AGAT Laboratories

Cold Traps & Clean Peaks

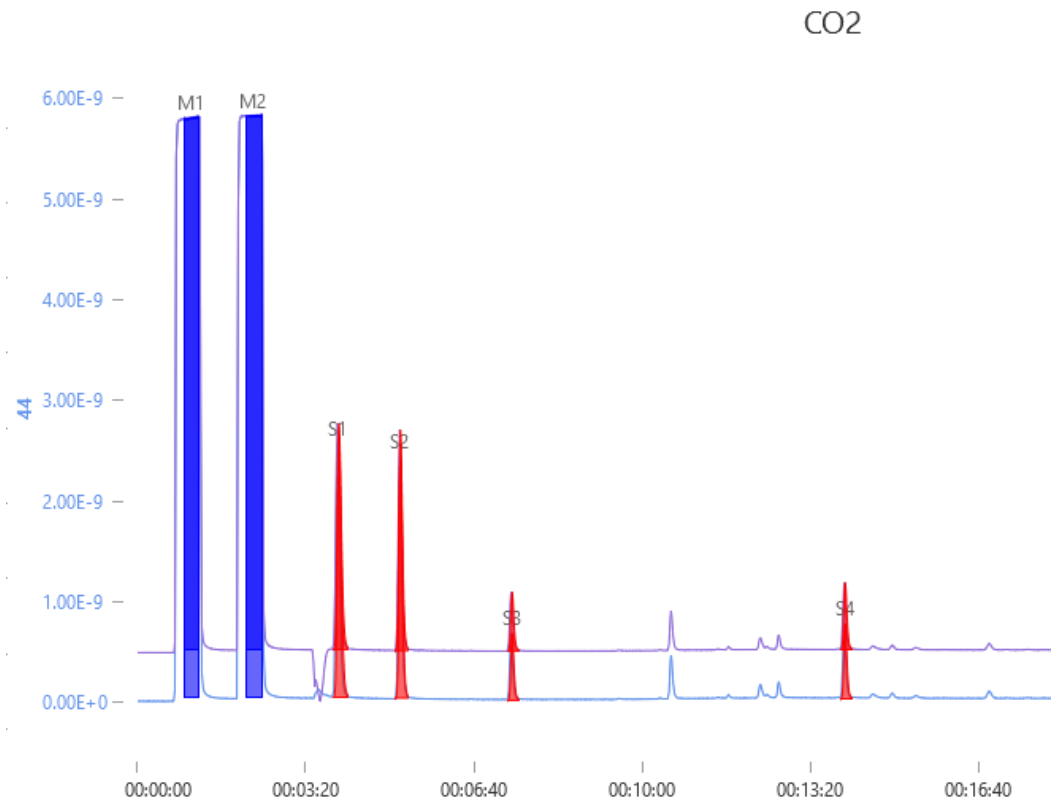
Cryogenic Approaches to Atmospheric Methane Analysis with GC-IRMS

James Ravenhill, Andrew Kingston, Fereshteh Meshkani

AGAT Laboratories, Calgary, AB

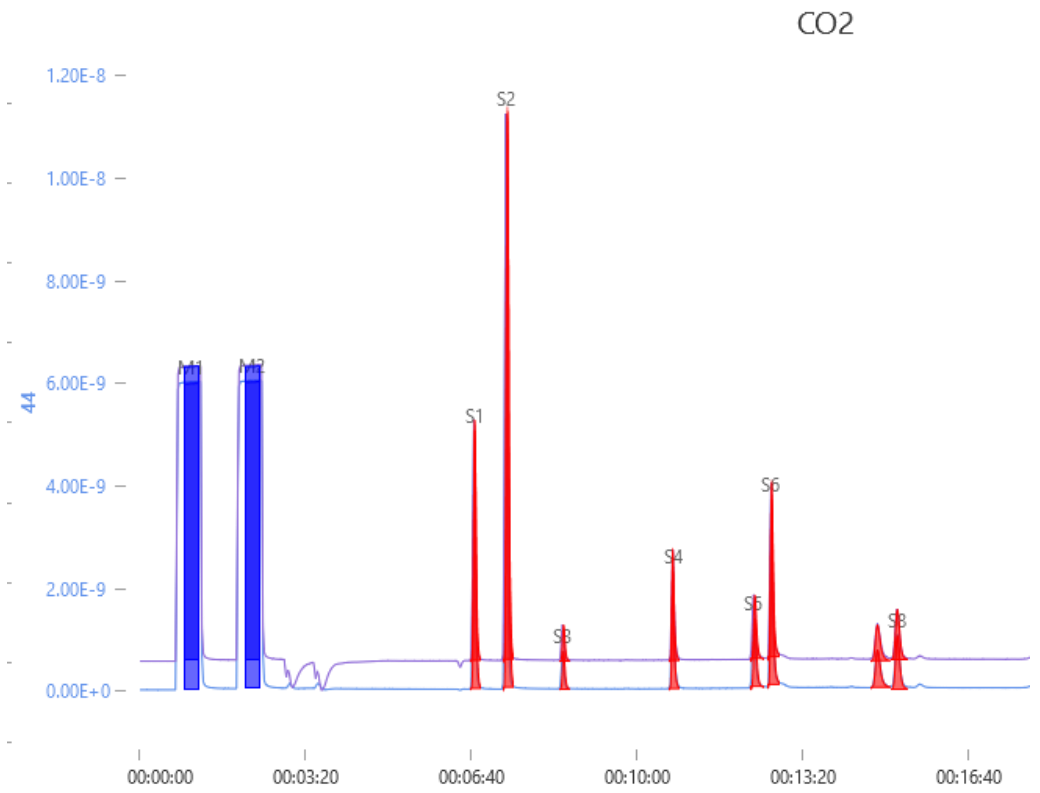
The struggle

- CH_4 peaks co-elute with air (N_2+O_2) on some GC column phases
  - Source effects of air and CH_4 peaks cause large deviations to CH_4 values
- Exposure of filament to excessive air (i.e., O_2) in these samples reduces the life of the filament
- Low abundance samples require labor intensive concentration prior to analysis via GC-IRMS



