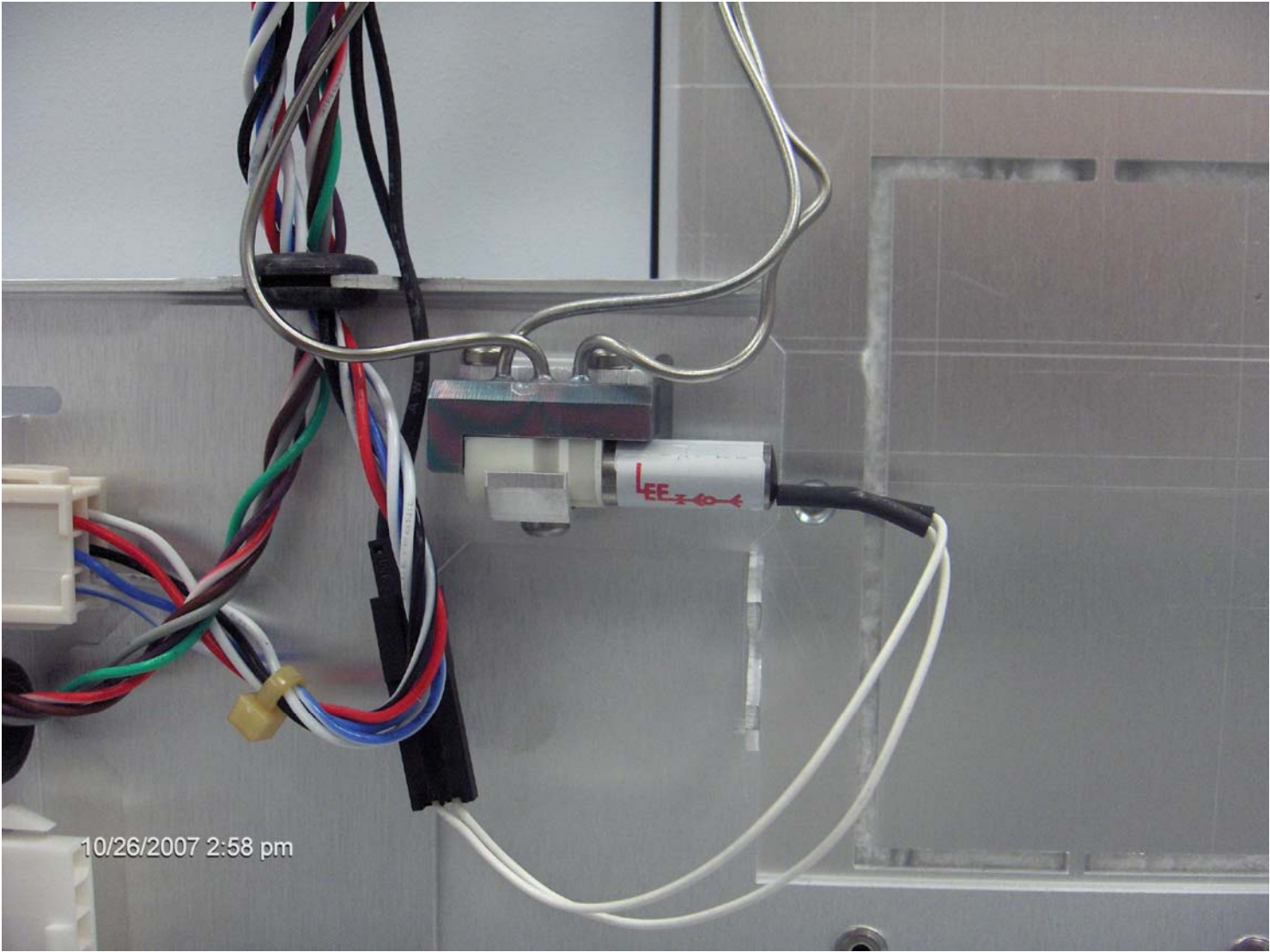
ChemStation Screen for Setting Modulation Times

Inject time is calculated from [mod period – sample time]

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Peak Area Check: Modulated (sum) vs. Un-modulated

C11
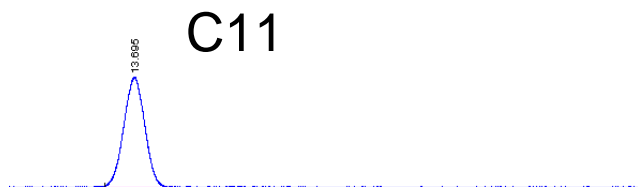
<u>Modulation</u>
Load: 1.45 s
Inject: 0.10 s

