

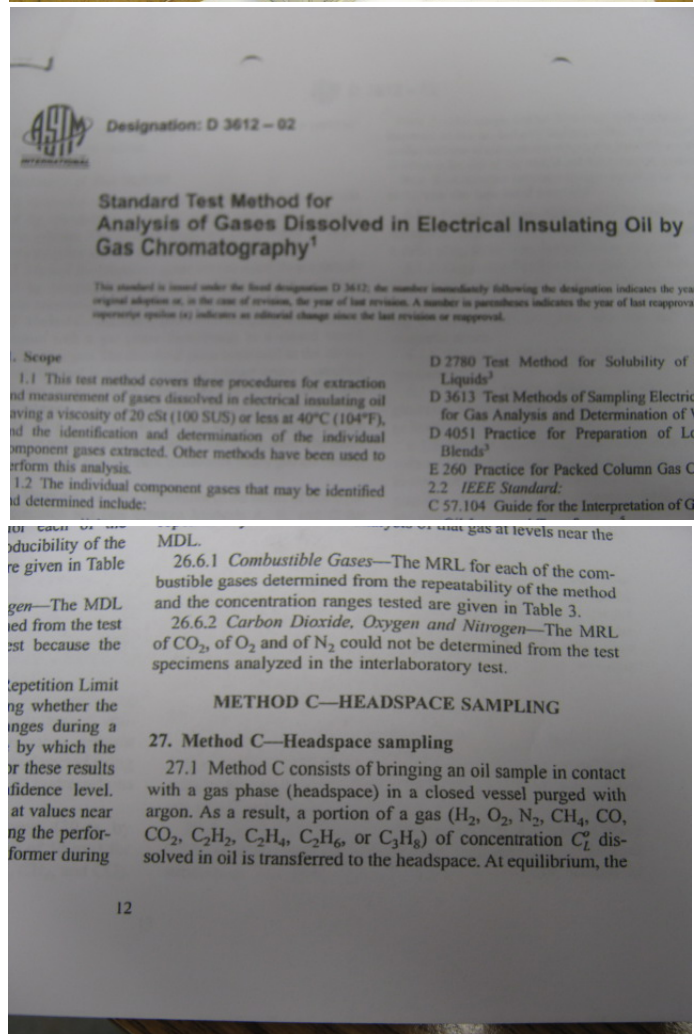
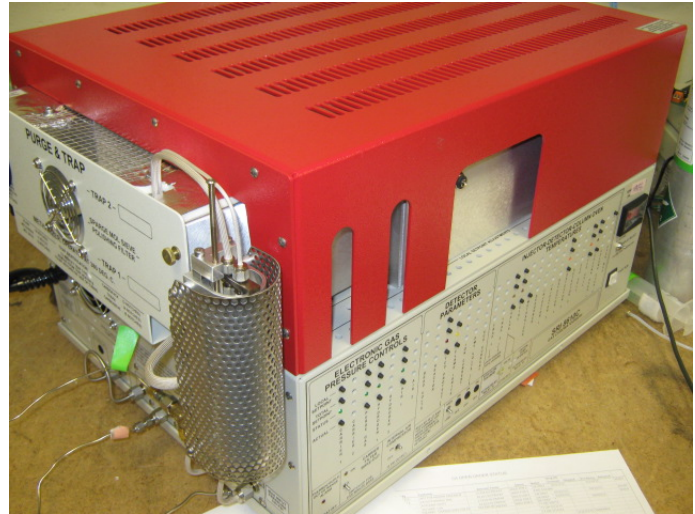
ASTM 3612/TOGA/Dissolved Gas GC

Revised October 2013

The SRI ASTM 3612/TOGA/ Dissolved Gas GC configuration (TOGA GC) permits measurement of gasses dissolved in water, oil or other liquids, and is based on the requirements of ASTM method 3612, option C, which specifies the use of headspace to extract the gas molecules from the liquid.



A headspace vial like the 40ml vial shown above is half filled (20ml) with liquid and then the gas above the liquid is purged with inert gas like argon, nitrogen or helium. Gases (CH₄, CO, CO₂ etc) which are dissolved in the liquid then escape into the inert headspace where they accumulate until an equilibrium is reached. Those gases are then injected into the GC.