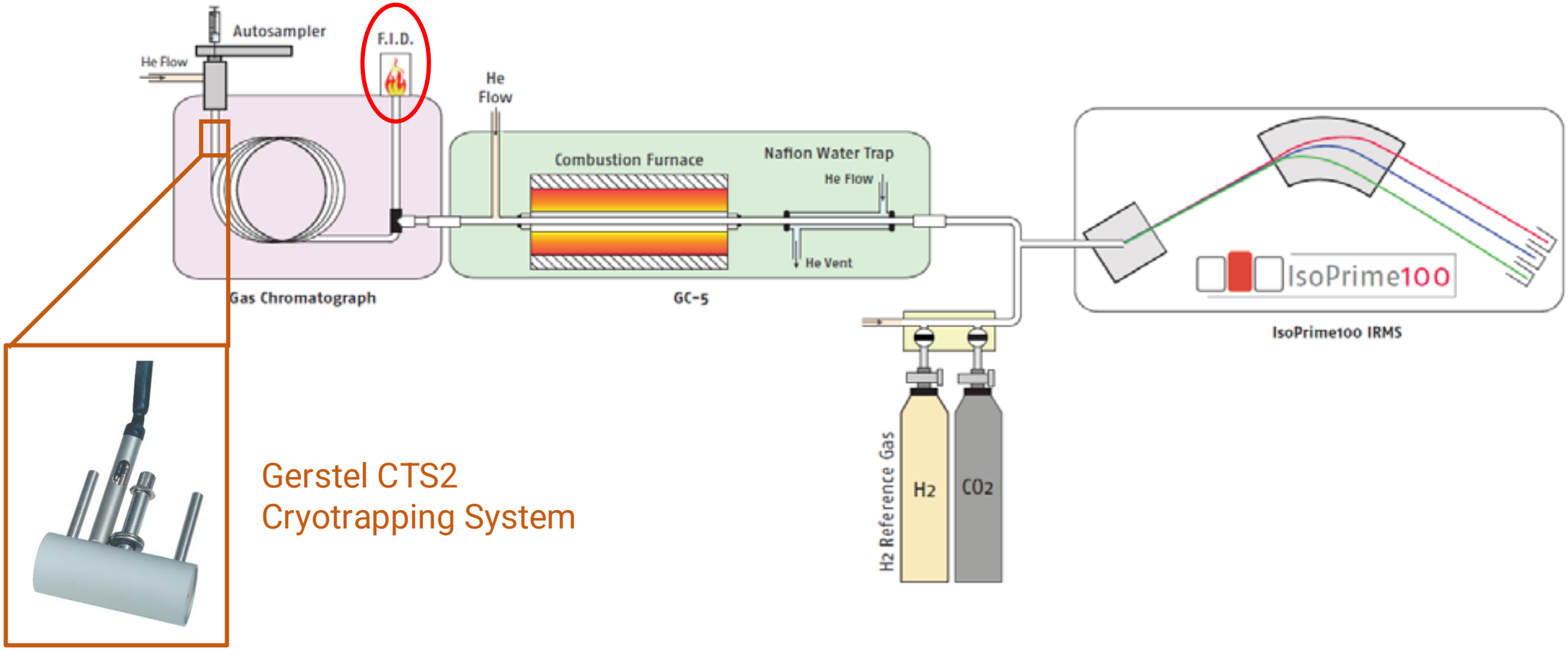
The benefits

- Can backflush or direct undesirable gases away from the IRMS
- Trapping of gas species, like CH_4, on-column permits analysis of low concentration samples via multiple injections or headspace analysis
  - automation
- Can tailor retention times of gas species to desired method requirements



