

Multiple Gas#5 GC configuration Revised

Jan 2018 *Updated Jan2016-19.16-23p*

History:

Unfortunately there is no single column that can separate:

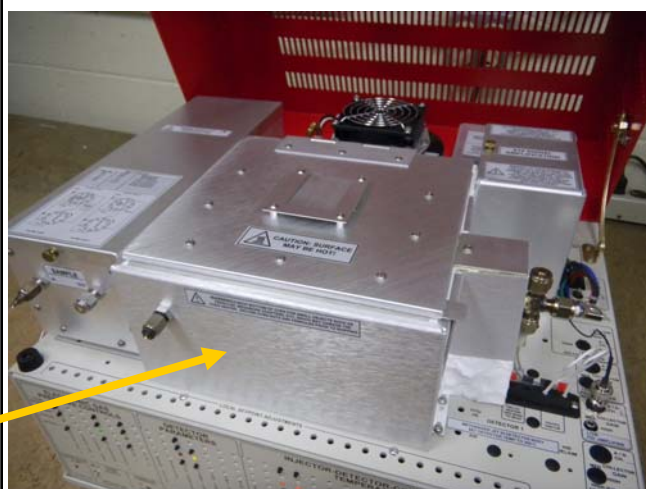
Hydrogen
Oxygen
Nitrogen
Methane
CO
CO₂
Ethane
Water
Propane
Butane
Pentane

Over the years SRI Instruments has devised several solutions to this analytical problem, starting with the MultipleGas#1 configuration and evolving to the present MultipleGas#5 configuration.

Like the earlier MG GCs the 8610C chassis includes an ambient to 400C programmable column oven.

Inside the column oven are three columns. There can be additional columns, but the basic MG5 includes:

.5 meter Haysep-D precolumn
2 meter MoleSieve 5A column
2 meter Haysep D column



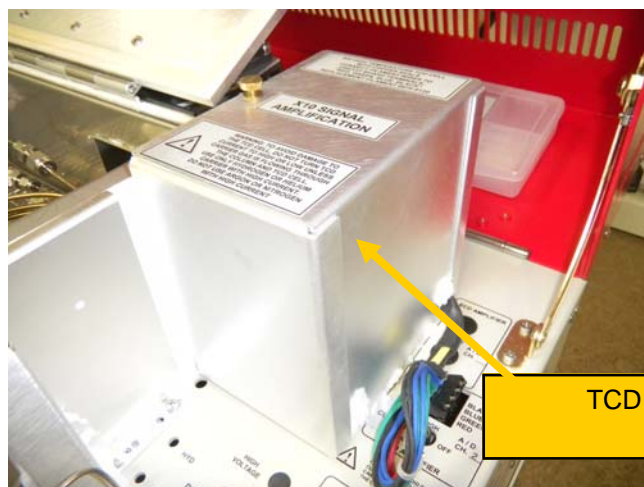
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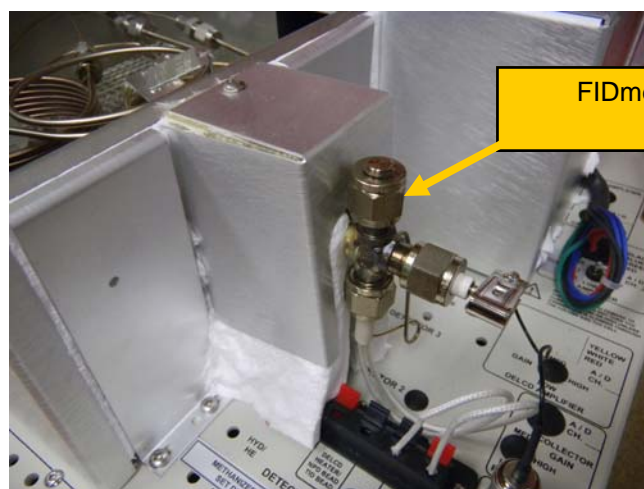
On the right side of the column oven is located the Thermal Conductivity Detector (TCD) which detects all the gases from 200ppm to 100% except hydrogen (see detailed explanation for this later).

Most MG5 configurations will also include a Flame Ionization Detector (FID) usually also including a Methanizer (FIDmeth) to enable the FID to also detect CO and CO₂ from 1ppm to 50,000ppm. The FID can only detect hydrocarbons like methane and ethane, but when equipped with a methanizer, CO and CO₂ are reacted to methane and thus detected at the same sensitivity as methane.

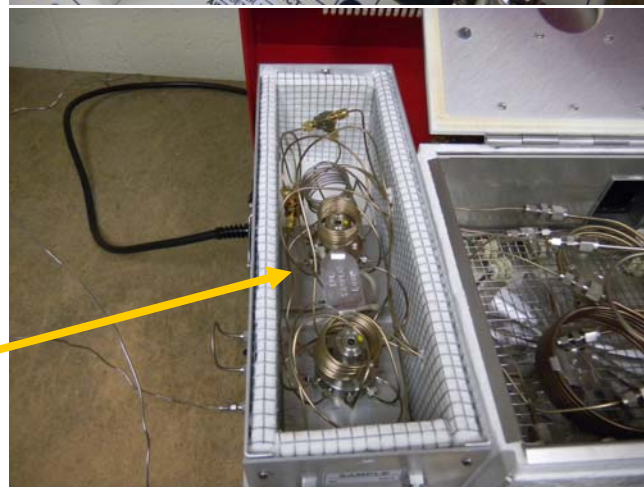
On the left side of the column oven is the valve oven, which contains two 10port Valco valves and lots of 1/16" stainless steel tubing.



TCD



FIDmeth



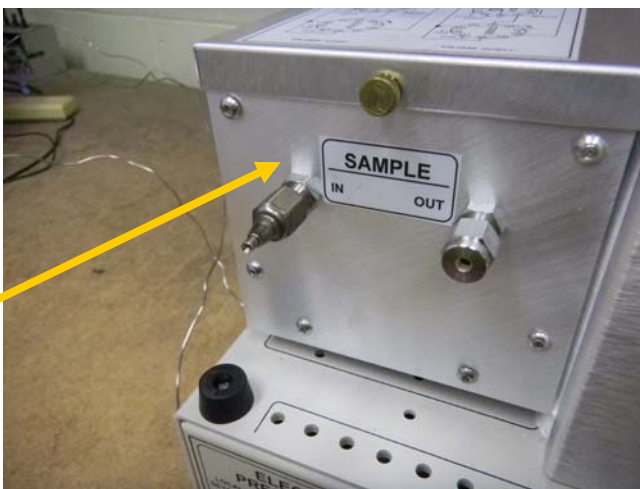
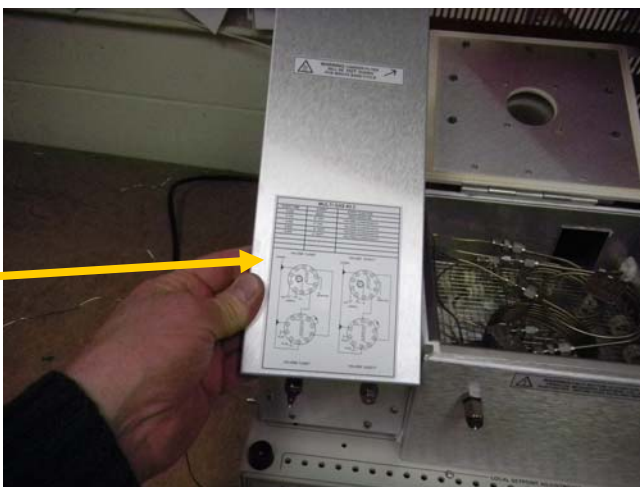
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The Valco 10port gas sampling valve (GSV) looks like this. There is an electric motor inside the GC which turns a Teflon seal inside the valve at a specific time during the analysis to change the carrier gas flow path.

We put a map on the cover of the valve oven so you can follow the carrier gas flow path in both positions (load and inject). It is important to understand the flow path to troubleshoot and optimize the analysis. It is also critical to understand that the valve does not “open” or “close”. Rather, the carrier flows in one path or the other, but it always flows continuously.

The sample to be analyzed is loaded at the front of the valve oven. The sample can flow from the “sample IN” through the “loop” and then out the “Sample OUT” continuously, or it can be flushed with new sample prior to starting an analysis. Normally it takes a minimum of 10ml of sample to flush the loop. There is no restriction or pressure to work against. You could blow through from “In” to “Out” with your mouth.



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The carrier gas is connected to the left side of the GC. The carrier gas can be helium, hydrogen, nitrogen or argon. Inside the GC there is a very precise pressure regulator called an “Electronic Pressure Controller” (EPC) which supplies the carrier gas at a stable pressure to the valves and columns.

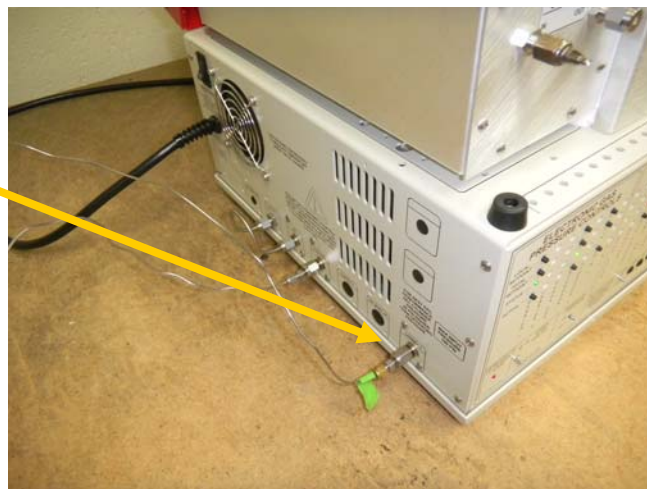
Helium is the most common choice because it gives the best overall results. However the sensitivity is not as good for hydrogen as it is for the other gases. This is because the TCD sensitivity depends on the difference of the “thermal conductivity” of the carrier gas relative to the sample molecule. The “thermal conductivity” difference between helium and hydrogen is very small

Hydrogen is sometimes used as carrier, but when it is, there is no sensitivity for hydrogen at all.

Nitrogen is sometimes used especially where it is important to measure hydrogen. Naturally, if nitrogen is used as carrier gas, there is no sensitivity to measure nitrogen.