Inlet: 0.8 ml/min, constant flow
PCM: 20 ml/min, constant flow

#	Time	Area	Height	Width	Area%	Symmetry
7	6.31	3.2	1.5	0.0267	0.024	1.106
8	6.41	56	24.7	0.0283	0.414	1.08
9	7.485	5131.7	1807.1	0.0365	37.965	1.333
10	7.871	57.2	24.5	0.0305	0.423	1.017
11	9.709	65.6	27.2	0.0301	0.485	0.971
12	11.706	141.3	58.8	0.0314	1.045	1.022
13	13.695	73.7	30.4	0.0298	0.545	1.061
14	15.614	303.4	124.5	0.0288	2.245	1.062
15	19.143	156.8	65	0.0297	1.160	1.1
16	20.764	79.1	33.2	0.0286	0.585	1.087
17	22.302	160.2	67.2	0.0322	1.185	1.1
18	23.755	80.5	34.6	0.0302	0.596	0.929
19	25.137	35.5	15.1	0.0304	0.263	0.911

C11

Areas should agree to within 4%

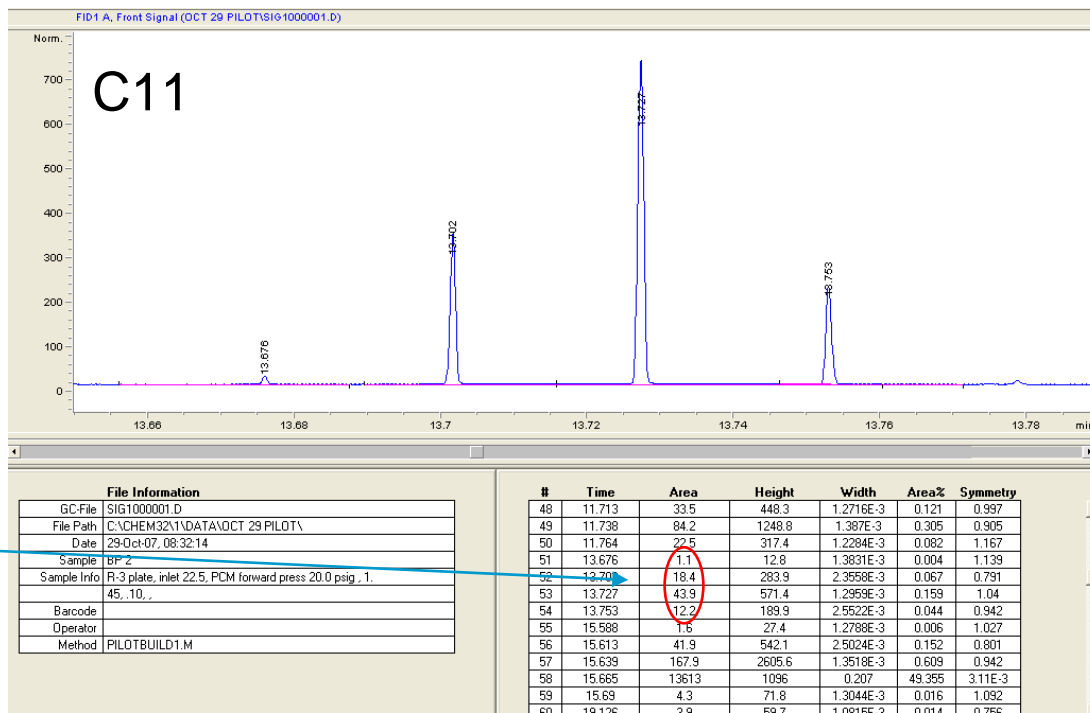|	File Information
GC-File	SIG1000001.D
File Path	C:\CHEM32\1\DATA\OCT 29 PILOT\
Date	29-Oct-07, 08:32:14
Sample	BP 2
Sample Info	R-3 plate, inlet 22.5, PCM forward press 20.0 psig , 1. 45, .10, ,
Barcode	
Operator	
Method	PILOTBUILD1.M