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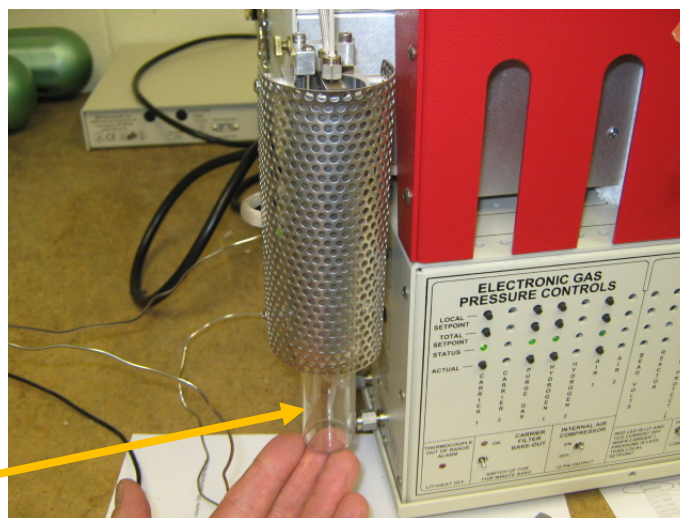
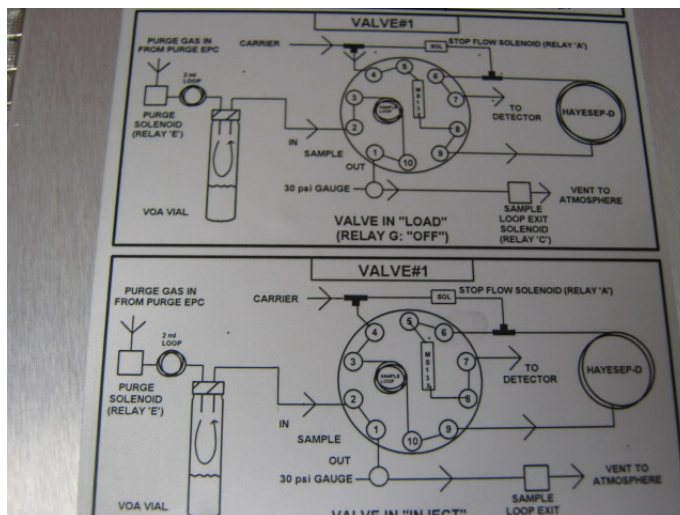
The GC is configured with two detectors (TCD and FID/Methanizer) which are connected in series at the end of the two separation columns (Haysep-D and Haysep-N).

A 10port gas sampling valve (GSV) injects 1ml of headspace gas into the columns where the various gas molecules are separated. The valve is connected as shown. This diagram is also displayed on the cover of the GC's valve oven.

The valve is plumbed to backflush the columns when the peaks of interest (H₂, CO, CO₂, ethane, ethylene and acetylene have eluted.

Before measuring liquids, it is helpful to inject the calibration gas itself with no liquid in the vial. This permits the operator to optimize the separation of the gases of interest, identify and calibrate the peaks etc.

Take a new empty 40 ml vial with septum cap (CRS part# 279545 www.chromres.com) and slide it into the headspace sampler from the bottom.



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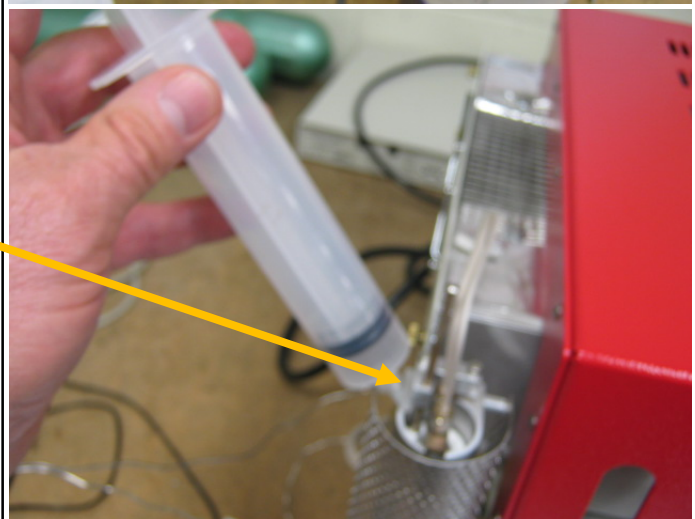
Make sure the 40ml vial is inserted all the way so you can see the septum. As the vial is pushed upwards, the septum is pierced by two needles.