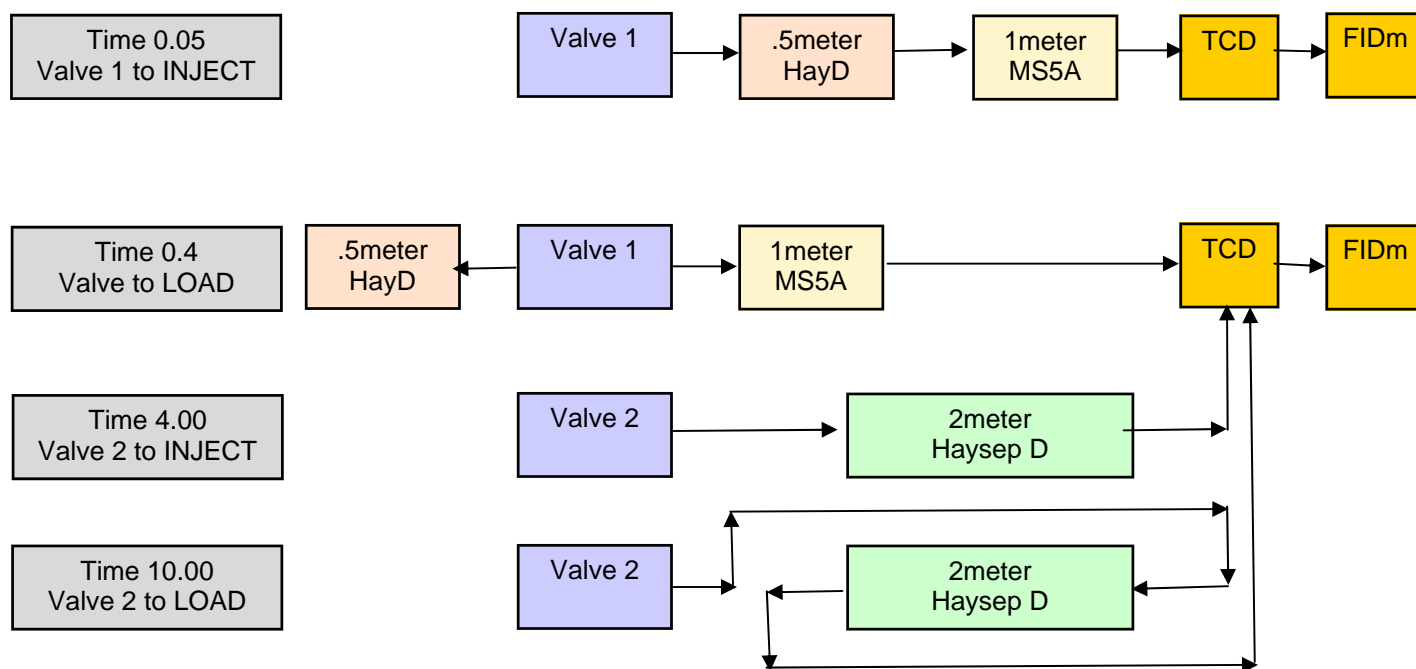
Argon is used where it is important to measure hydrogen and also oxygen and nitrogen.

If an FIDmethanizer detector is also installed, then hydrogen is also connected on the left side of the GC. Air is typically supplied from the built-in air compressor, but can also be supplied from an external air cylinder. Both hydrogen and air are required for the FID flame.



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The schematic above shows the 4 steps in the MG5 analysis after the sample has been loaded into the loop of each valve.

STEP 1: Valve1 is turned to the INJECT position (Relay G on). The carrier gas pushes the sample out of the valve loop onto the 5.meter Haysep D column. H₂, O₂, N₂ CH₄ and CO migrate through the .5meter HayD column very quickly and land on the 1meter MS5A column.

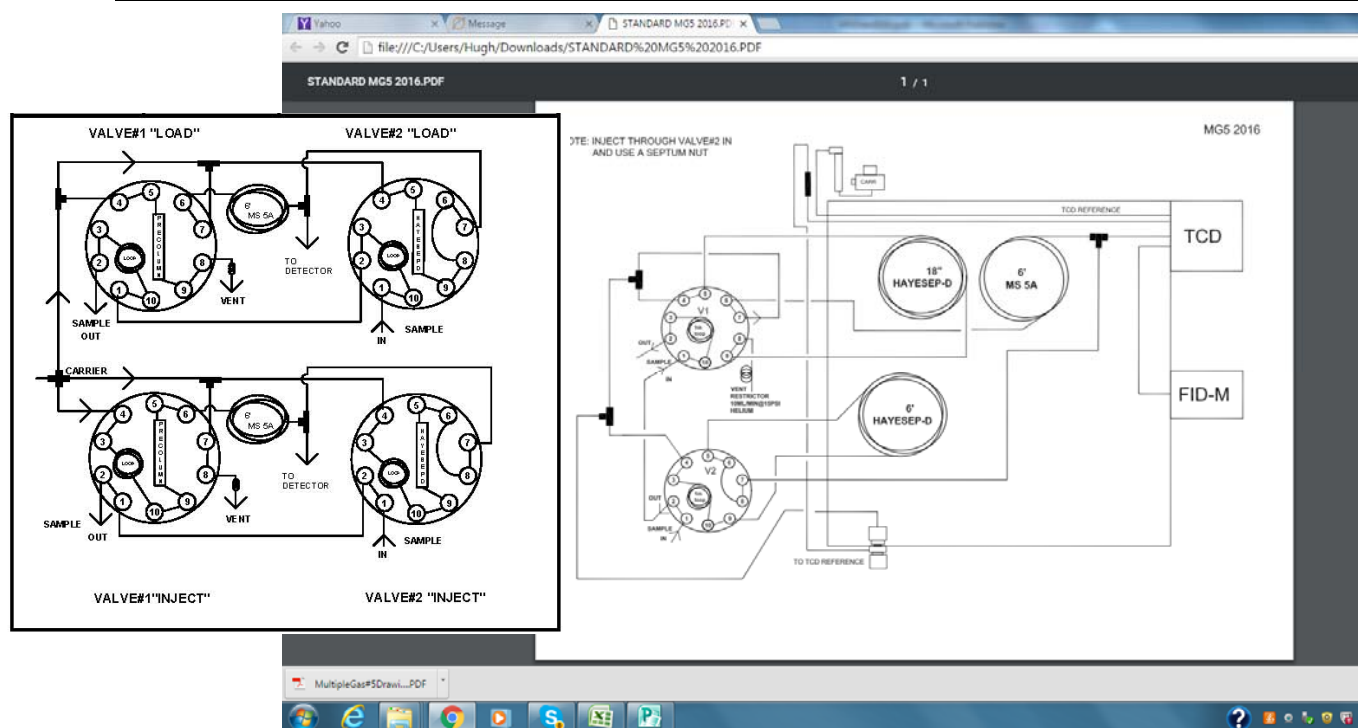
STEP 2: Valve1 is turned back to the LOAD position (Relay G off). Carrier gas continues to push the H₂, O₂, N₂, CH₄ and CO molecules through the MS5A column towards the detectors. Also carrier gas backflushes any remaining molecules backwards through the .5meter HayD column out to vent (not through the detectors). The molecules which remain on the .5meter column are CO₂, Water, and C₂ and higher hydrocarbons. These molecules would get stuck on the MS5A column if they were allowed onto the MS5A column. However, they easily backflush out of the HayD.

STEP 3: Valve2 is turned to the INJECT position (Relay F on). The carrier gas pushes the molecules in the loop of Valve2 onto the 2meter HayD column in the “forward” direction. H₂, O₂, N₂ and CO elute from the column very quickly as one peak, followed by the CH₄ peak, the CO₂, water and the hydrocarbons from C₂-C₆.

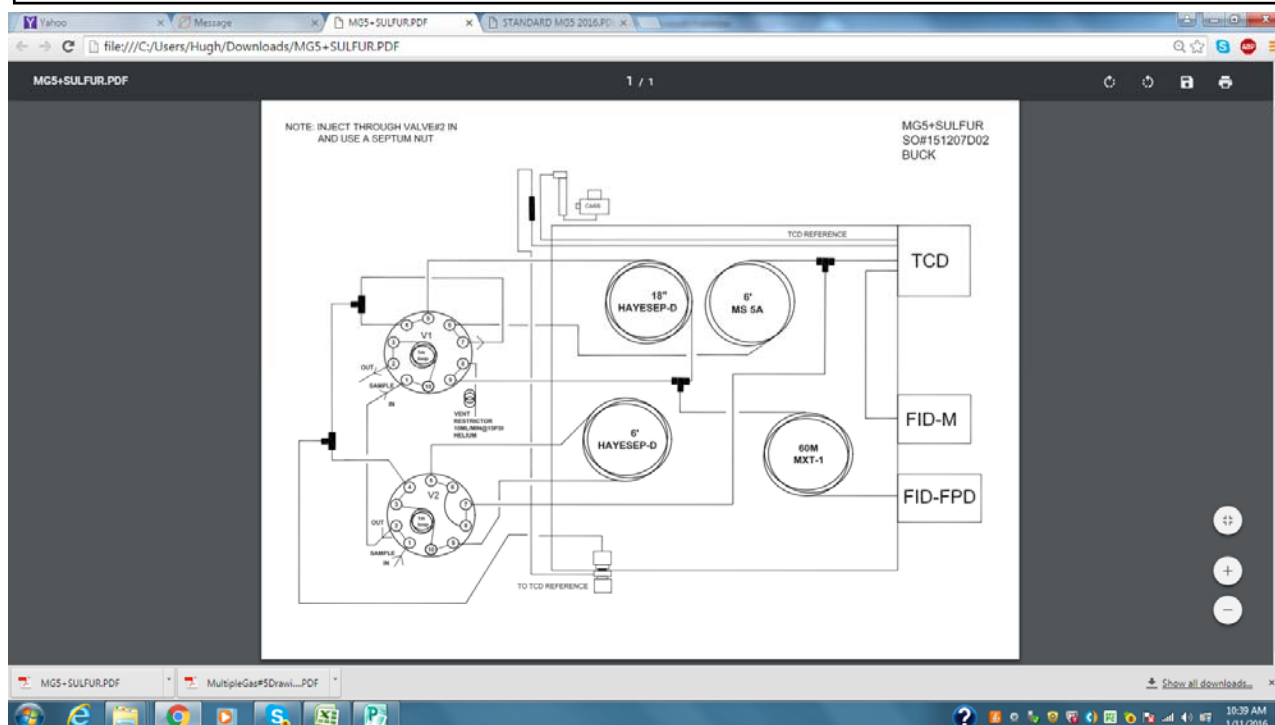
STEP 4: At some point in the analysis Valve2 is returned to the LOAD position. This reverses (back-flushes) the flow direction in the HayD column. Any peaks which have not yet exited the HayD column now back out of the column and into the detector. If, for example the analysis had no peaks after CO₂ (or you did not care about any peak after CO₂), then you would backflush after the CO₂ peak. Any peaks remaining in the HayD column would come out in a “lump”.

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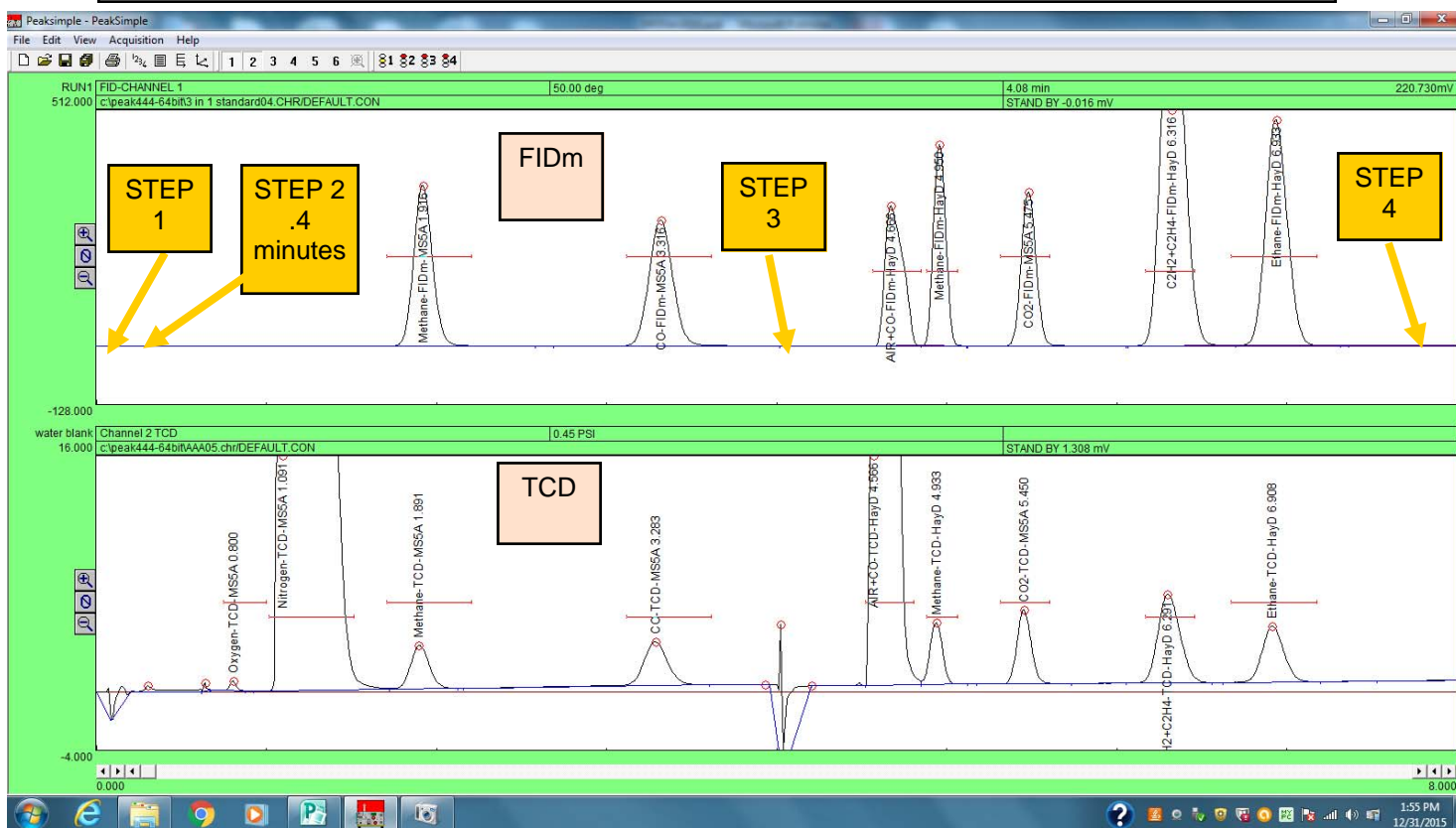


