

Aromatics and Oxygenates in Gasoline

June 2018

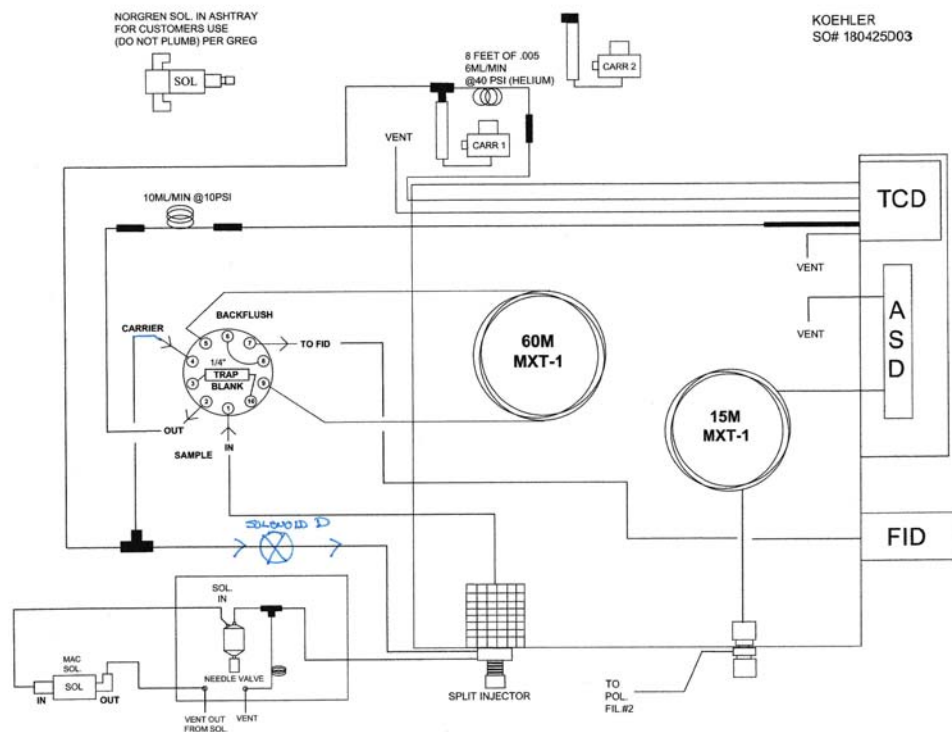
SRI has configured in a single GC two common tests performed on gasoline.

The first test is a simplified version of ASTM 4815, oxygenates in gasoline.

The second test is a simplified version of ASTM 3606, Benzene and Toluene in gasoline.

The photo at right shows two syringes loaded with 1ul gasoline each, poised for injection. Both analyses can be performed simultaneously.

A schematic of the GC is shown here.