Find some calibration gas which contains the molecules you want to measure in the liquid. In this example we are using a mix which contains 1% each of H₂, O₂, CO, CH₄ and CO₂ in nitrogen. Other gas mixes are available which might also include C₂H₆, C₂H₄, C₂H₂ and others.



Withdraw 20ml of the calibration gas into a 60ml syringe with 27gauge needle (supplied with GC) and then push the calibration gas into the vial as shown. Pierce the vial's septum with the 27 gauge needle at an angle.

Use a new septum each time since the holes from a previous puncture will leak.



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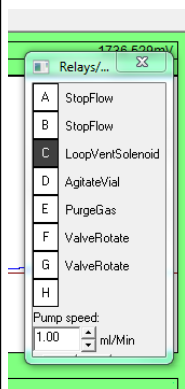
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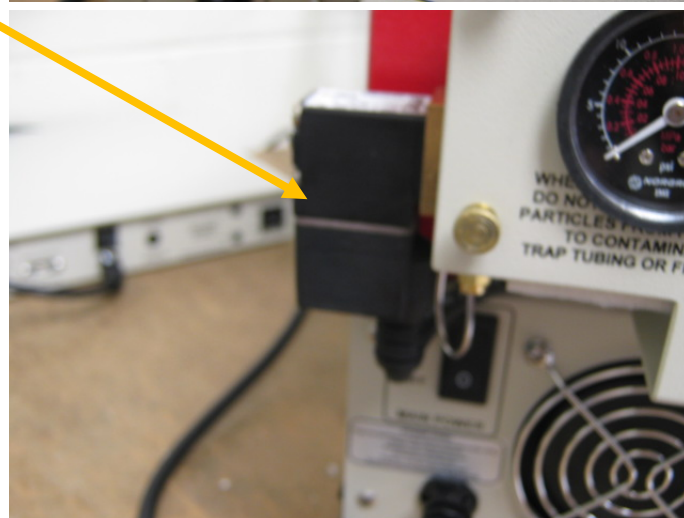
As you push the calibration gas into the vial you should see the vial pressure increase.

20ml into a 40ml vial should result in a pressure of .5bar (8psi). The pressure will remain indefinitely if the vial is not leaking. Because 20 ml of calibration gas was added to 40ml of air in the vial the resulting concentration of the calibration gas in the vial is 3 times less that it was coming out of the calibration gas cylinder.

Use the View/Relay-Pump Window to actuate Relay C. This opens the solenoid mounted at the rear of the valve oven which releases the pressure in the vial through the 1ml sample loop. (See the valve diagram to visualize the path that the gas takes).



The loop is now filled with diluted calibration gas.