The diagram above shows a schematic of the "basic" MG#5 configuration with both valves in the INJECT position. A similar diagram below shows the "basic" MG#5 plus an additional column and FPD/FID detector to measure sulfur gases like H₂S, CO₂, SO₂, mercaptans, DMS etc.



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This is a typical chromatogram of gases at 1% in Nitrogen. The FIDmethanizer chromatogram is on the top and the TCD on the bottom.

STEP 1: Valve1 is turned to the INJECT position (Relay G on). The carrier gas pushes the sample out of the valve loop onto the 5.meter Haysep D column. H₂, O₂, N₂ CH₄ and CO migrate through the .5meter HayD column very quickly and land on the 1meter MS5A column.

STEP 2: Valve1 is turned back to the LOAD position (Relay G off) at .4 minutes. Carrier gas continues to push the H₂, O₂, N₂, CH₄ and CO molecules through the MS5A column towards the detectors. Also carrier gas backflushes any remaining molecules backwards through the .5meter HayD column out to vent (not through the detectors). The molecules which remain on the .5meter column are CO₂, Water, and C₂ and higher hydrocarbons. These molecules would get stuck on the MS5A column if they were allowed onto the MS5A column. However, they easily backflush out of the HayD.

STEP 3: Valve2 is turned to the INJECT position (Relay F on). The carrier gas pushes the molecules in the loop of Valve2 onto the 2meter HayD column in the "forward" direction. H₂, O₂, N₂ and CO elute from the column very quickly as one peak, followed by the CH₄ peak, the CO₂, Water and the hydrocarbons from C₂-C₆.

STEP 4: At some point in the analysis Valve2 is returned to the LOAD position. This reverses (back-flushes) the flow direction in the HayD column. Any peaks which have not yet exited the HayD column now back out of the column and into the detector. If, for example the analysis had no peaks after CO₂ (or you did not care about any peak after CO₂), then you would backflush after the CO₂ peak. Any peaks remaining in the HayD column would come out in a "lump".

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The screen at right shows the oven temperature program used.

STEPS 1 and 2 occur while the column oven is at 50C. After 1 minute, the column temperature increases to 90C and stays there until after STEP 3. Then the column temperature increases to 270C.

At some point while the column temperature increases, STEP 4 occurs, backflushing any un-eluted molecules.

The channel 1 Event table is shown at right.

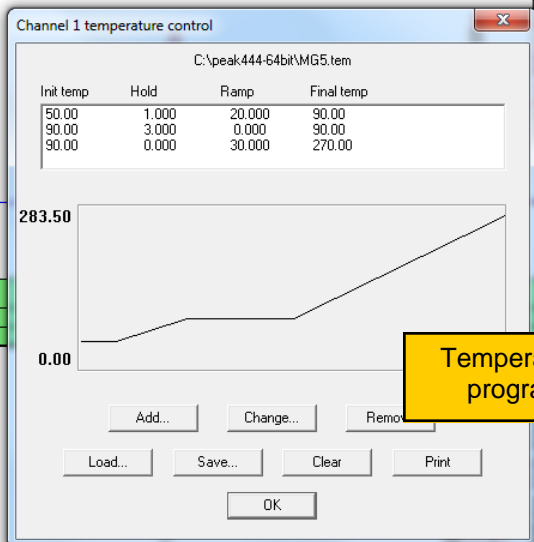
At time 0.05 Relay G turns on. This initiates STEP 1.

At time 0.4, Relay G turns off.

At time 4.00 Relay F turns on initiating STEP 3.

At time 8.0 Relay F turns off back-flushing the Haysep D column to the detectors.

The exact times may change if the carrier flow rate changes or if a different carrier gas is used. The back-flush time (STEP 4) especially may change depending on what molecules are in the sample.



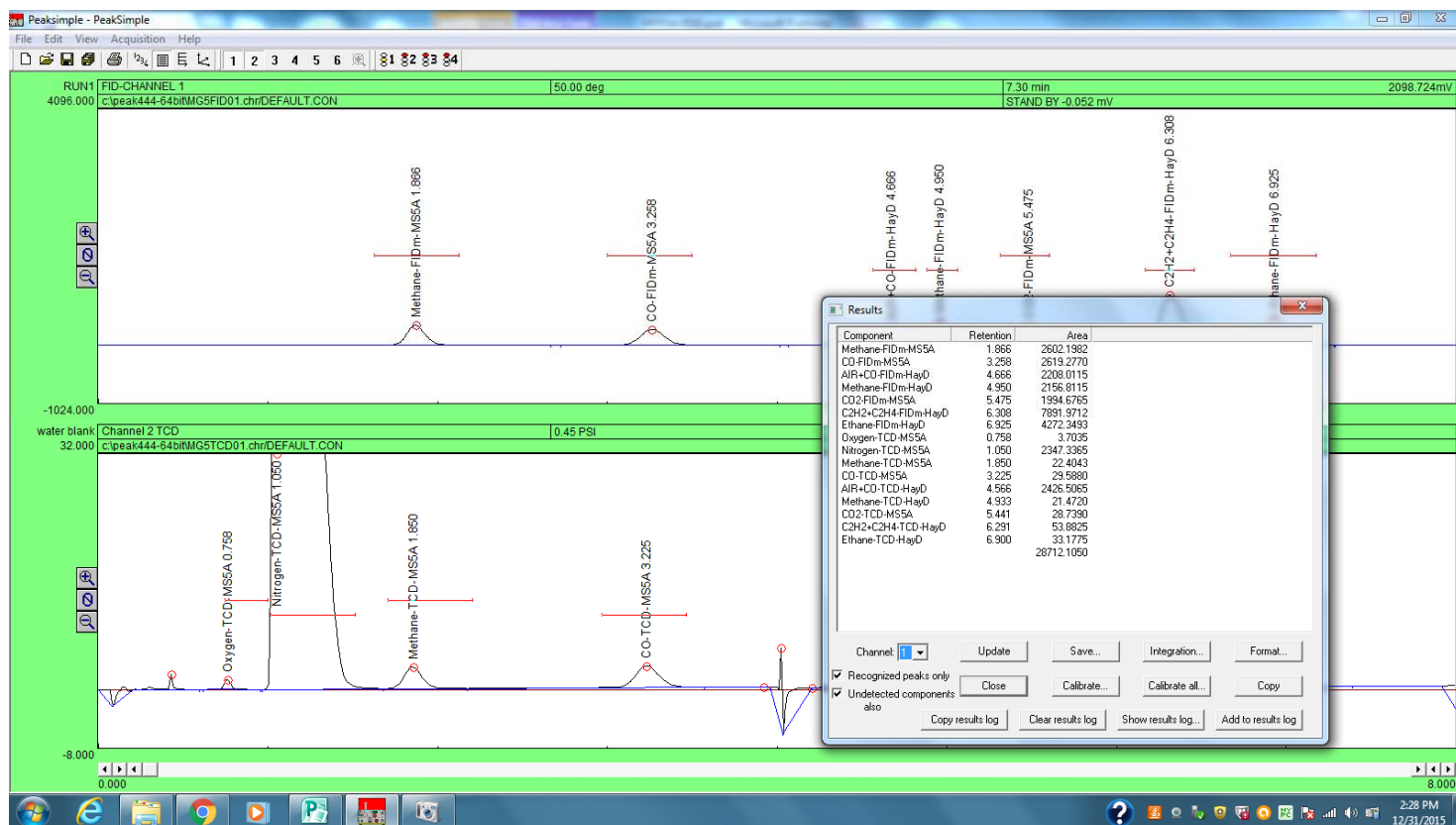
The screenshot shows the 'Channel 1 events' window. It contains a table with the following data:

Time	Event
0.000	ZERO
0.050	G ON (Valve1)
0.400	G OFF (Valve1)
4.000	F ON (Valve2)
8.000	F OFF (Valve2)

A yellow callout box labeled 'Channel 1 Event table' points to the table.

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The sample above (helium carrier at 15psi) shows 1% each methane, CO, CO2, ethane, ethylene and acetylene with a little oxygen, and nitrogen balance. Note that the area of the methane, and CO peaks are about the same on the FIDm, and similar but not identical on the TCD.

This shows that the methanizer is working 100% since every molecule of CO is converted to one molecule of methane.