#	Time	Area	Height	Width	Area%	Symmetry
48	11.713	33.5	448.3	1.2716E-3	0.121	0.997
49	11.738	84.2	1248.8	1.387E-3	0.305	0.905
50	11.764	22.5	317.4	1.2284E-3	0.082	1.167
51	13.676	1.1	12.8	1.3831E-3	0.004	1.139
52	13.702	18.4	283.9	2.3558E-3	0.067	0.791
53	13.727	43.9	571.4	1.2959E-3	0.159	1.04
54	13.753	12.2	189.9	2.5522E-3	0.044	0.942
55	15.588	1.6	27.4	1.2788E-3	0.006	1.027
56	15.613	41.9	542.1	2.5024E-3	0.152	0.801
57	15.639	167.9	2605.6	1.3518E-3	0.609	0.942
58	15.665	13613	1096	0.207	49.355	3.11E-3
59	15.69	4.3	71.8	1.3044E-3	0.016	1.092
60	19.126	3.9	59.7	1.0815E-3	0.014	0.756

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Overlay of Nine Modulated Runs: C10

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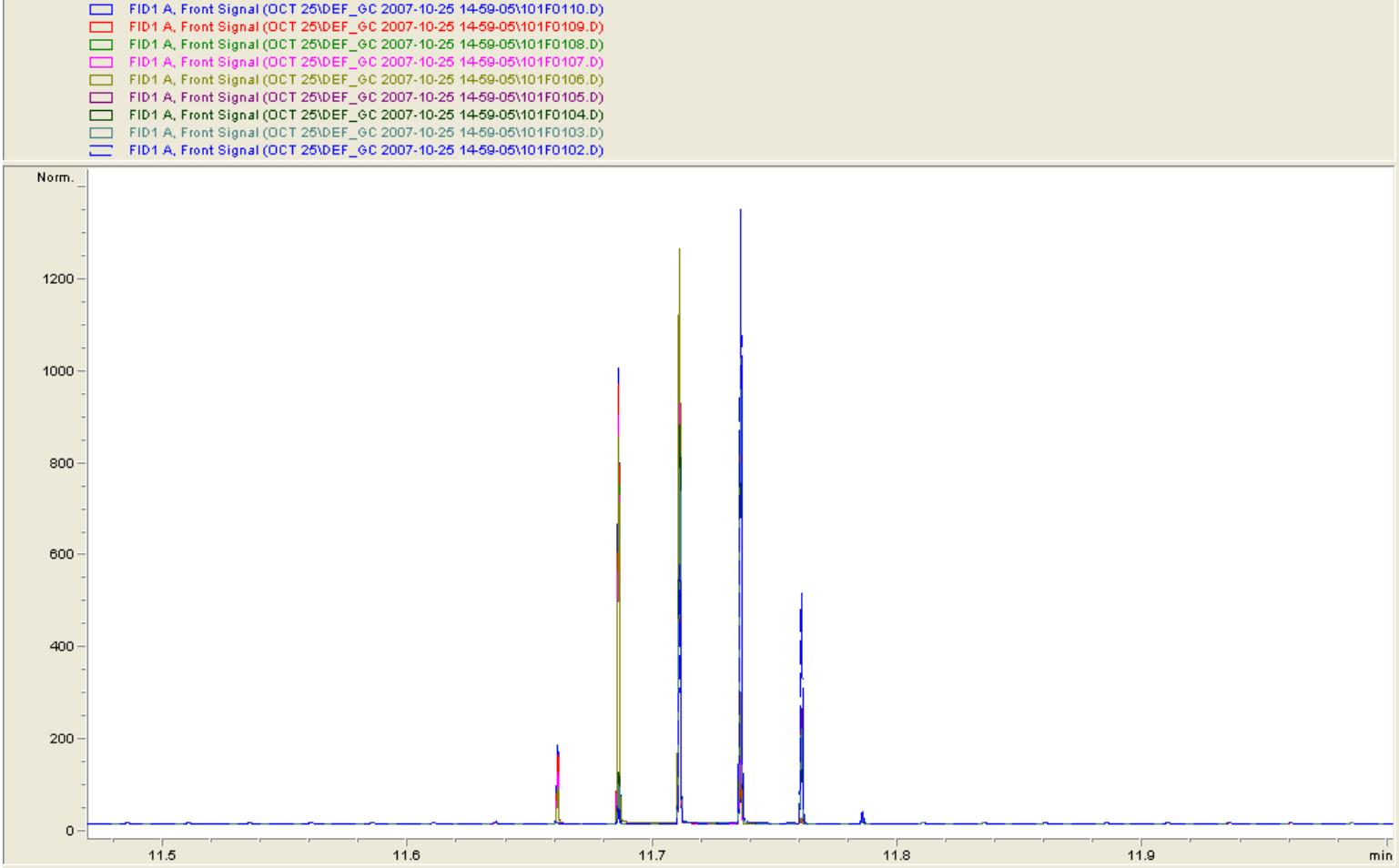
Overlay of One Modulation of C14

FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000005.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000006.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000007.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000009.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000009.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000010.D)
FID1 A, Front Signal (OCT 31 PILOT\DEF_GC 2007-10-30 14-48-19\SIG1000011.D)

High demands are placed on the system from auto injector, EPC flow control, and modulation Timing to achieve this repeatability.