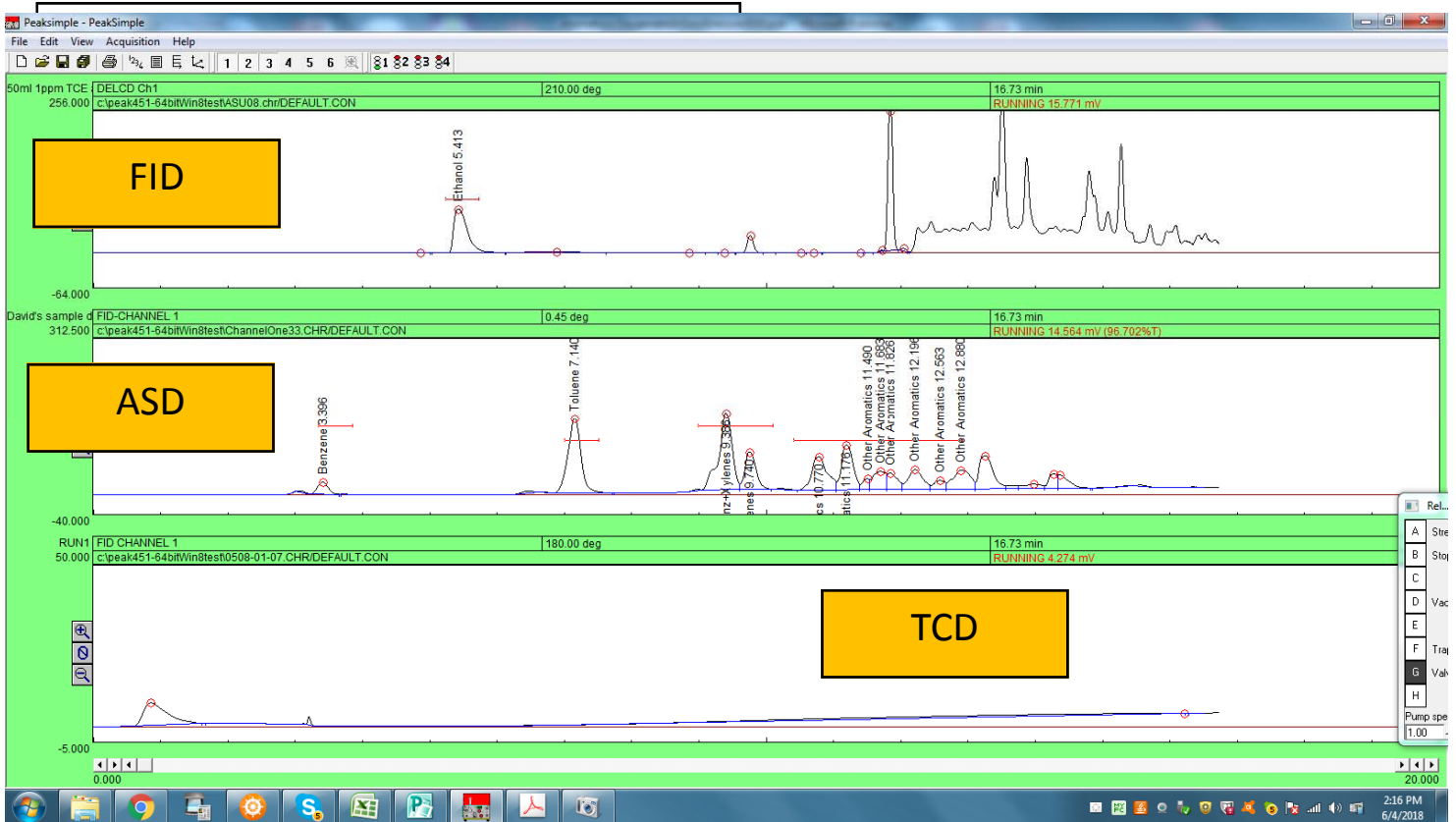


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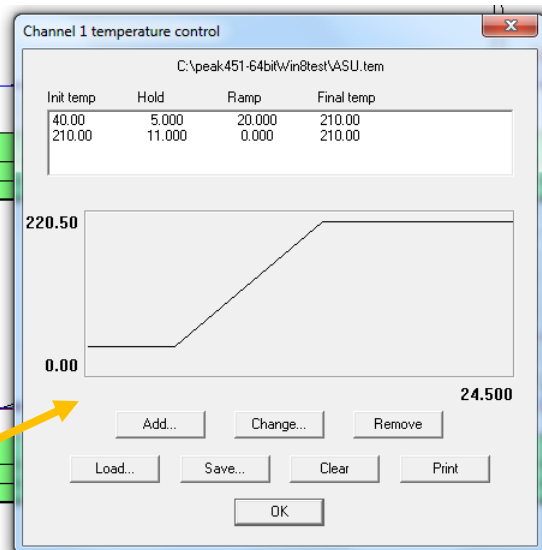


A typical chromatogram looks like this above. The FID (Flame Ionization Detector) is displayed on Channel 1.

The ASD (Aromatic Selective Detector) is displayed on Channel 2.

The TCD (Thermal Conductivity Detector) is displayed on Channel 3.

The Channel 1 temperature program is shown here.



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The Event tables for Channel 1,2 and 3 are shown here. The mechanical events which operates the valve, solenoids and heat are placed in Channel 1's event table for simplicity.

The Events are explained below:

0.00 Zero This autozeros the FID signal

0.00 Sound This makes a sound on the computer to verify that the analysis has begun

.010 A on This turns on a solenoid valve which allows the injector's split vent to open. The normal injection volume of 1ul gasoline needs to be split, otherwise the system can be overloaded. The remaining flow carries a portion of the gasoline to the TCEP trap where the oxygenates migrate very slowly, but the volatile non-oxygenates flow quickly through the trap and are detected by the TCD detector on Channel 3.

1.5 D on This turns on another solenoid which stops the entire gas flow to the heated injector. The flow through the TCEP trap must be halted prior to heating the trap, otherwise the peaks remaining on the trap will be lost. The exact time D turns on is determined by injecting just methanol, which is the first oxygenate. Observe the TCD signal on channel 3. When the TCD signal first begins to rise, this is the methanol exiting the TCEP trap, and the time the flow trough the trap must stop to avoid losing the methanol.

1.6 A off. This turns off the split vent which is no longer needed since all the gasoline molecules have now been transferred to the TCEP trap.

2.0 F on This turns on the TCEP trap heat (135C). The flow through the trap is zero at this point. It takes about 1 minute for the trap to heat to 135C, which is just below the TCEP material's upper limit.