FPD sig



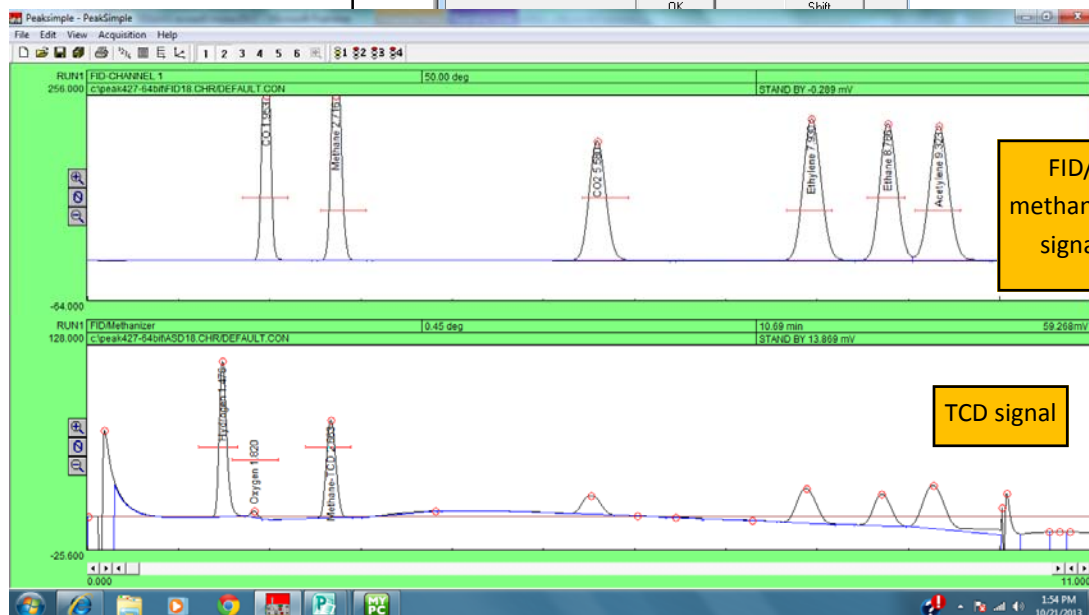
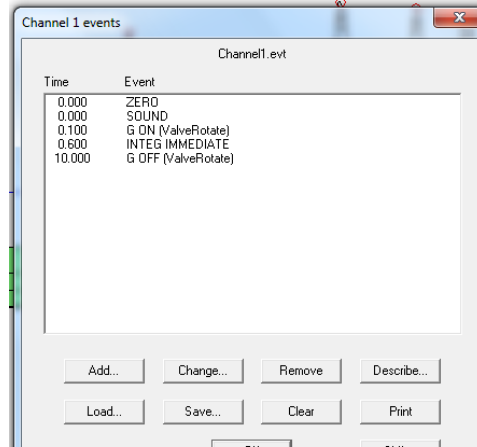
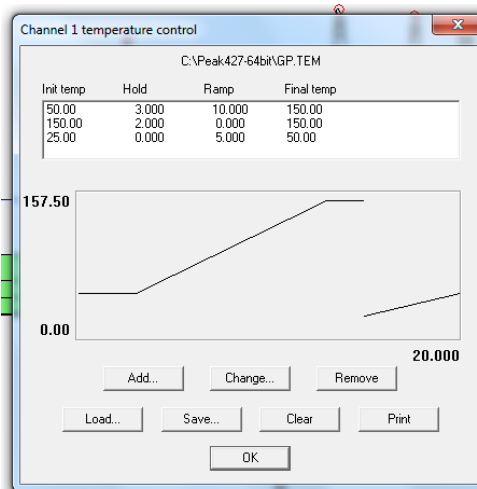
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We used the Temperature program and Event table shown at right for this analysis. Nitrogen carrier was set at 20psi on the GC. The two columns were 2meter Haysep-D and 2meter Haysep-N in series. The Haysep-N was the upstream column with the valve in the INJECT position.

A chromatogram such as the one shown should result from the injection of a calibration gas standard containing CO, CO₂, methane, ethane, ethylene and acetylene. The TCD measures hydrogen and oxygen, while the FID/methanizer shows CO, CH₄, CO₂ and the C₂ compounds. This chromatogram was run using nitrogen carrier gas.



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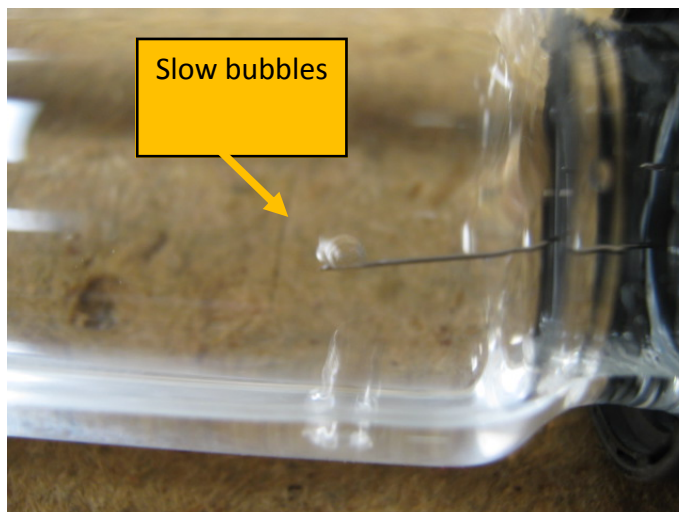
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Gas calibration standards are readily available, but liquid standards (known amounts of gases dissolved in liquids) are not easily found, so you might have to make your own. ASTM 3612 has a procedure, but it is cumbersome. Another standard preparation method is to bubble calibration gas through a liquid until the liquid and calibration gas are in equilibrium. Supplied with the TOGA GC system is a pressure regulator, restrictor tube, silicone tubing with Luer lock, and two needles for this purpose.