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Heavy Gasoline

60m x 0.25mm x 0.10um DB5-ms
5m x 0.25mm x 0.10 Wax

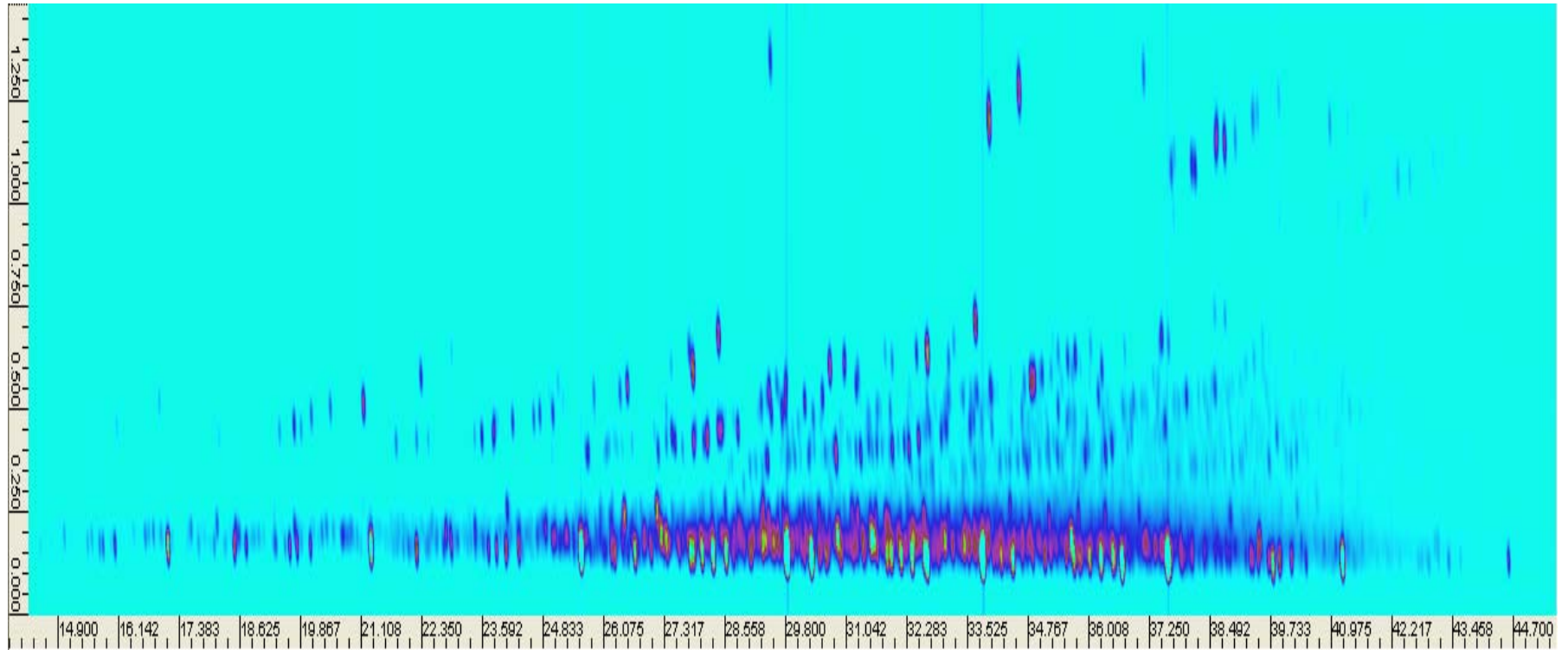40 C (1 min) to 250 C (5min) @3.5 C/min