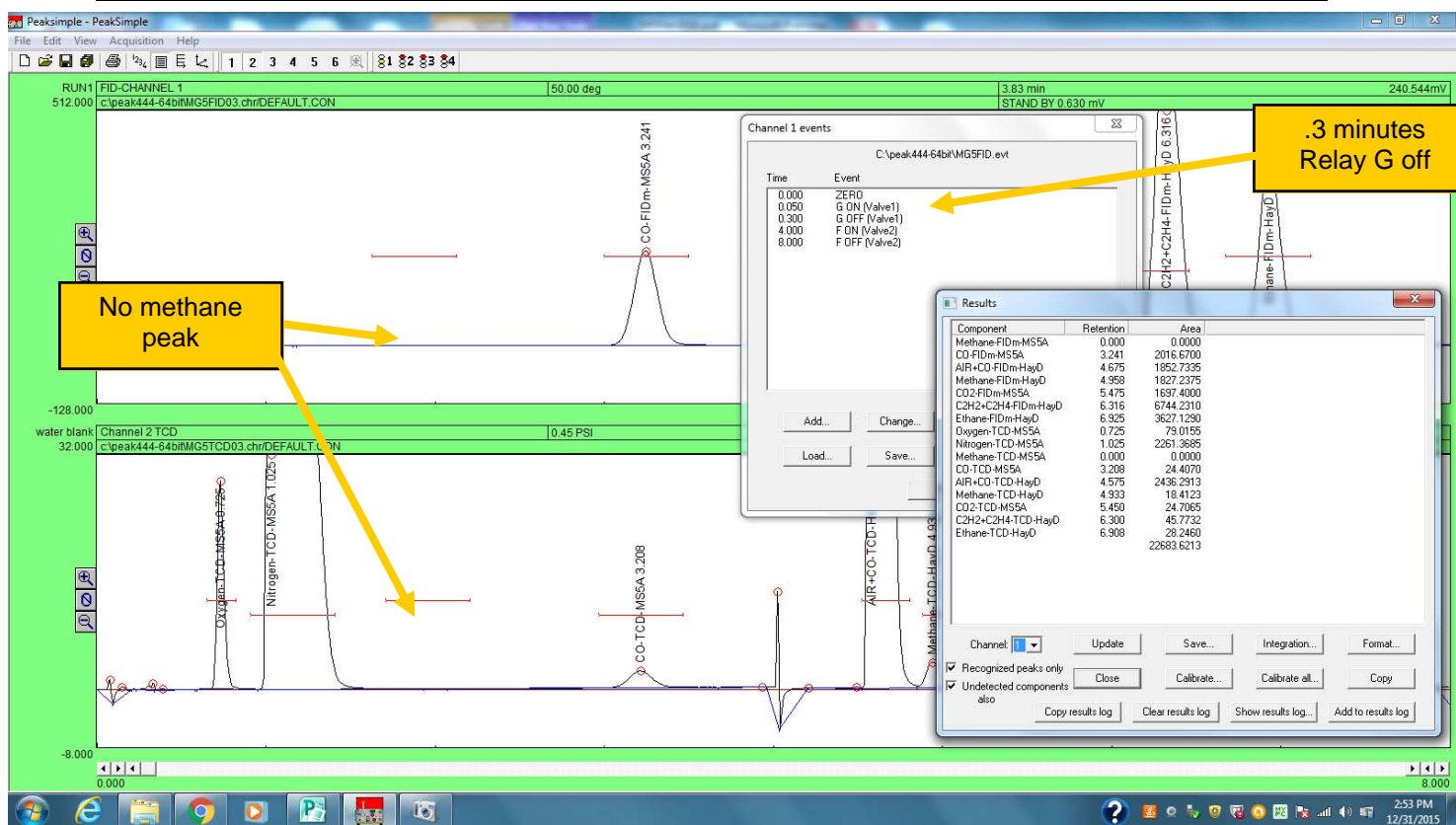
It also shows that the Valve 1 timing (Relay G off at .4 minutes) is correct.

Methane and CO have different thermal conductivities so on the TCD the peak areas are slightly different from each other.

Note that on a HaysepD column, ethylene and acetylene co-elute. A different flavor of Haysep (Haysep N for example) can be substituted to separate these two molecules.

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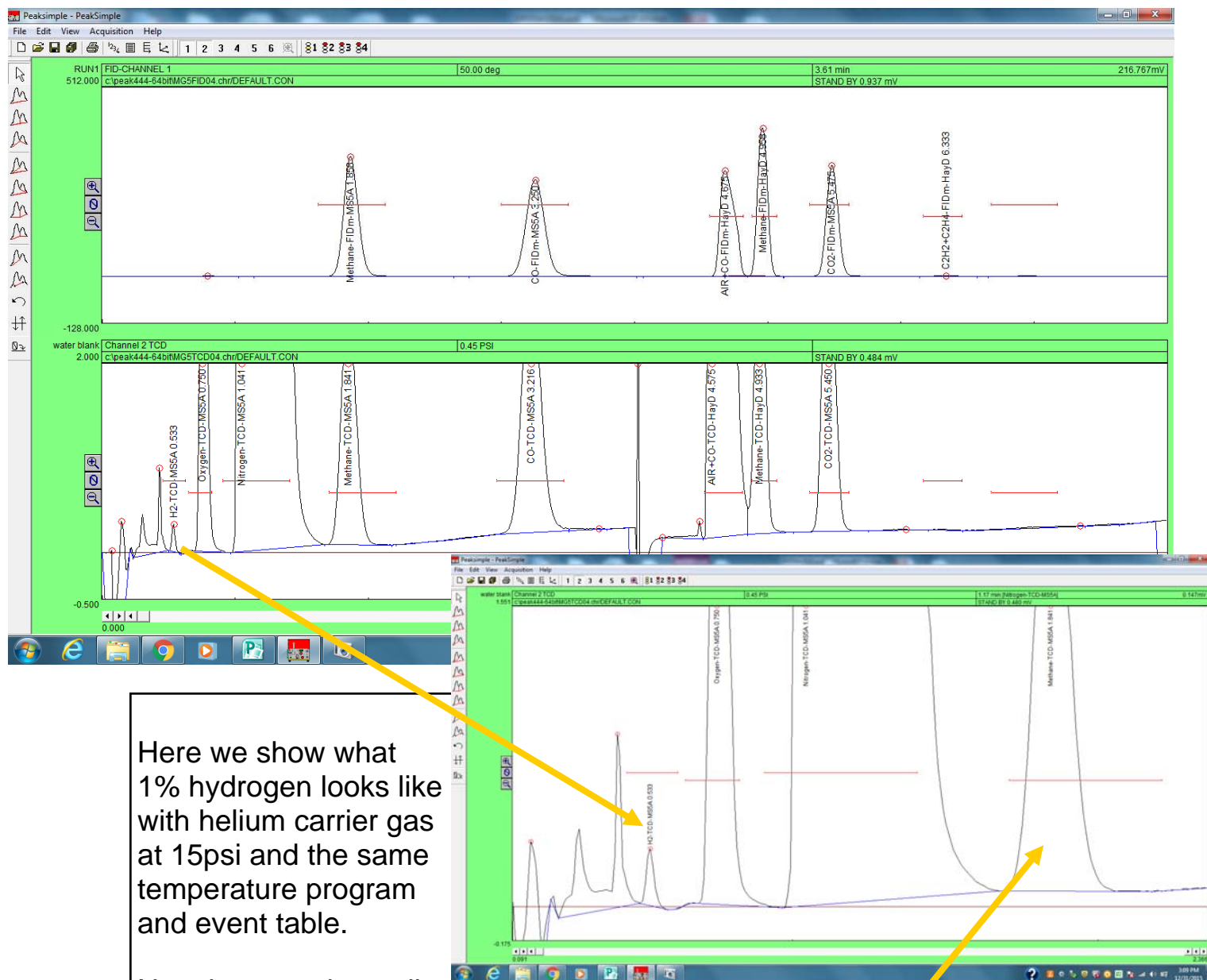


Compare the same sample but with Relay G off at .3 minutes instead of .4 minutes as in the previous page. The methane peak has disappeared because the time that Relay G turned off was too early, so the methane peak did not make it onto the MS5A column and was back-flushed off the pre-column (.5meter HayD) to vent.

If you change carrier gas types (argon instead of helium), carrier flow rates, column types (MS13X instead of MS5A), or column lengths, you will have to determine the correct timing by trial and error.

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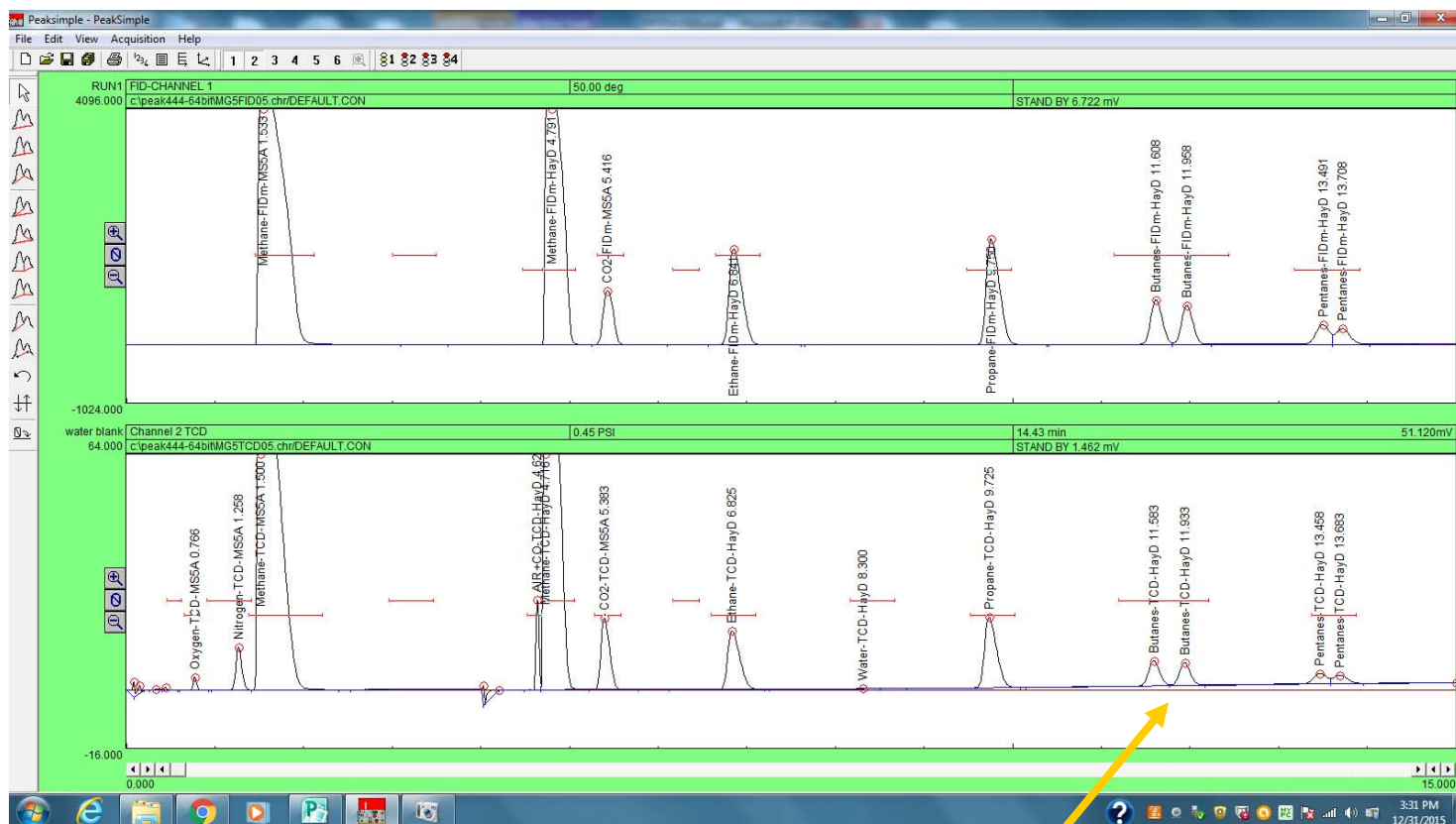


Here we show what 1% hydrogen looks like with helium carrier gas at 15psi and the same temperature program and event table.

Note how much smaller the 1% hydrogen peak is than the 1% methane peak.