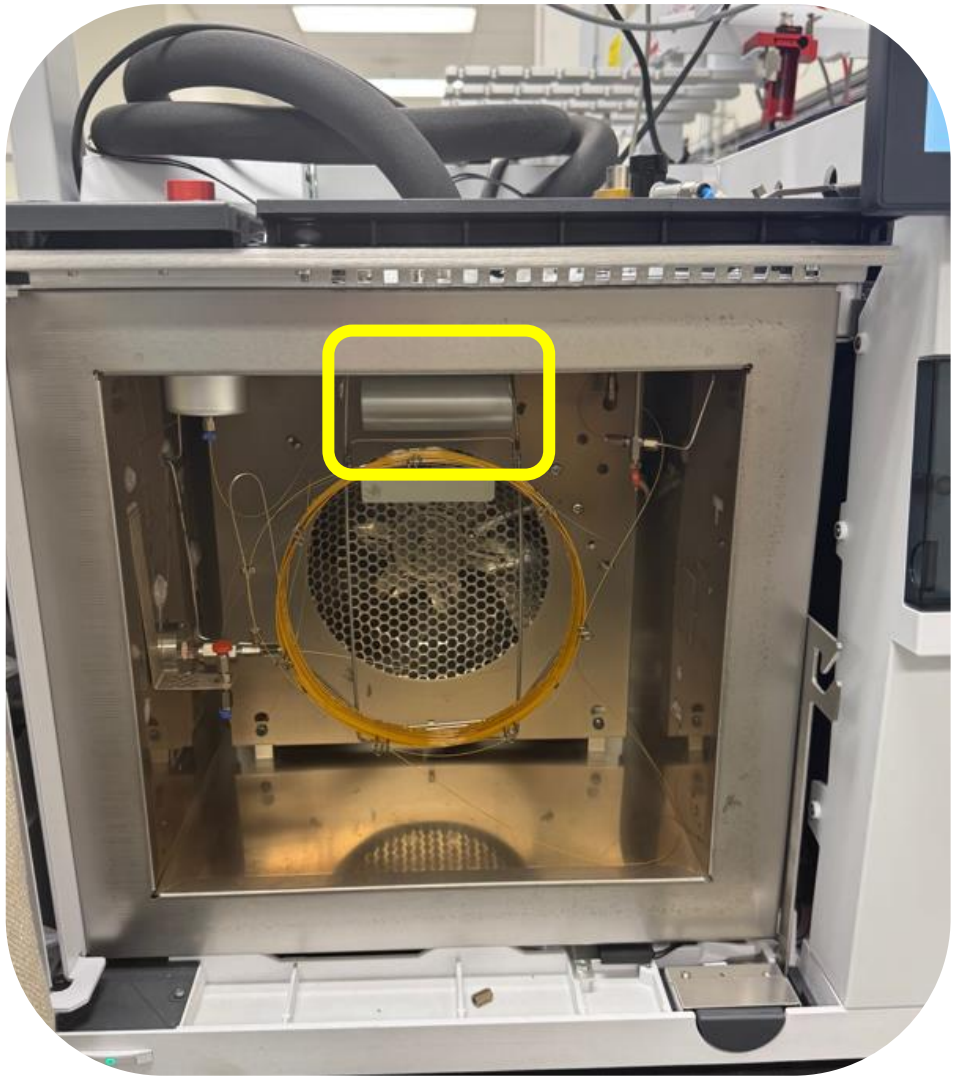
GC-IRMS at AGAT Labs

Cryotrapping System coupled to GC-IRMS



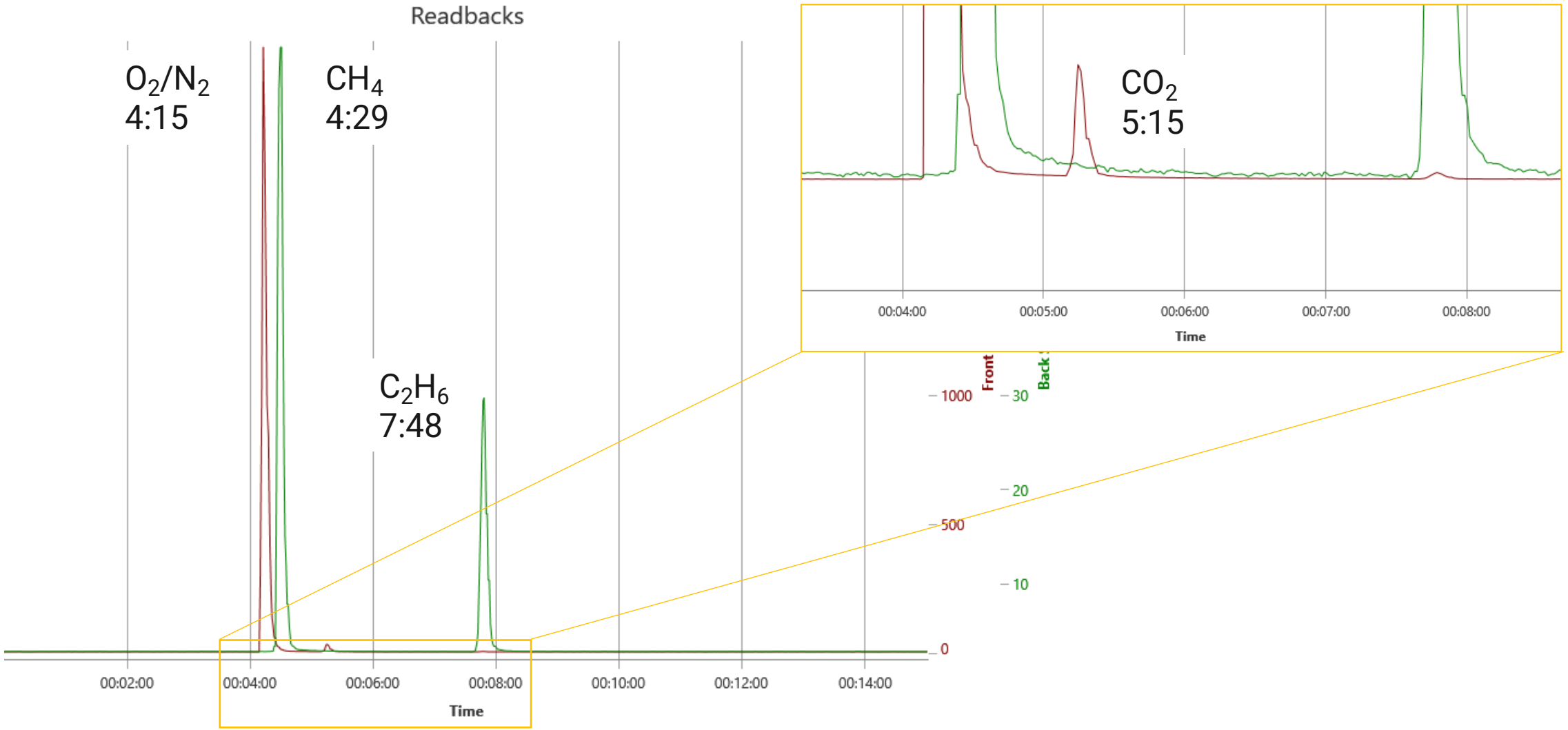
Gerstel CTS2
Cryotrapping System

Gerstel CTS2 Cryotrapping System

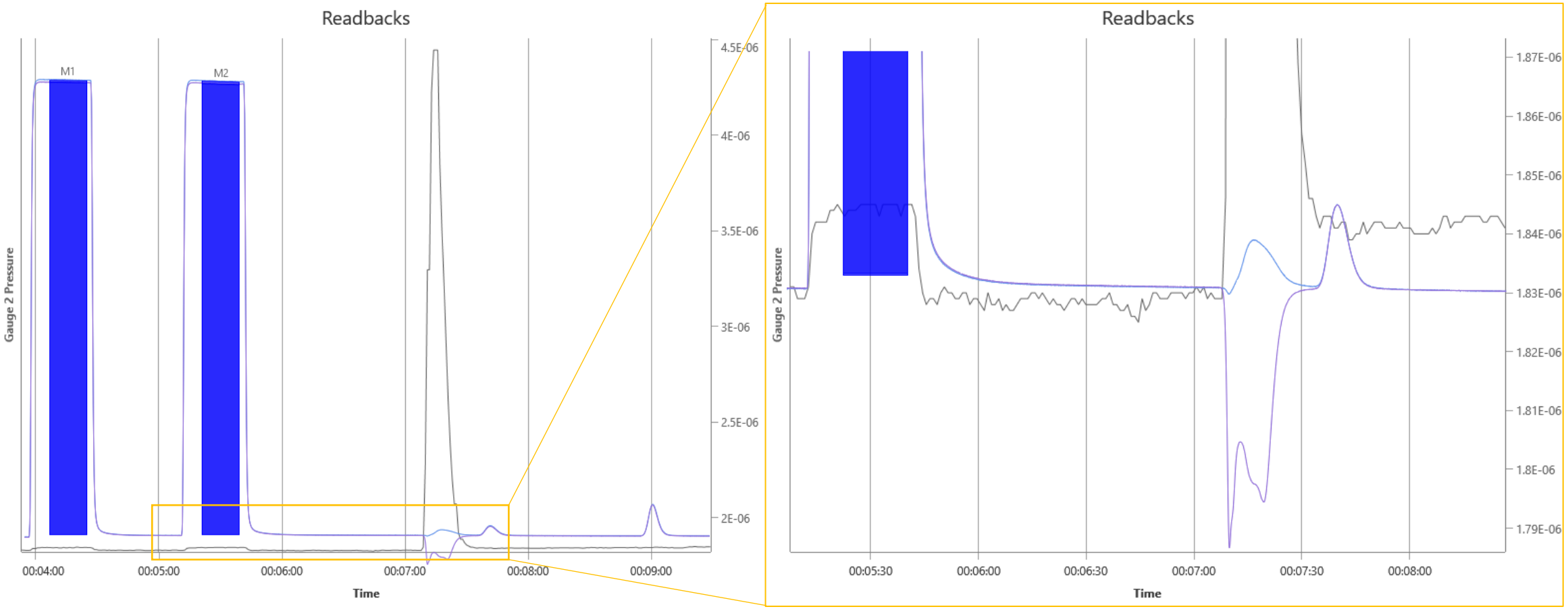


- Minimum temperature: –150°C
  - LN_2 cooling liquid
- Maximum temperature: +400°C
  - integrated heater
- Two temperature ramps
- Max. ramp rate of 20°C/sec
- 80mm of capillary in cooling zone
- Up to 1 mm OD capillary
- Controlled via Maestro software

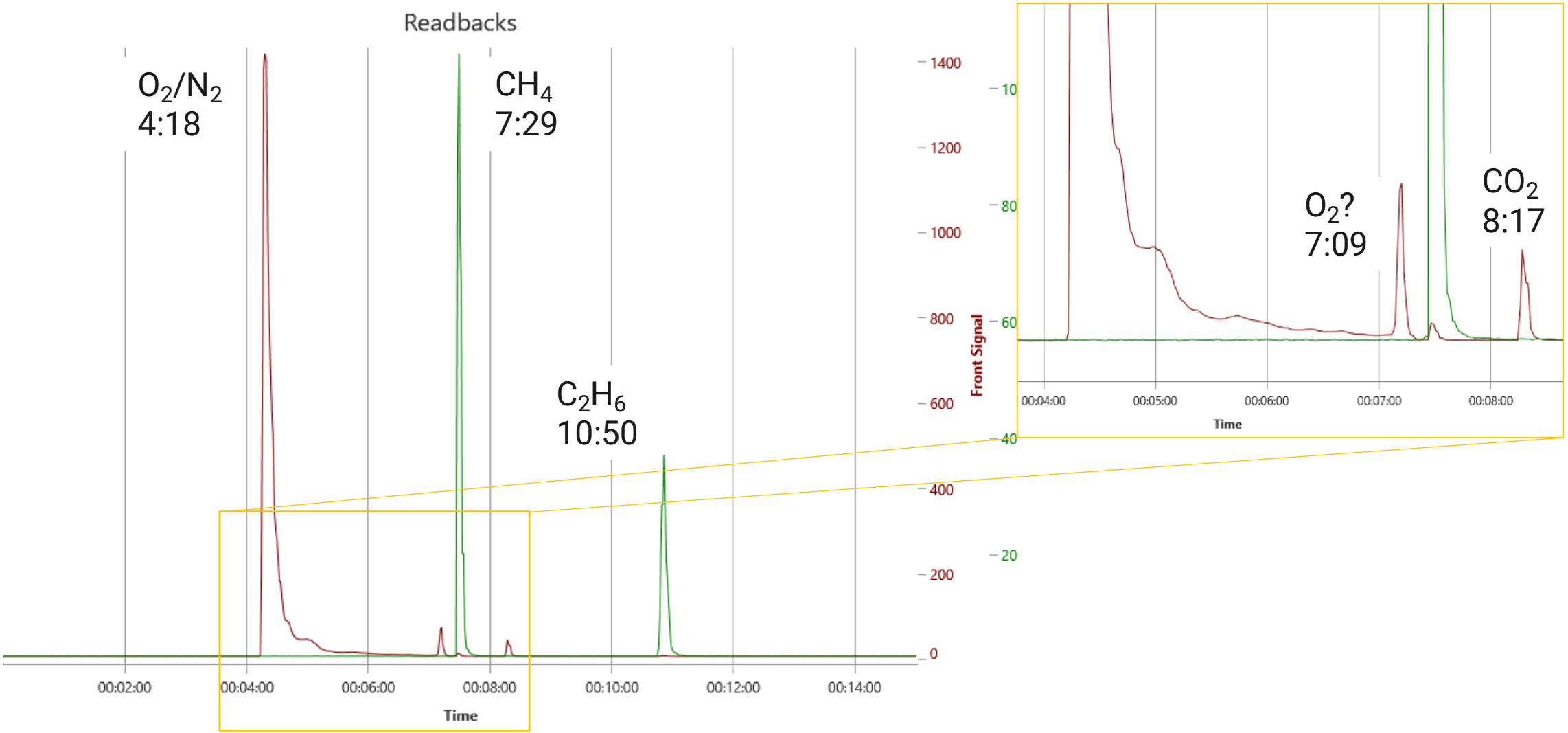
$CH_4 + C_2H_6 + CO_2$ in Air on HP PLOT-Q: +50°C (CTS ambient)