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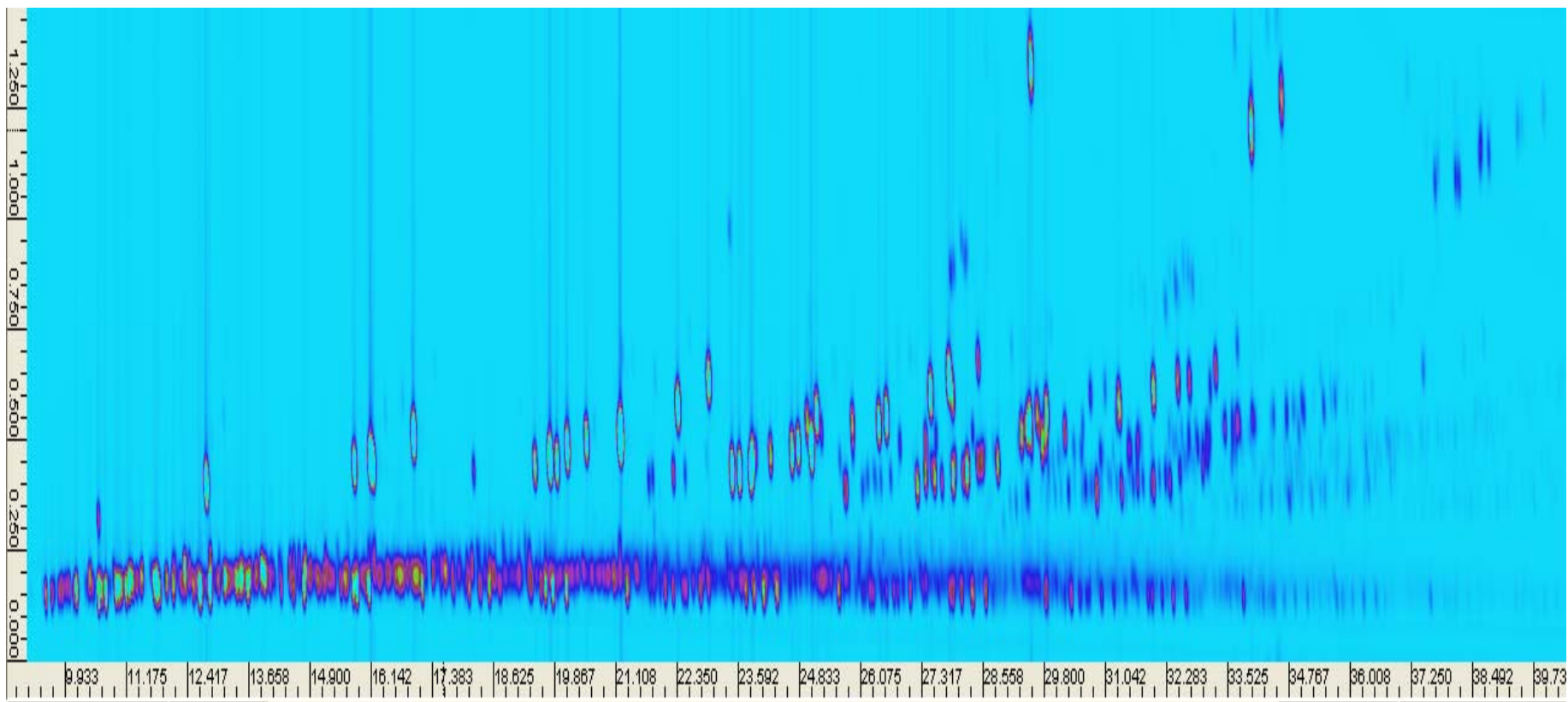
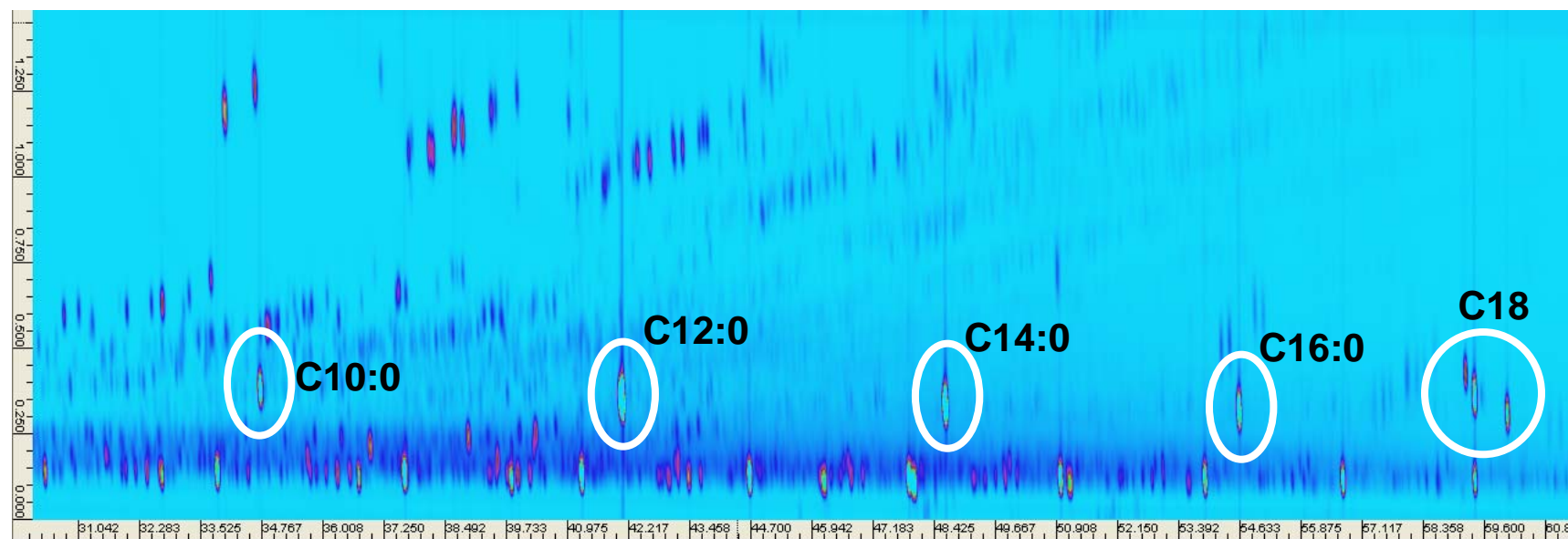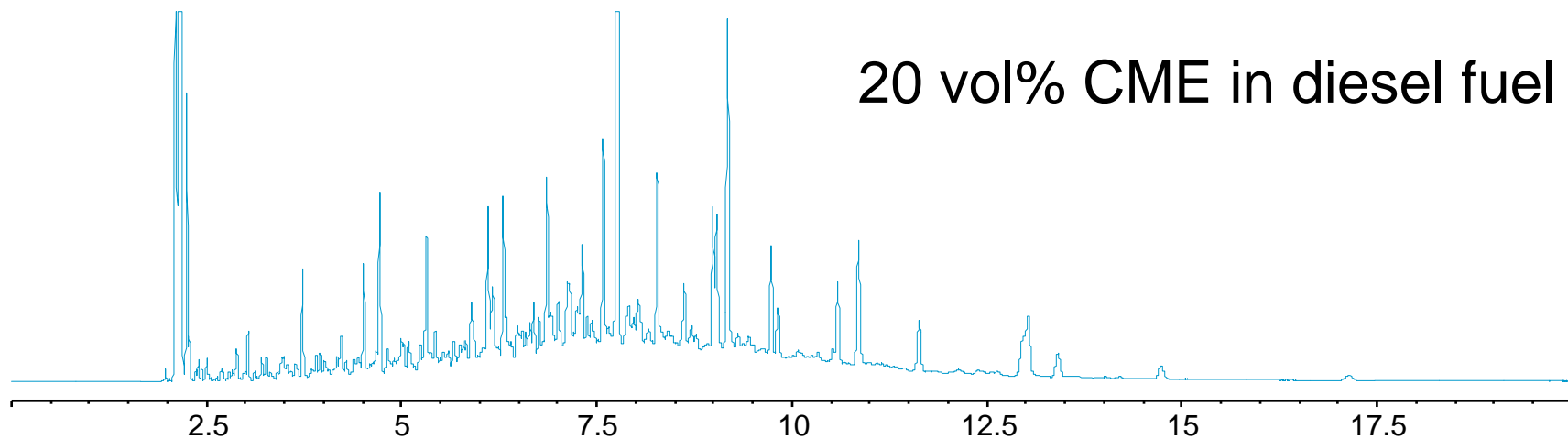# Kerosene