Connect the regulator to the calgas cylinder as shown and adjust the pressure so a slow stream of bubbles comes out of the needle which is positioned below the surface of the liquid. You may have to lay the VOA vial down on its side. The 2nd needle (27gauge) is inserted to vent the calgas from the top of the vial. After one hour or so, the calgases dissolved in the liquid should have reached equilibrium. From the Internet you can get a table which shows the amount of each gas which will be dissolved in the liquid once equilibrium is achieved, at least for water.

The solubility of gases in transformer oil is assumed to be the same as for water, although this is not completely accurate, and different oil types will exhibit different solubilities.



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When gases are dissolved in liquids the concentration of those gases can be described by the volume of gas in a volume of water (volume%) or by weight of gas in a weight of liquid, or volume of liquid, or by moles. There is a very large difference between volume%, weight% and mole%. Volume% is the method many people use.

For example:

From the Internet we learn that the weight of CO₂ in 100ml of water when completely saturated with a pure CO₂ purge gas is 0.169grams. By multiplying this by a series of unit conversions we get 1.45ml CO₂ in every ml of water, or 145%. If our calgas contains 1% CO₂ (which it does in this case) then the water would contain 1.45% CO₂ (14,500ppm) by volume.

By weight% the answer comes out to be 16.9 ppm

By mole% the answer comes out to be 1.08ppm

So there is at least a factor of 10000 difference between vol% and mole%

Volume% calculation assuming 100% CO₂ at 1 atm and saturated

.169gramCO ₂	1moleCO ₂	24litersCO ₂	1000mlCO ₂	= 1.45ml CO ₂
100mlH ₂ O	28gramCO ₂	1moleCO ₂	1literCO ₂	1.00ml H ₂ O

*Grams of gas dissolved in 100 g of water when the total pressure above the solution is 1 atm.

Oxygen .0043	Acetylene .117
Nitrogen .0019	Hydrogen .00016
Methane .0023	CO .0028
CO ₂ .169	Ethane .0062
Ethylene .0149	

Reference: G.W.C. Kaye and T.H. Laby, "Tables of Physical and Chemical Constants," 15th ed., Longman, NY, 1986, p. 219