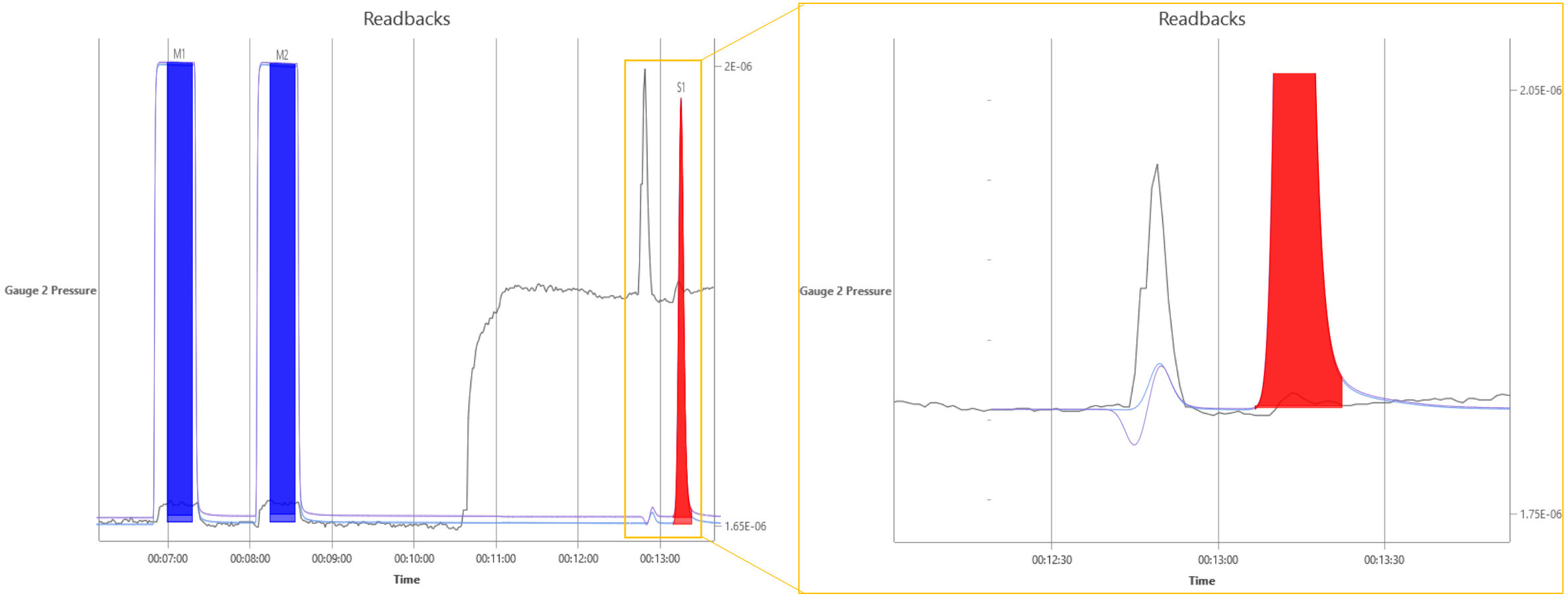
Vacuum Instability with Large Volume Injections



O_2? Partial Retention on HP PLOT-Q: -150°C



Vacuum Instability Greatly Reduced with Cryofocusing

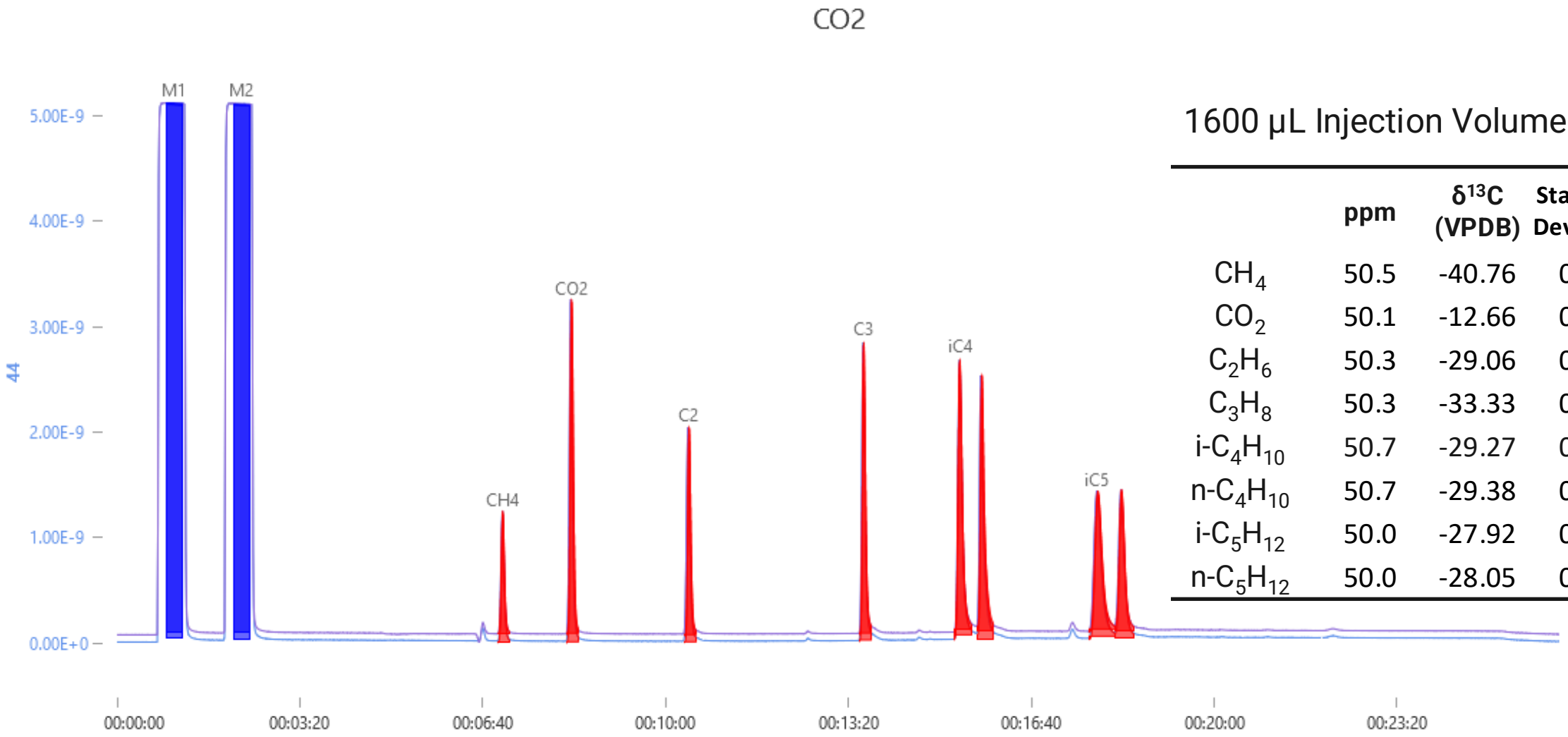


Routine Cryogenic Method Parameters

Total Injection Volume: **1600 µL**

Gerstel CTS2		**Agilent 8890**	
Syringe	1000 µL	Split Ratio	2:1
Injection Volume	2 x 800 µL	Column Flow	1.2 mL/min
Injection Speed	100 µL/s	Oven Initial Temp	40°C
CTS2 Initial Temperature	-150°C	Oven Initial Hold Time	7 min
CTS2 Initial Hold Time	3 min	Oven Ramp Rate	20°C/min
CTS2 Ramp Rate	20°C/s	Oven Final Temperature	200°C
CTS2 Final Temperature	60°C		