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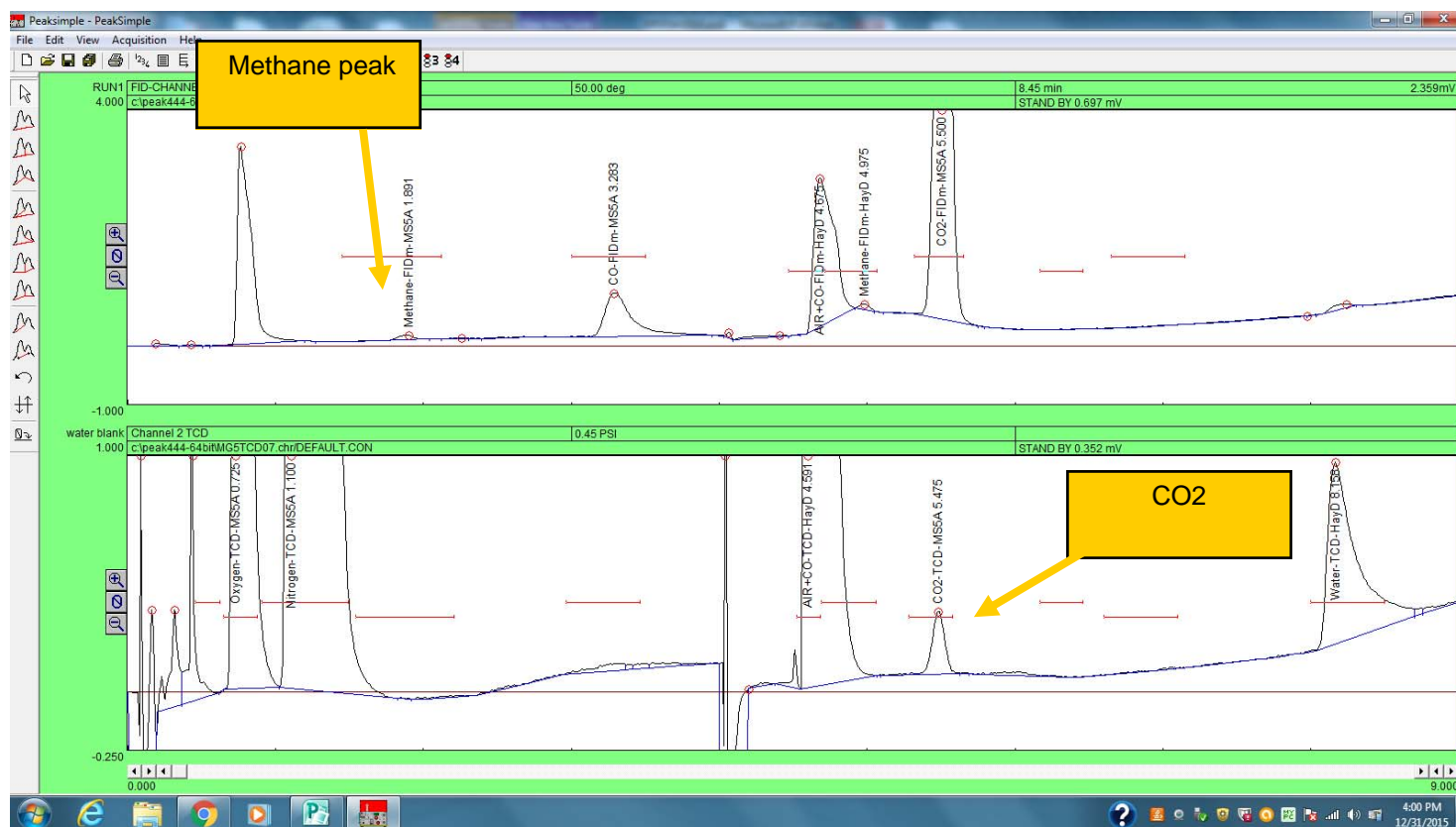
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This is natural gas. Notice there is no CO, but plenty of butanes and pentanes. There is also a water peak on the TCD.

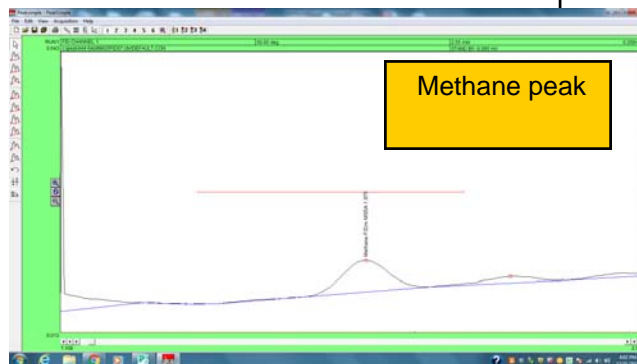
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This is room air which has 2ppm of methane, 400ppm of CO₂ and 10,000ppm of water.

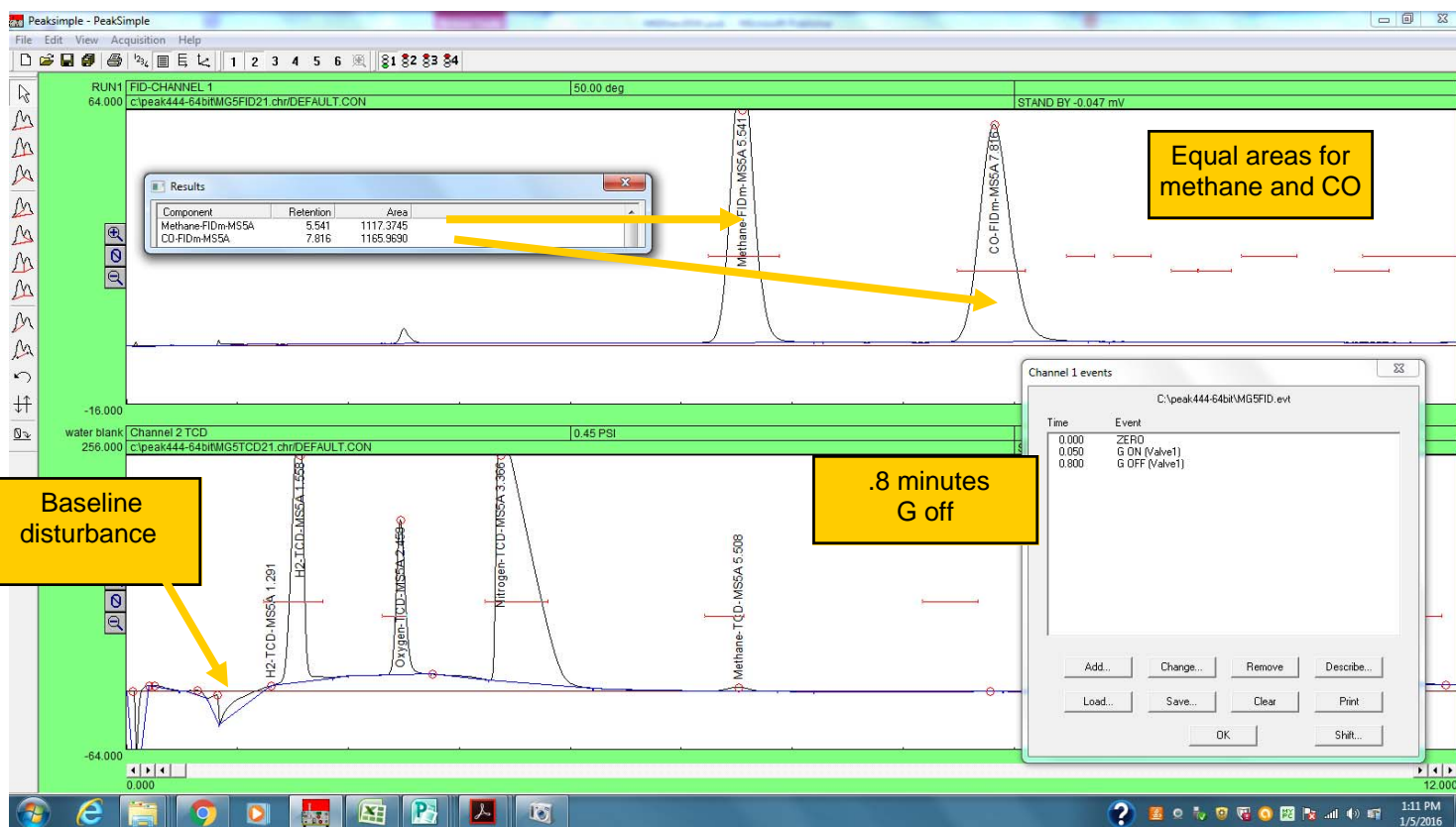
Notice the 2ppm methane peak is easily detectable on the FIDmethanzier, and the 400ppm CO₂ peak easily detectable on the TCD.



The room air in this case also apparently had some CO.

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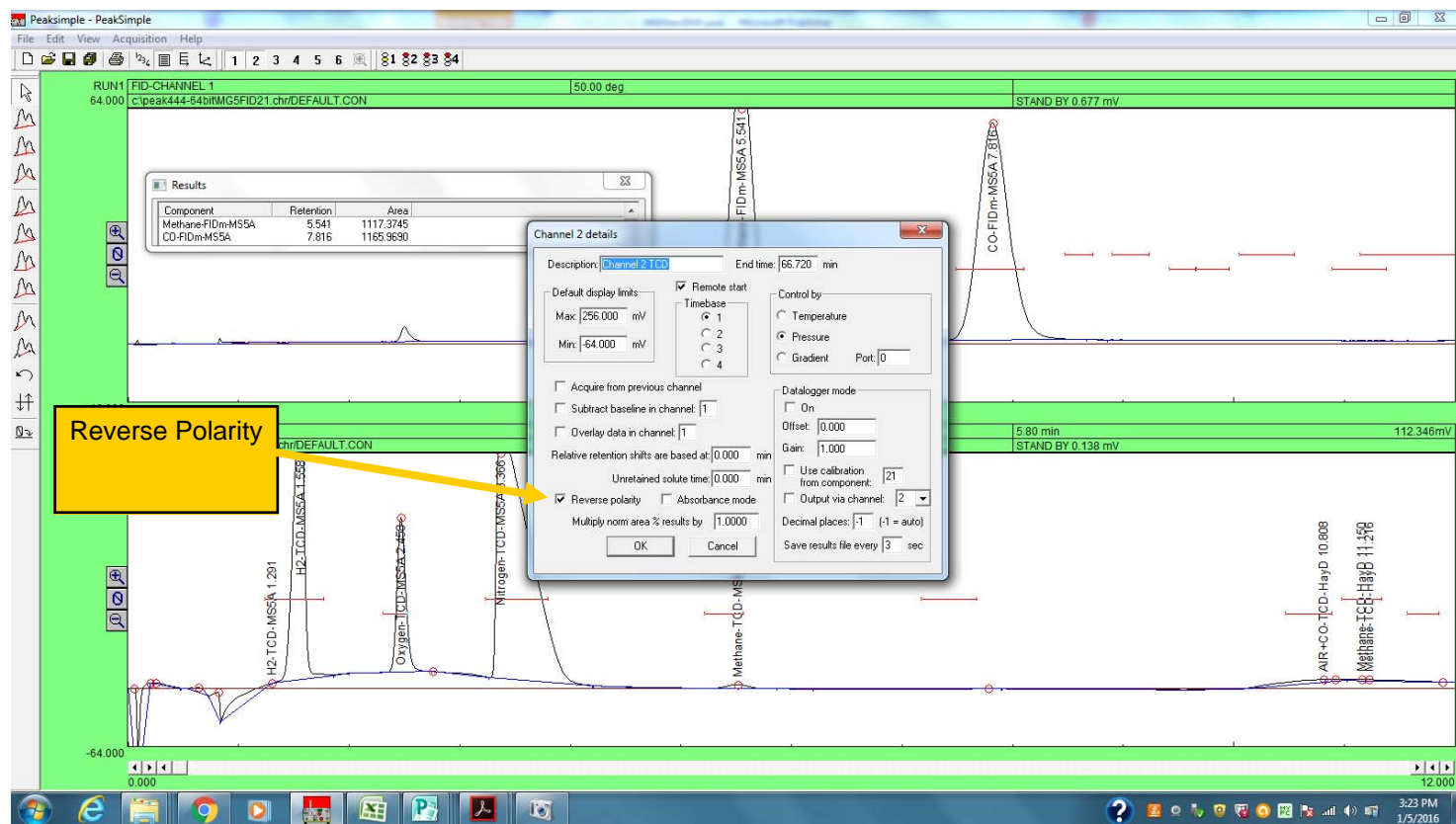
If hydrogen measurement is a priority its is best to use Argon carrier gas instead of helium. Because there is an un-avoidable baseline disturbance when Relay G turns off and backflushes the pre-column, it may make sense to use a 6 foot MS5A column instead of the 3 foot MS5A column. The 6' column makes the Hydrogen peak come out a little later giving the baseline a chance to stabilize before the H2 peak begins.