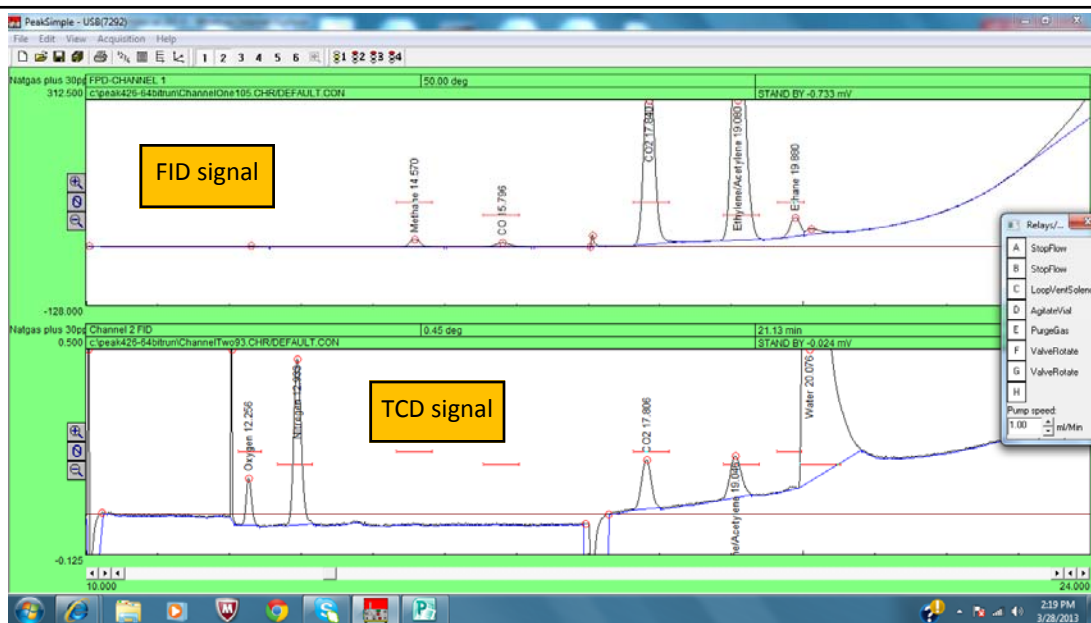


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The chromatogram at right show the results for a 20ml water standard which was saturated with a 1% calgas in Nitrogen. The volume% concentrations in the water would have been:



Hydrogen 192ppm

Oxygen 64.5ppmv

Nitrogen 1539ppmv Since this was the 94% balance in the calgas

CO 33.6ppmv

Methane 34.5ppmv

CO2 14,500ppmv

Had they been present in the calgas, the C2s would have been:

Ethylene 128ppmv

Acetylene 108ppmv

Ethane 49.6ppmv



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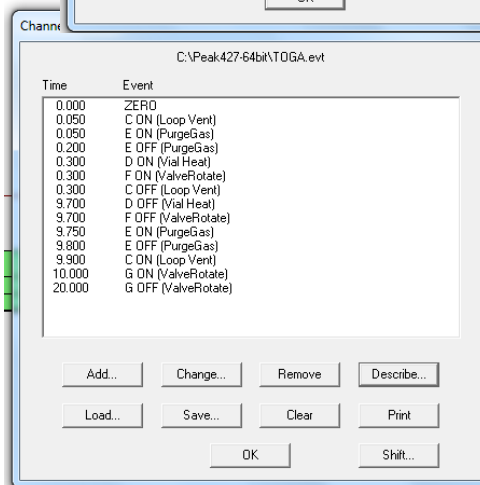
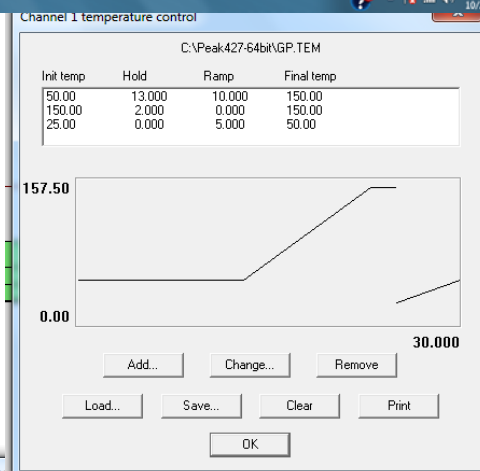
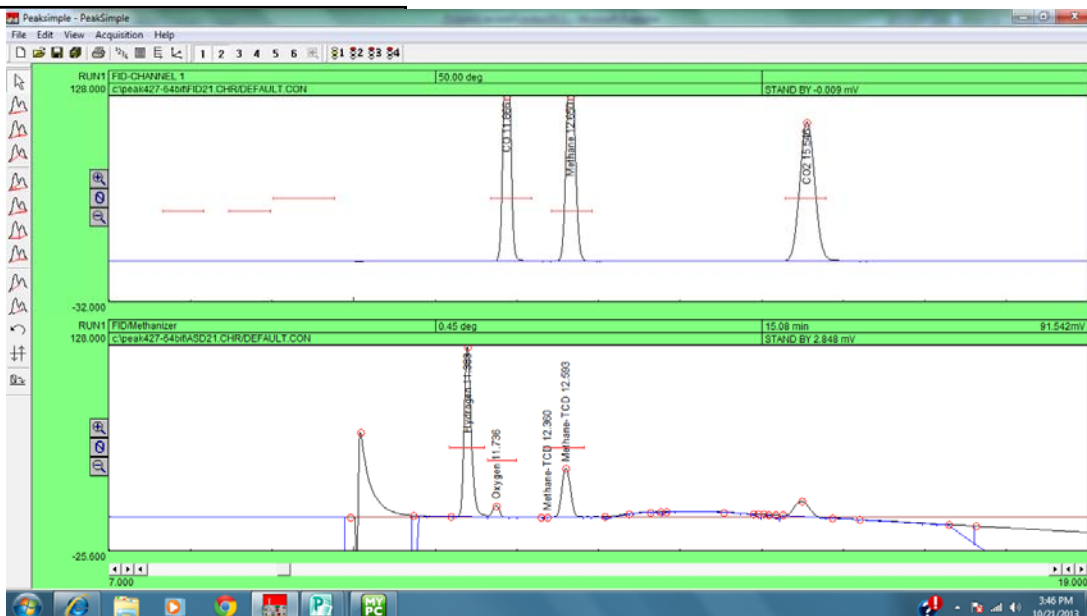
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The temperature program and event table had to be modified from the previous ones to run this sample because a 10 minute "headspace" time had to be included in the analysis. This required holding the initial oven temperature at 50 degrees for 13 minutes instead of 3 minutes as before.