60m x 0.25mm x 0.10um DB5-ms
5m x 0.25mm x 0.10 Wax

40 C (1 min) to 270 C (5min) @3.5 C/min

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Biodiesel: Coconut Oil FAMEs in B20 Blend

20 vol% CME in diesel fuel

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System Layout for GCxGC FID/MSD

Auto-sampler

Switching valve

PCM

FID

s/s inlet

MS Tee

Column 1

Column 2

Flow modulator

MSD

1st column

modulated

2nd column

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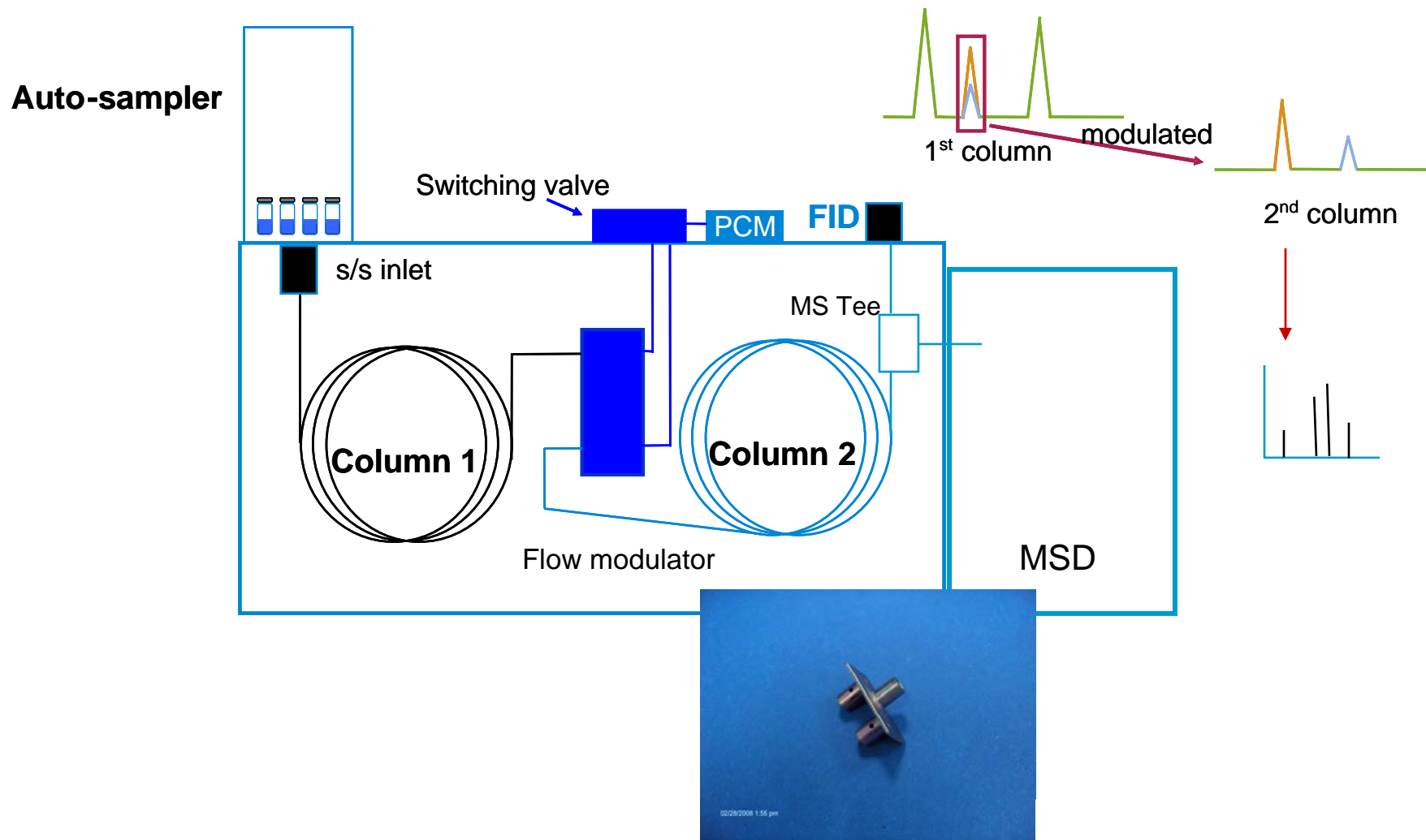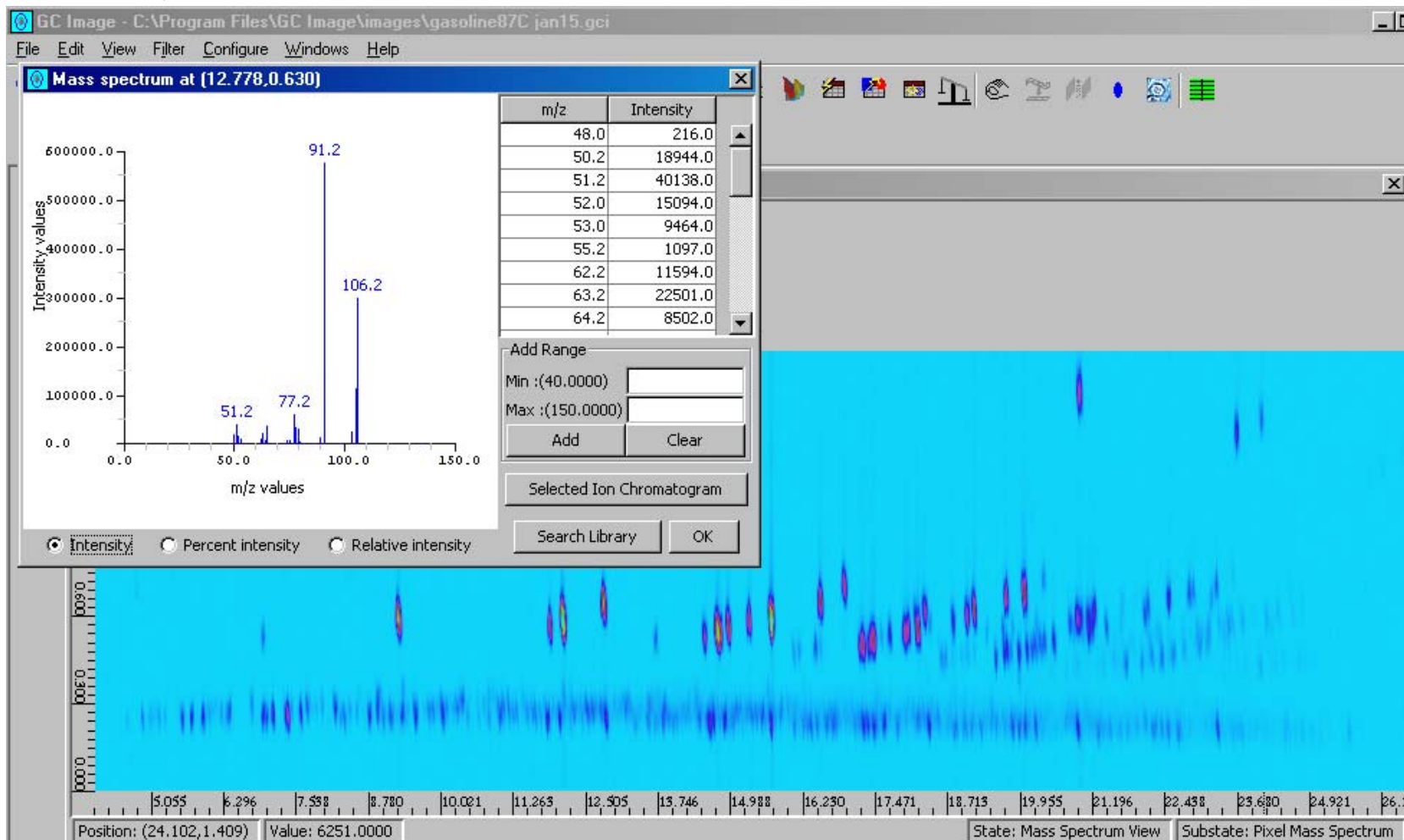
TIC of Gasoline Sample