6' and 3' MS5A columns

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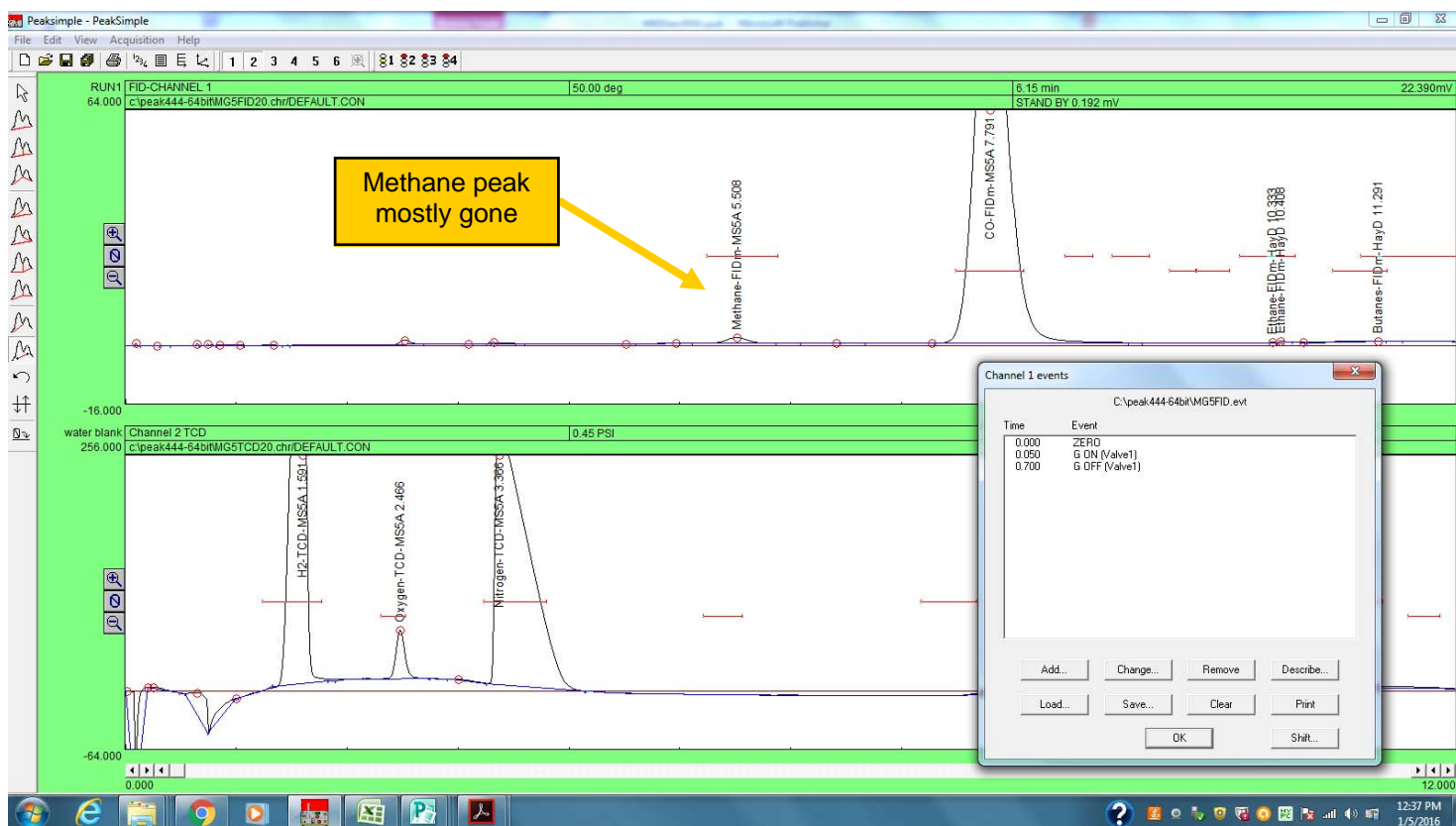
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When using Argon or Nitrogen carrier gas the peaks come out upside down. In the channel 2 Details screen, click the box labelled “Reverse Polarity” so the peaks will come out in the positive direction.

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The exact time for Relay G off (backflush pre-column) will be different using Argon vs Helium. By trial and error move the Relay G off time earlier and earlier until you see the methane peak disappear.

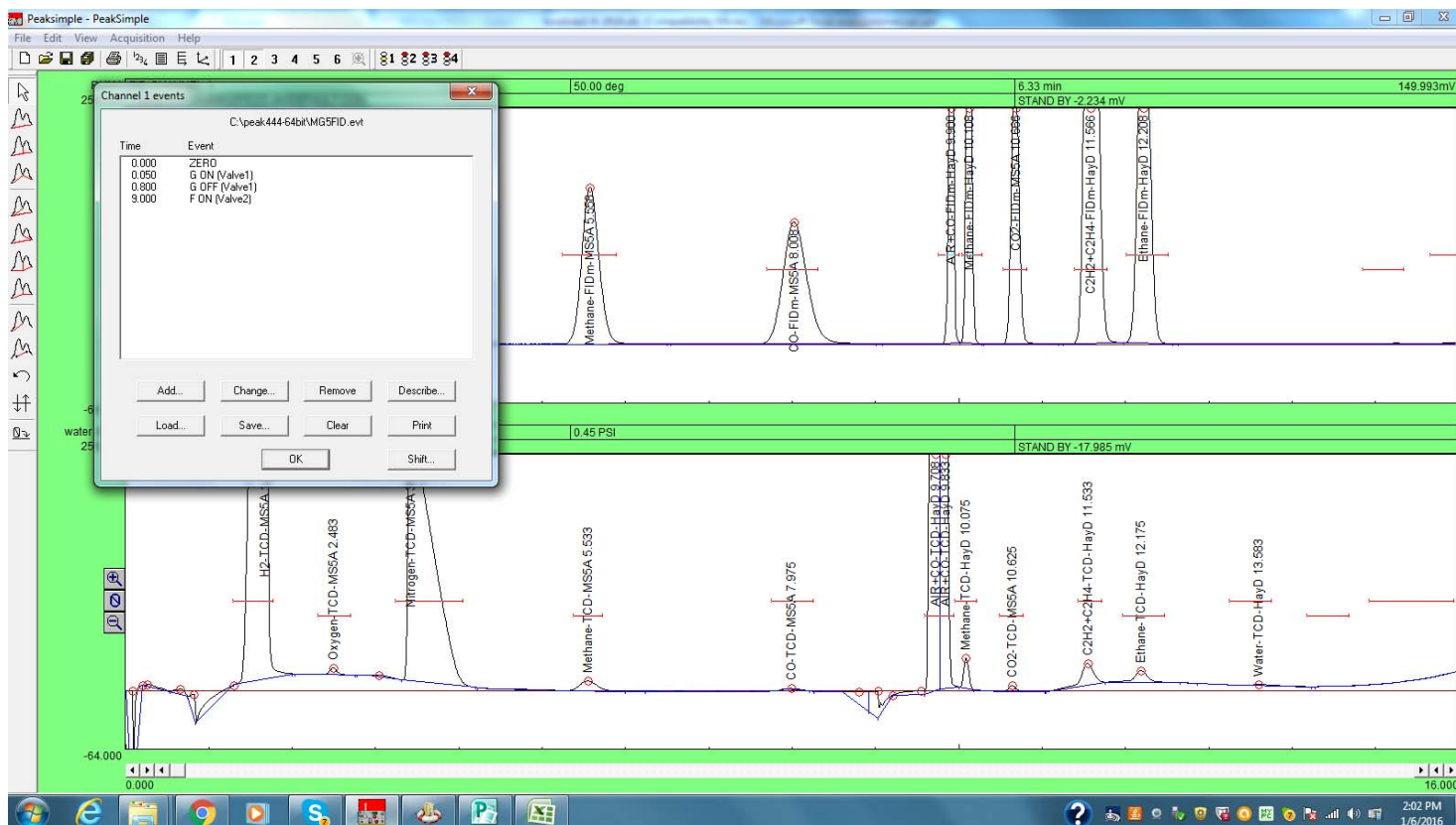
Compare this analysis to the same analysis on page 13.

Both methane and CO are present in the sample at 1% and have similar area count in the page 13 analysis with Relay G off set to .8 minutes.

In the analysis above the Relay G off time is .7 minutes which was early enough to backflush the methane peak (which was still on the pre-column) , yet allow the CO peak to make it through onto the MS5A column.

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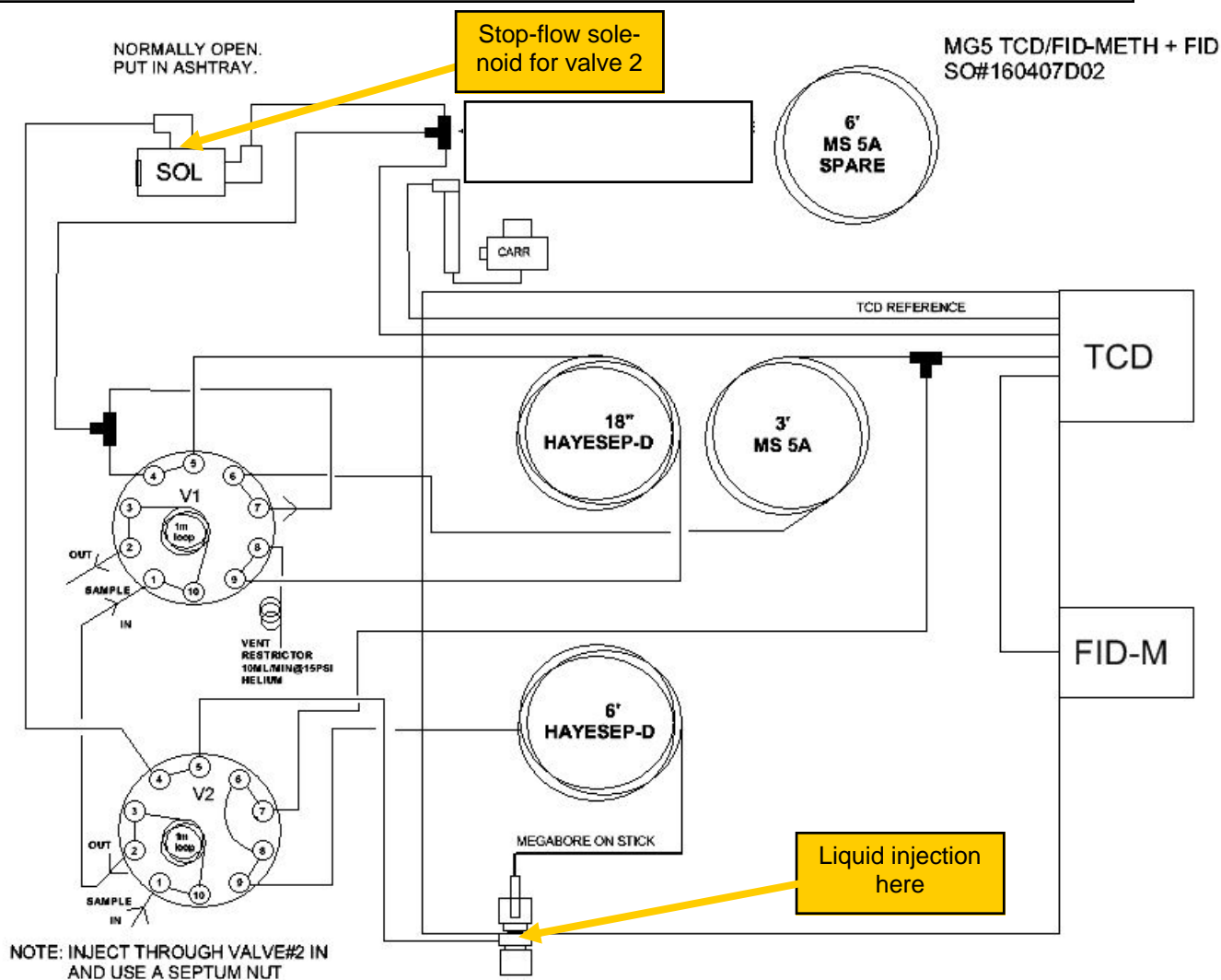
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The chromatogram above shows the full analysis including the C2 peaks. Note that the Relay F on time (inject onto the Haysep column) had to be delayed until 9 minutes to allow the CO to elute from the 6'MS5A column before making the injection onto the Haysep column.