Also the Event table was modified to shake (Relay D) and heat the 40ml vial (Relay F) for the first 10 minutes of the analysis.

The existing headspace in the vial was also purged for .2 minutes (Relay E and Relay C) at the very beginning of the analysis. This may not be necessary or required for real samples which have been inserted into pre-purged vials and remained in the 40 ml vials for some time prior to analysis. As the samples sit in the vial, they are already in the process of equilibrating the headspace so no flushing may be necessary.

Notice that to purge the headspace in the vial at time 0.05 minutes, Relay C is turned on first, and off last, so that the purge gas can flush out the headspace and then depressurize through the Relay C solenoid. When the vial is pressurized at 9.8 minutes however Relay C remains off until 9.8 minutes so the headspace gas has a few seconds to homogenize before being released through the loop.



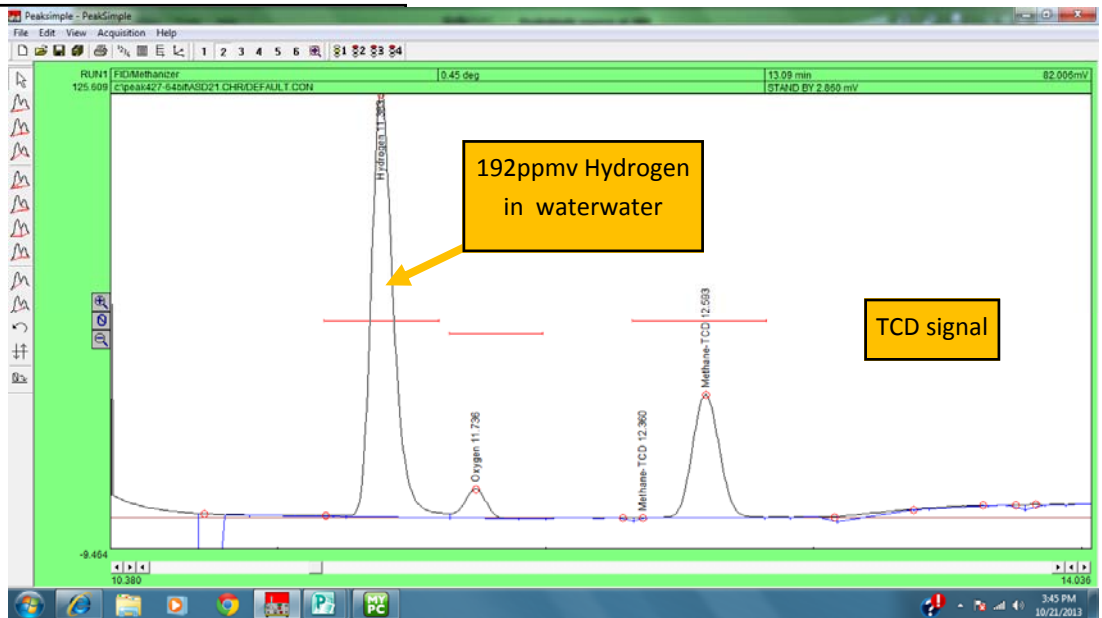
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Shown at right is the 1% gas mix (equilibrated into water) using nitrogen carrier gas and high (120ma) filament current.

Nitrogen carrier enables detection of hydrogen in liquids to 5ppm but sacrifices detection of nitrogen.



The FID/Methanizer detects Methane, CO, CO₂, ethane, ethylene, and acetylene and other hydrocarbons down to 1ppmv.



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