GC Image 2D plot showing Mass spectrum
Approximately 28 scans/second: 5975C MSD

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Summary: flow modulation GC x GC

- **<u>Reliable Setup:</u>** Based on capillary-flow- technology, easy to setup, high performance chromatography, and reliable.

- **<u>Run Time:</u>** Chromatographic runs are than half the time of thermal systems

- **<u>High temperature operation:</u>** Operation to 350 C expands applications

- **<u>No Cryogen Required:</u>** Flow modulation means no tanks of Liquid N_2 or CO_2

- **<u>7890A Enabled GC x GC:</u>** Capillary- flow-technology ready, synchronized periodic events ensure precise modulation, control from 7890A logic board

- **<u>Comparable resolution without N2:</u>** Cap Flow Technology allows low dead volume and precise flow control, resulting in minimum peak broadening even without cryo-focusing . Peak widths on the second column are typically 60 to 100 ms at half maximum.

- **Sensitivity:** Approaches that obtained by thermally modulated systems

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Typical Pressures at 50 C

Split/Splitless Inlet

0.8 ml/min

Column head pressure: 23.5 psi

Inject Flow direction

Column 1 (25 – 30 M)

Pressure supplied By PCM: 20.0 psi

H_2

Modulation Valve

Collection channel

Pressure drop across channel: < 0.1 psi

Pressure at head of Column 2: 19.7 psi

Column 2 (5M)

FID

Flow Modulator

Approx. 21 ml/min

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