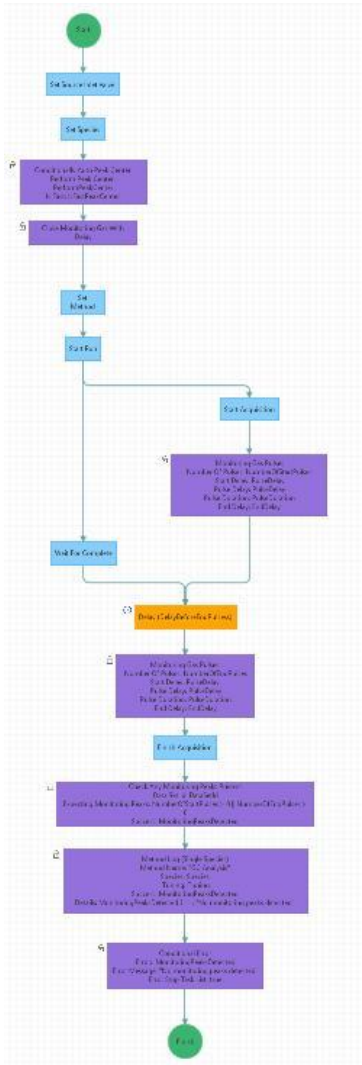
Routine Cryogenic Injections on HP PLOT-Q



1600 µL Injection Volume (n=3)

	ppm	$\delta^{13}C$ (VPDB)	Standard Deviation
CH_4	50.5	-40.76	0.28
CO_2	50.1	-12.66	0.28
C_2H_6	50.3	-29.06	0.33
C_3H_8	50.3	-33.33	0.26
i-C_4H_{10}	50.7	-29.27	0.33
n-C_4H_{10}	50.7	-29.38	0.28
i-C_5H_{12}	50.0	-27.92	0.31
n-C_5H_{12}	50.0	-28.05	0.34

Standard LyticOS Method for GC-IRMS Injections



Instrument prep

START

IRMS and GC Run

Data Analysis

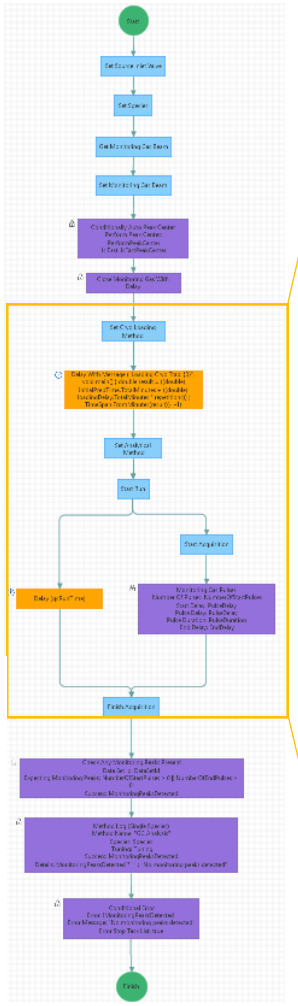
LyticOS Method Changes for Larger Volume “Injections”

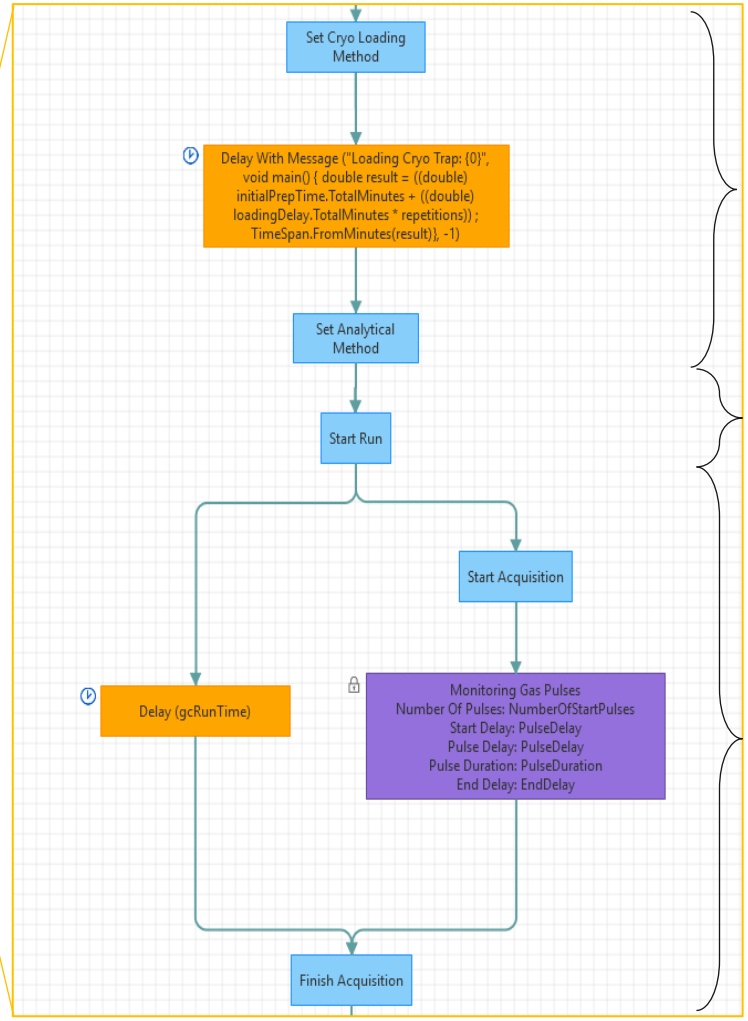
Needs:

1. Create Custom “Cryogenic Loading GC Method”
   1. Constant Oven Temperature
   2. Shortest possible time
2. Enable LyticOS to run multiple GC methods within a single task
3. Programmable time delay between loading different GC methods

Input Parameters

Name	Default Value	Editable In Task List
IRMS		
Agilent		
Gerstel		
Repetitions	3	☑
Loading Delay	00:01:15	☑
Initial Cool Time	00:01:30	☐





Cryogenic Sample Loading

START

IRMS and GC Run

Large Volume Cryogenic Method Parameters

Total Injection Volume
6400 µL

Sample Loading

Gerstel CTS2		Agilent 8890	
Syringe	1000 µL	Split Ratio	2:1
Injection Volume	6 x 800 µL	Column Flow	1.2 mL/min
Injection Speed	100 µL/s	Oven Temperature	40°C
CTS2 Temperature	-150°C	Oven Hold Time	0.01 min