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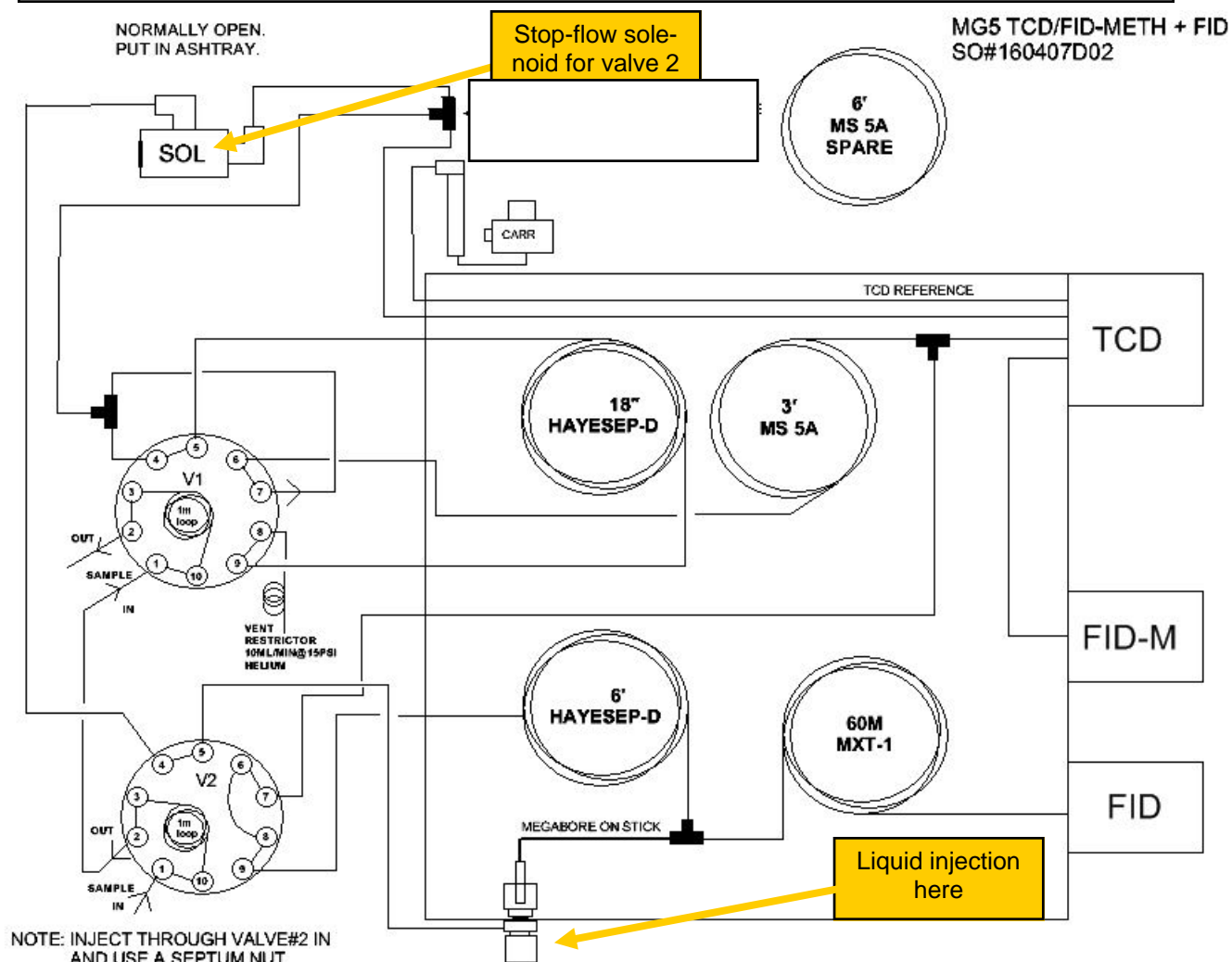


Starting in March of 2016 all MG5 configurations were slightly modified:

- 1) The Haysep D column (and sometimes a capillary column) are connected to the injector port to make it easy to perform a liquid injection or small volume gas injection **without** using the gas sampling valves, and without having to reconnect columns inside the column oven. The low volume or liquid injection can only be made into the Haysep column, not the Mole sieve.
- 2) A solenoid valve can interrupt the carrier gas to the Haysep valve and column. This allows both valves to inject at the same time if that is critical to the analysis (the normal MG5 valve sequence injects valve 1 immediately, and valve 2 some minutes later). When injecting both valves simultaneously, the solenoid is closed (Relay A ON usually) just after the valve injection to stop-flow the peaks in the Haysep D column until the MoleSieve peaks have eluted. An example of this is shown later in this document.

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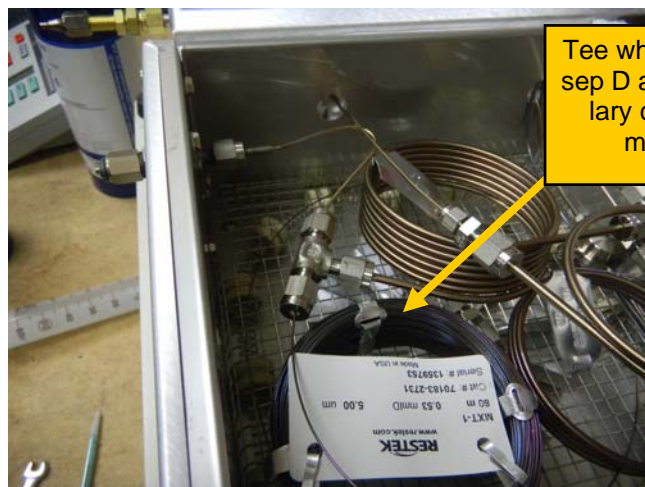
This drawing shows a capillary column and extra FID detector connected at a "tee" fitting so a liquid injection (or low volume gas injection) splits onto the capillary and the Haysep column.

In this configuration neither Valve 1 or Valve 2 is actuated at the beginning of the analysis. Valve 2 may optionally be rotated to the Inject position to backflush the Haysep column after the capillary peaks have eluted. See next page.

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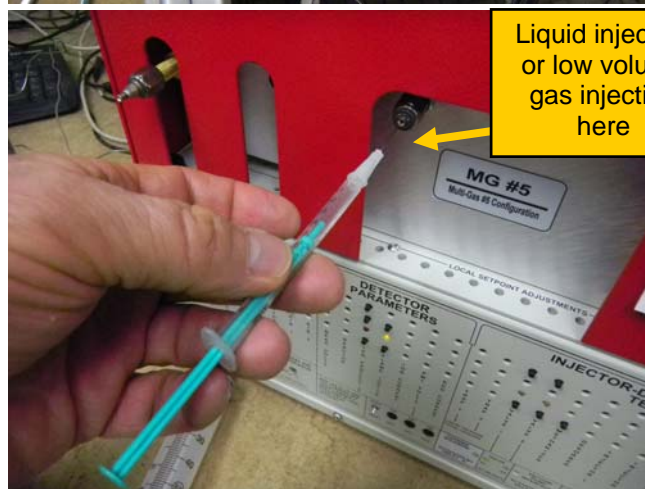
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When a capillary column is configured along with the Haysep column it can be connected at one of two places. Here it is shown connected to a "tee" fitting where one leg of the tee is the capillary column, the second leg is the Haysep column and the third leg is connected to the on-column injection port using a small adapter.



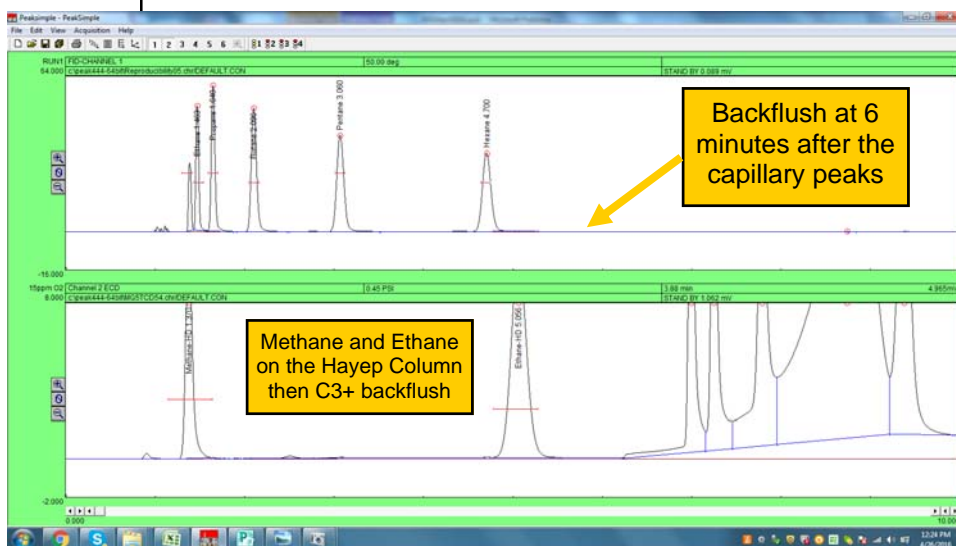
Tee where Haysep D and capillary column meet.

When making a low volume gas injection you do not need to use the gas sampling valves at all, unless you want to backflush the Haysep column after the capillary column peaks have eluted.



Liquid injection or low volume gas injection here

Here is a chromatogram of C1-C6 hydrocarbons injected via a gas tight syringe and backflushed at 6 minutes after all the peaks had eluted from the capillary column.