Analysis

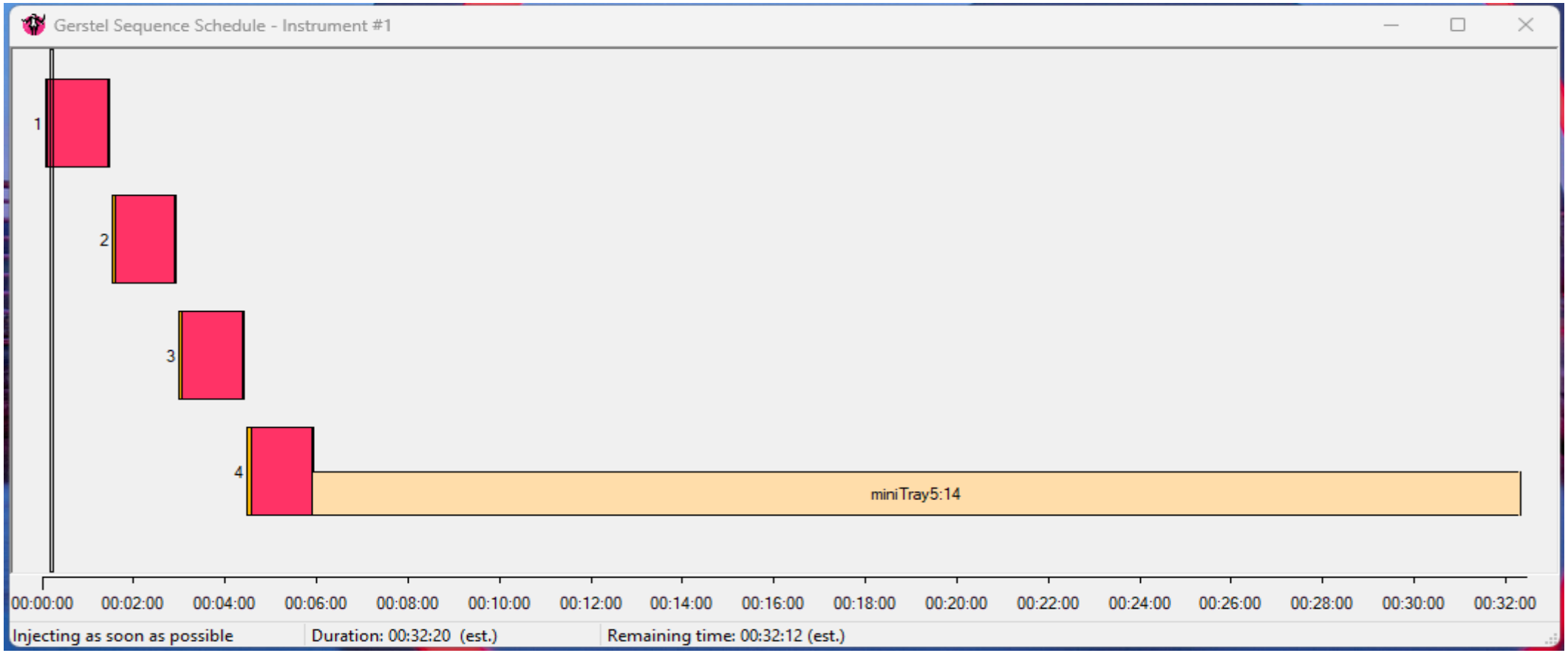
Gerstel CTS2		Agilent 8890	
Syringe	1000 µL	Split Ratio	2:1
Injection Volume	2 x 800 µL	Column Flow	1.2 mL/min
Injection Speed	100 µL/s	Oven Initial Temp	40°C
CTS2 Initial Temperature	-150°C	Oven Initial Hold Time	7 min
CTS2 Initial Hold Time	3 min	Oven Ramp Rate	20°C/min
CTS2 Ramp Rate	20°C/s	Oven Final Temperature	200°C
CTS2 Final Temperature	60°C		

Gerstel Injection Sequence for Single Sample

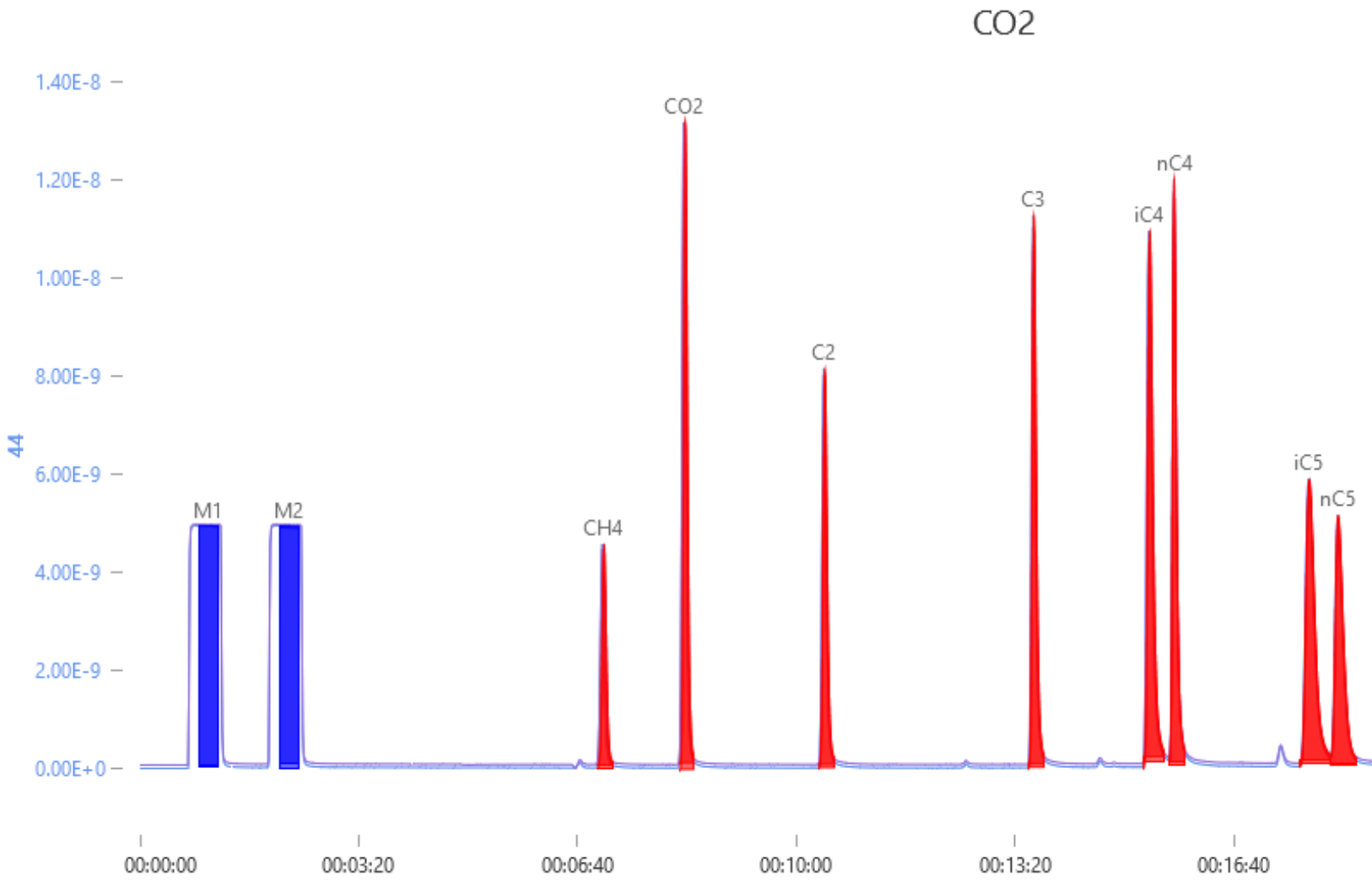
Cryogenic Sample Loading

START

IRMS and GC Run



Large Volume Cryogenic Injections on HP PLOT-Q



6400 µL Injection Volume (n=3)

	ppm	$\delta^{13}C$ (VPDB)	Standard Deviation
CH_4	50.5	-40.11	0.05
CO_2	50.1	-12.26	0.06
C_2H_6	50.3	-29.67	0.02
C_3H_8	50.3	-33.48	0.06
i-C_4H_{10}	50.7	-28.67	0.05
n-C_4H_{10}	50.7	-28.91	0.05
i-C_5H_{12}	50.0	-27.57	0.01
n-C_5H_{12}	50.0	-27.86	0.04

Atmospheric Cryogenic Method Parameters

Total Injection Volume
20,000 µL (20 mL)
(GHG: 100 mL)

Sample Loading

Gerstel CTS2		Agilent 8890	
Syringe	2500µL	Split Ratio	2:1
Injection Volume	6x 2500µL	Column Flow	1.2mL/min
Injection Speed	100µL/s	Oven Temperature	50°C
CTS2 Temperature	-150°C	Oven Hold Time	0.01 min

Analysis

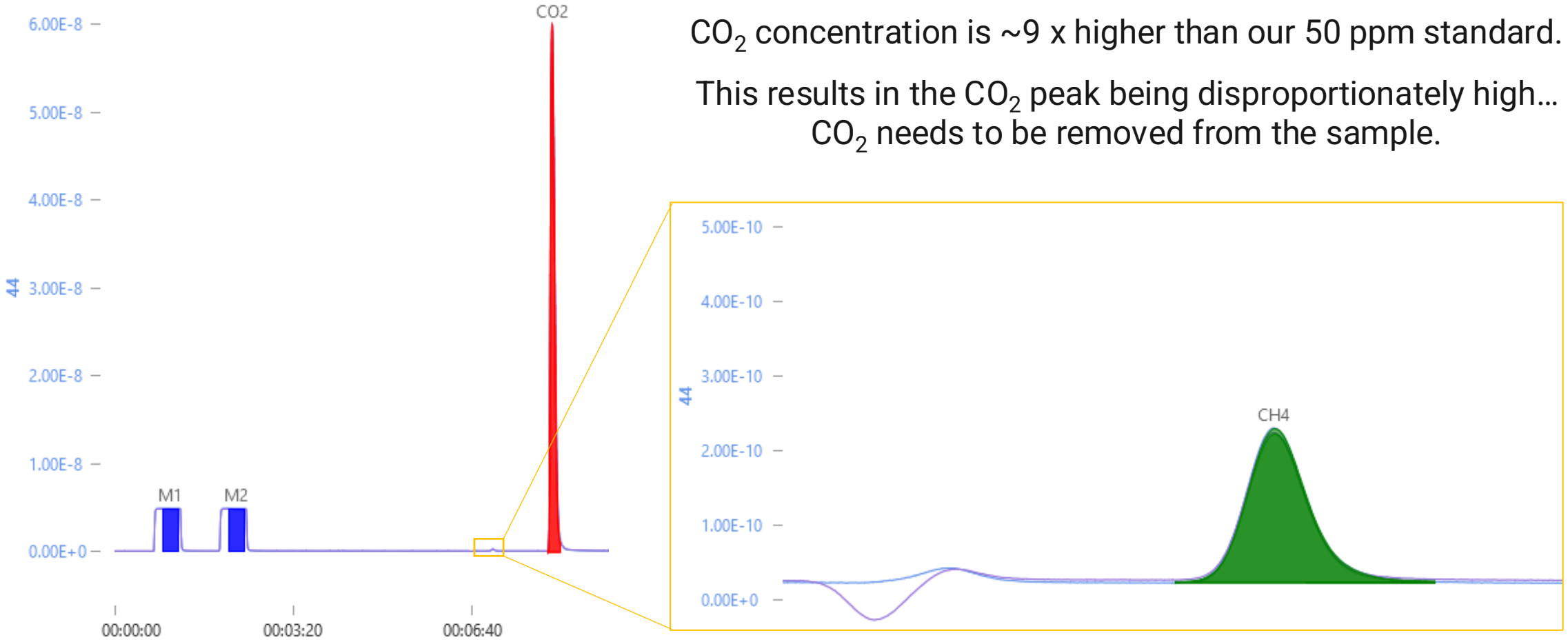
Gerstel CTS2		Agilent 8890	
Syringe	2500µL	Split Ratio	2:1
Injection Volume	2x 2500µL	Column Flow	1.2mL/min
Injection Speed	100µL/s	Oven Initial Temp	50°C
CTS2 Initial Temperature	-150°C	Oven Initial Hold Time	10 min
CTS2 Initial Hold Time	5 min	Oven Ramp Rate	20°C/min
CTS2 Ramp Rate	20°C/s	Oven Final Temperature	200°C
CTS2 Final Temperature	60°C		

Atmospheric Cryogenic Method Challenges

CH_4 concentration is ~25 x lower than our 50 ppm standard.

CO_2 concentration is ~9 x higher than our 50 ppm standard.

This results in the CO_2 peak being disproportionately high…
CO_2 needs to be removed from the sample.



Atmospheric Cryogenic Possible Workarounds

Inject more sample!

6.4 mL had good results with 50 ppm, so inject more sample to see if peak heights can be increased.

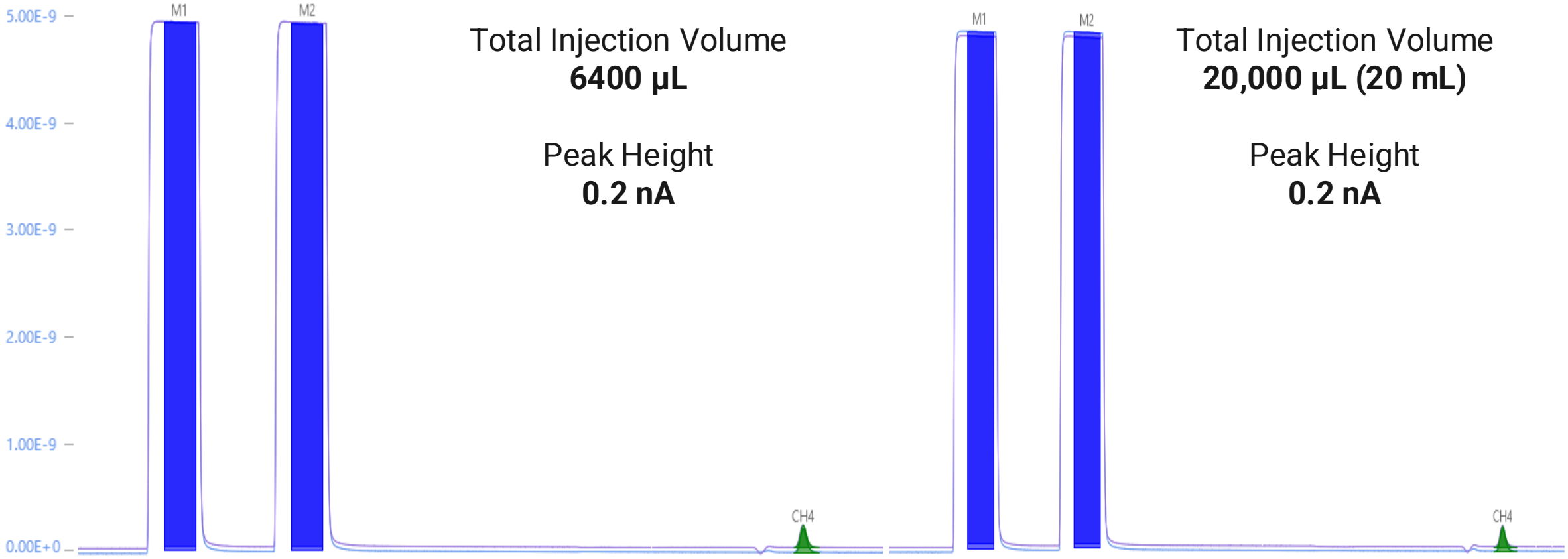
Hopefully this allows more methane to be trapped on the frozen section of column inside the CTS-2

Dual column setup!

20 mL sample is loaded onto a frozen section of Molesieve column at -100ºC.
Sample is then released at 60ºC and run through a 30 m Molesieve column before being trapped again on HP PLOT-Q at -150ºC
Focused sample is released through HP PLOT-Q and analyzed.