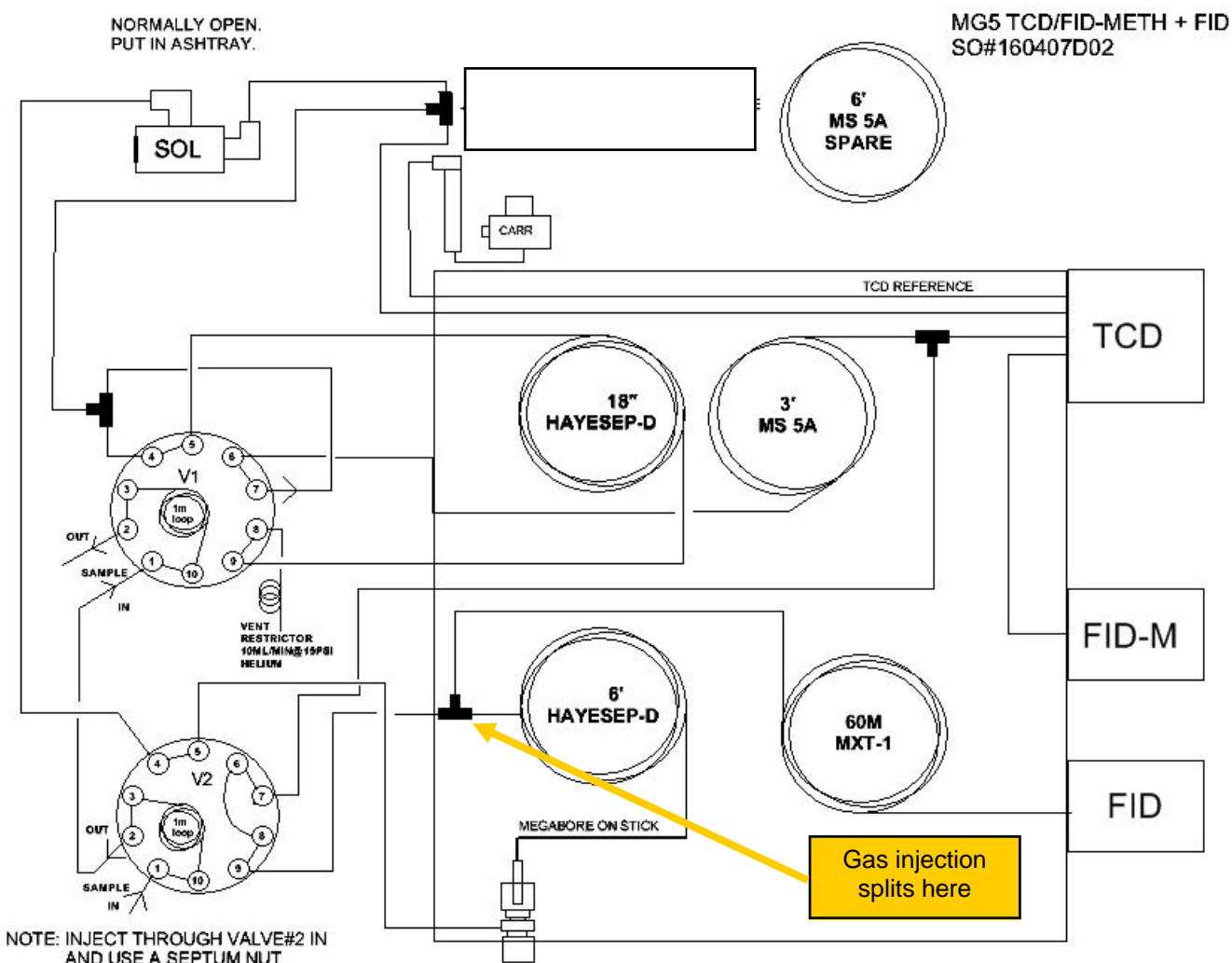
Backflush at 6 minutes after the capillary peaks

Methane and Ethane on the Haysep Column then C3+ backflush

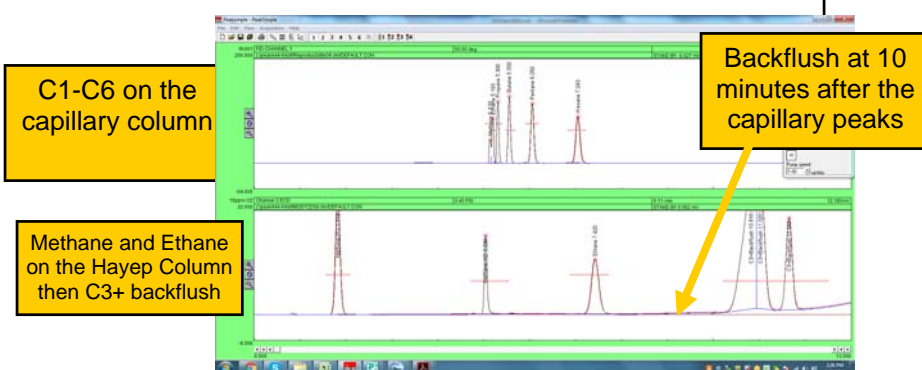
If you need to quantitate the backflush, the gas sampling valve loop must have a carrier gas purge to avoid injecting peaks which might be in the loop. See the diagram to understand.

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- 1) This drawing shows a capillary column set up for gas injection from the gas sampling valves onto both the Haysep and capillary column.

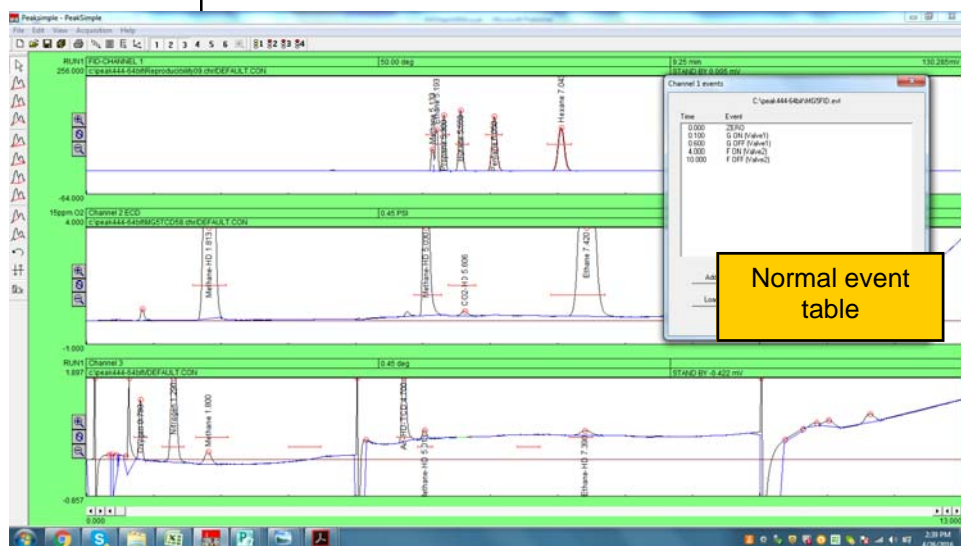


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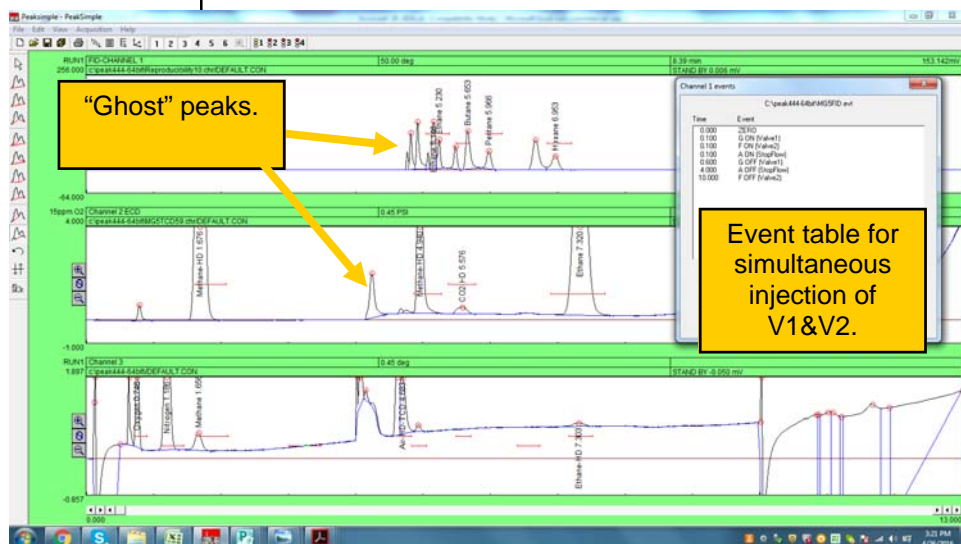
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There are some applications where the time delay between injecting the sample in Valve1 and Valve2 is important and un-desirable.

The top chromatogram shows the normal MG5 valve sequence/event table. The sample was 1000ppm C1-C6 aliphatic hydrocarbons. V1 injects at .1minutes. V2 injects at 4 minutes.



This chromatogram shows the same sample but with Valve 1 and 2 injected simultaneously. Relay A is turned ON at the same time (.1minute) which stops the carrier gas flow in the Haysep and capillary columns. This creates some extra "ghost" peaks but does not substantially affect the analysis. The stop-flow solenoid is turned OFF (re-establishing the flow) at 4minutes.



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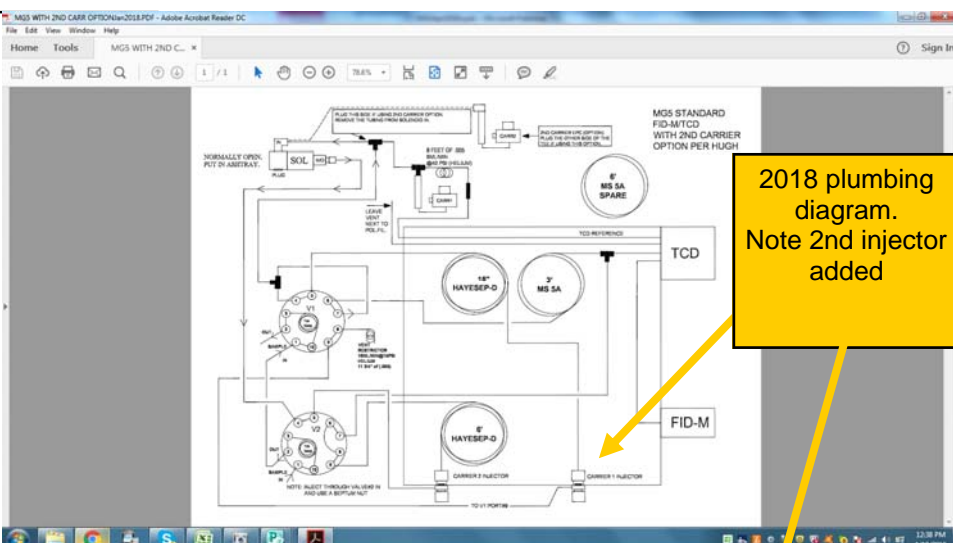
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All Multiple Gas#5 GCs built after January 1 2018 also include a second on-column injector to allow low volume syringe injections onto the MS5A column for separating H₂, O₂, N₂ CH₄ and CO.

Valve 1 (Relay G) must be placed in the INJECT position prior to making the syringe injection. Otherwise the analysis and event times are the same as when using the valve to make the injection.

The Valve 1 loop must be purged with carrier gas to avoid injecting whatever might otherwise be in the loop.

A simple way of purging the loop with carrier gas is to connect the "vent" output to the sample in port as shown.



Addendum - Chromalytic Technology 2014>

HayeSep-D ONLY elutes / separates CO / CO₂ and moisture adequately

- Understandably hydrophobic and not very selective for polar molecules
Other HS-X not very effective for CO/CO₂ etc (largely untested by us

Use High Purity Helium and/or OxyTrap as Carrier gas

HayeSep-D Bleeds badly >120DegC from our experience with sever +ve baseline drift and limits elution to about propanol / MEK at 200DegC (!0.1% 1ul)) on TCD & FID

- SRI TCD appears to suffer sever baseline drift during temp programming due to the use of EPC control and the inherent flow sensitivity of the TCD design.

- Conventional Mass Flow controllers are required for baseline stability during PTGC

upper T limit has not been determine by CT with decent Helium

Don't rely on commercial Helium Suppliers and their "high purity" gases