Hopefully this allows enough methane to be trapped and not have excess fixed gasses occupy the available active sites in the column within the CTS-2

Atmospheric Cryogenic Sample Volume Limitations



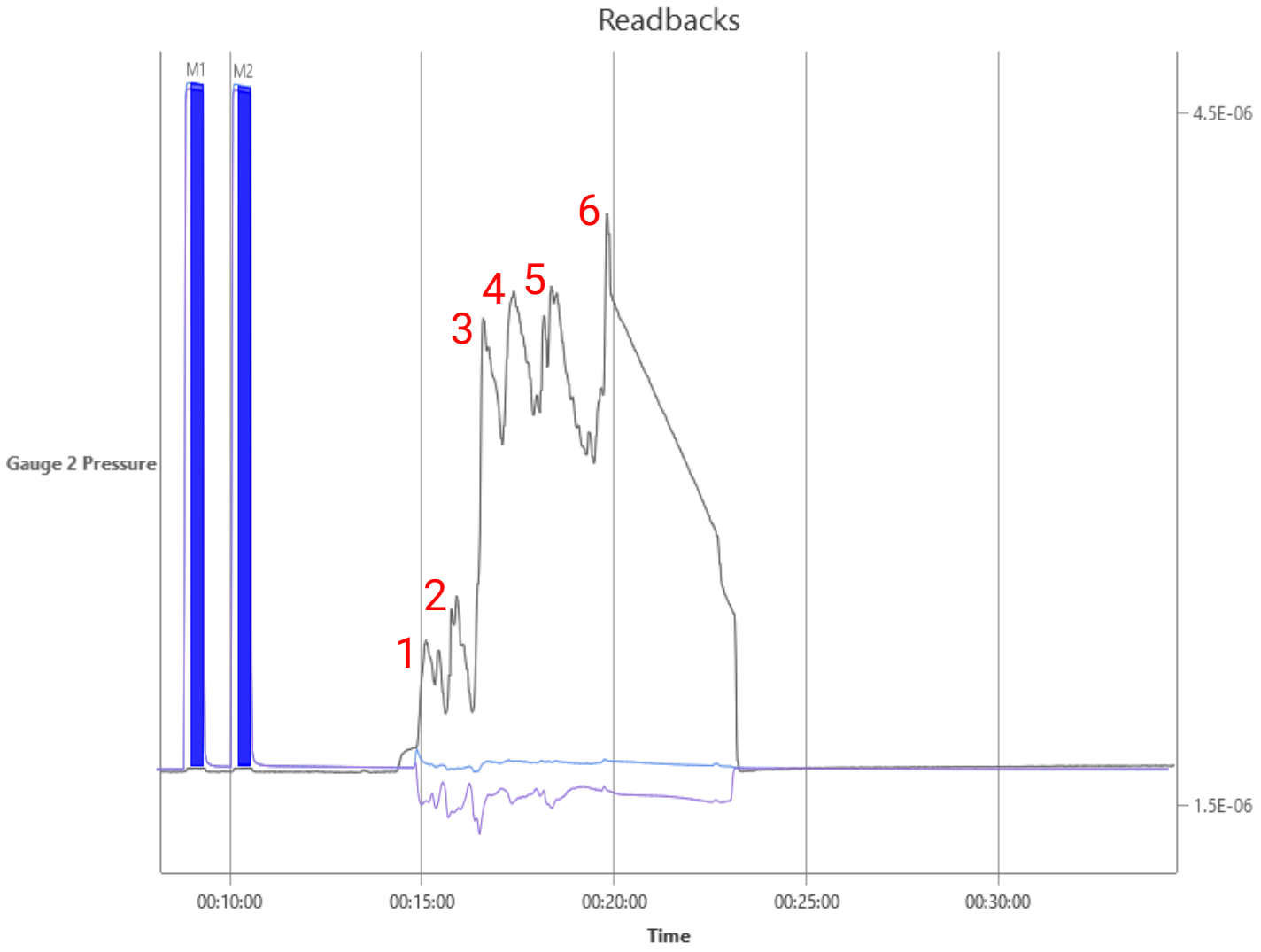
Total Injection Volume
6400 µL

Peak Height
0.2 nA

Total Injection Volume
20,000 µL (20 mL)

Peak Height
0.2 nA

Atmospheric Cryogenic Sample Volume Limitations



Method Timings are Critical

If the method timings are even slightly off, you don't trap things in the right order and you end up with all your individual injections showing up as distinct pulses to your MS.

Dual Column **Atmospheric** Methane Injection Sequence

MSD to "Waste"

Cryogenic Sample Loading

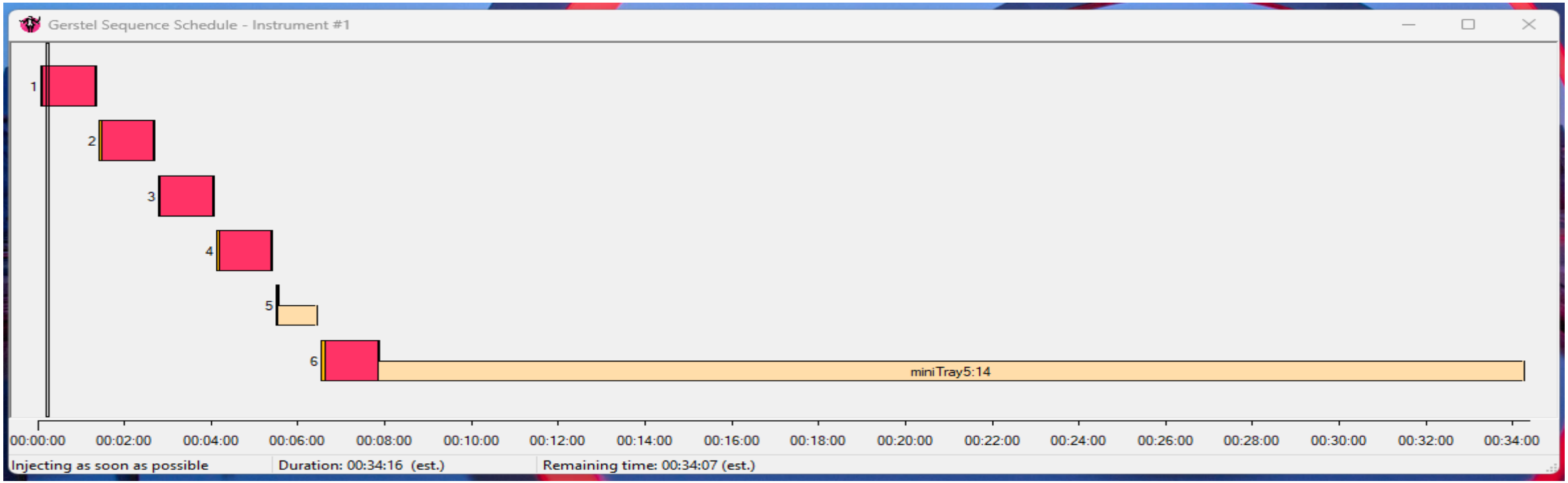
Sample Transfer

START

Methane Capture

CH_4 Release

IRMS and GC Run



Conclusions

Low Concentration Hydrocarbon Gasses:

- 50 ppm C_1-C_5 hydrocarbons can be effectively analyzed with 6.4mL injection volumes.
- There is minimal interference from the increased injection volume on the vacuum stability during analysis.
- There is some instability (linearity impacts) with peak heights ~2 nA larger injection volumes are better for increased stability.

6400 µL Injection Volume

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1600 µL Injection Volume

	ppm	$\delta^{13}C$ (VPDB)	Standard Deviation
CH_4	50.5	-40.76	0.28
CO_2	50.1	-12.66	0.28
C_2H_6	50.3	-29.06	0.33
C_3H_8	50.3	-33.33	0.26
i-C_4H_{10}	50.7	-29.27	0.33
n-C_4H_{10}	50.7	-29.38	0.28
i-C_5H_{12}	50.0	-27.92	0.31
n-C_5H_{12}	50.0	-28.05	0.34

Conclusions Continued…

Atmospheric Methane Analysis:

- Additional work is needed to identify a suitable method to remove the CO_2 from the sample prior to analysis.
  - Possibly a Molesieve column could be used, or Ascarite II and Magnesium Perchlorate to remove the CO_2 from the sample prior to placing into an autosampler bag.
  - Could a combination of Molesieve and PLOT-Q columns be used with varied trapping temperatures to effectively trap and focus enough of the sample to be useful?
- How much sample is too much?
  - Can more than 20 mL be injected at once before the cryo trap is overloaded?
  - Is 20 mL overloading the cryo trap already and that is causing the lower-than-expected CH_4 peak heights?

Acknowledgements

- Funding provided by AGAT's SRED Program
- Experiments by James Ravenhill, Andrew Kingston
- Support from Fereshteh Meshkani