3.0 G on This rotates the gas sampling valve, backflushing the TCEP trap onto the analytical column. The analytical column also backflushes, so when Relay G is turned off, the peaks remaining on the analytical column will be backflushed to the FID detector.

3.1 D off This de-actuates the solenoid so carrier gas now flows to the heated injector and TCD detector.

4.0 F off This turns off the heat to the TCEP trap.

The trap now returns to the starting temperature of 40C.

Channel 1 events
C:\peak451-64bit\Win8test\KoeblerCh1.evt

Time	Event
0.000	ZERO
0.000	SOUND
0.010	A ON (StreamSelectSolenoid)
1.500	D ON (VacuumPump)
1.600	A OFF (StreamSelectSolenoid)
2.000	F ON (TrapHeat)
3.000	G ON (ValveRotate)
3.100	D OFF (VacuumPump)
4.000	F OFF (TrapHeat)

Channel 2 events
ch2.evt

Time	Event
0.000	ZERO 100
3.000	INTEG IMMEDIATE

Channel 3 events
C:\peak451-64bit\Win8test\Channel3.evt

Time	Event
0.000	ZERO

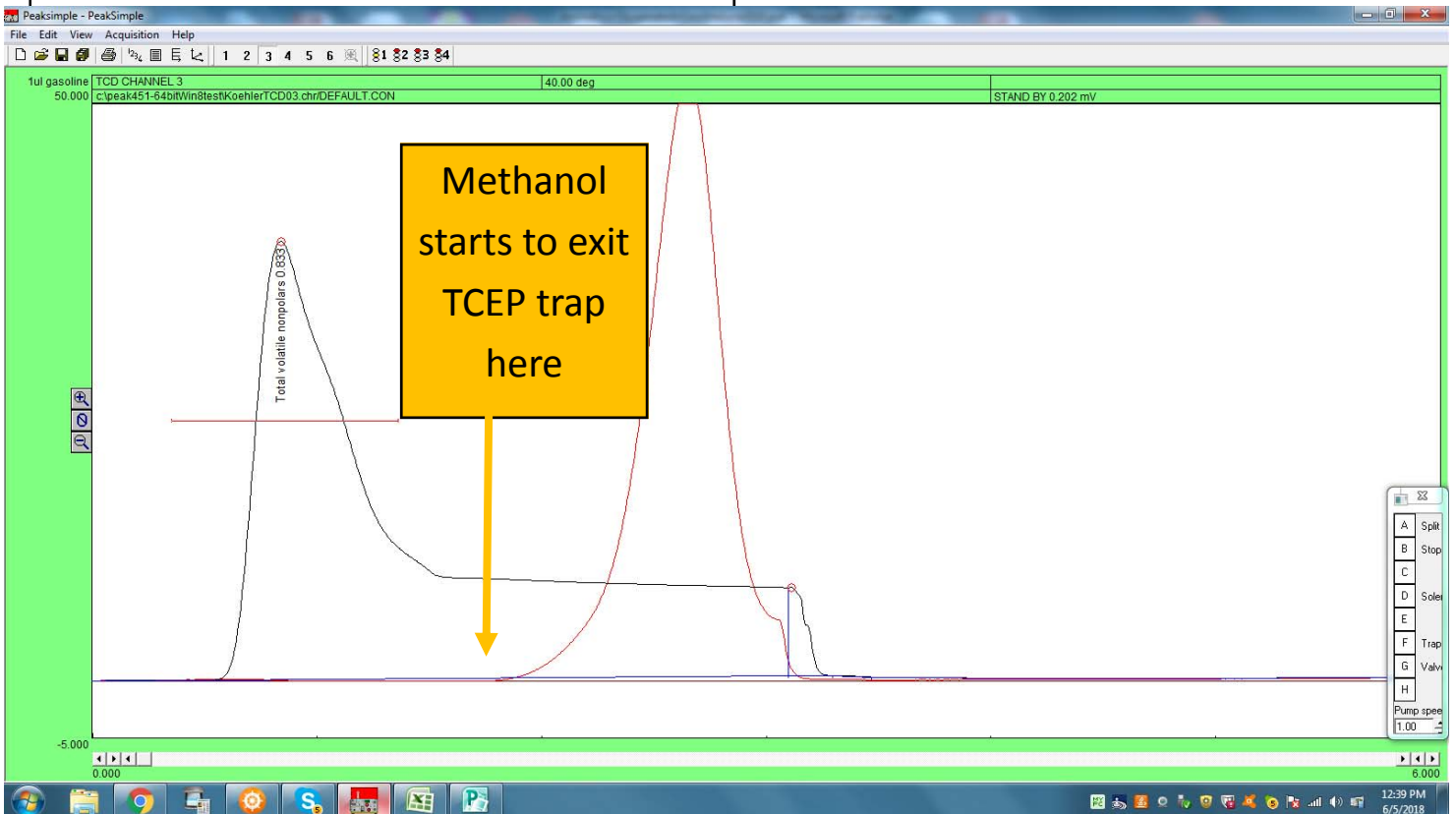


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The Channel 3 TCD signal above shows just methanol injected in RED and gasoline in BLACK. You can see that the methanol peak just begins to exit the TCEP trap at about 1.5 minutes, whereas the volatile gasoline peaks exit the trap much earlier. Relay D is actuated at 1.5 minutes to keep the methanol (and the other oxygenates) peak from exiting the trap. The higher boiling gasoline peaks are also retained by the trap, but when the trap is backflushed onto the analytical column, the oxygenates elute well before the higher boiling gasoline peaks with no interference from the volatile gasoline peaks.

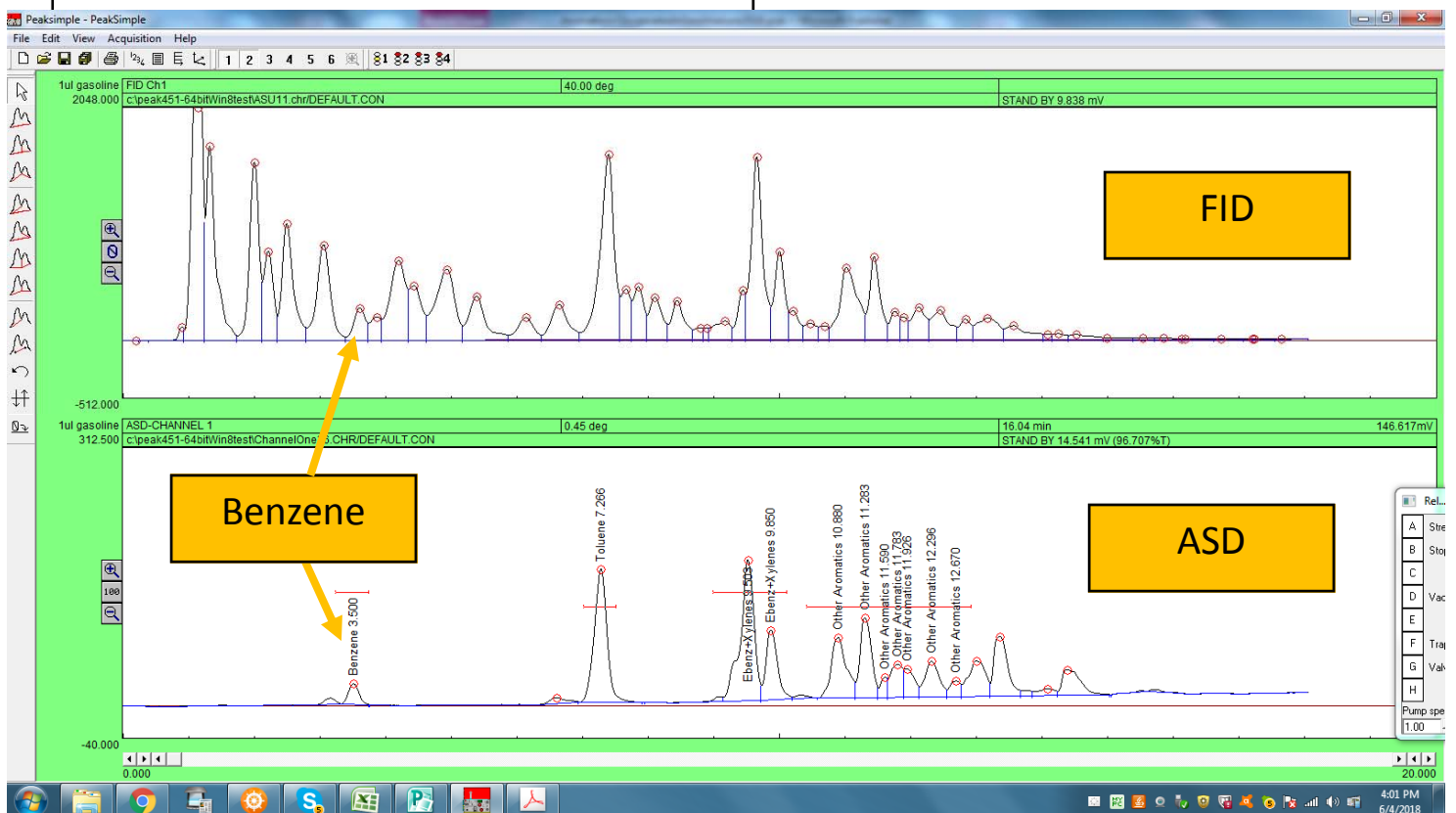


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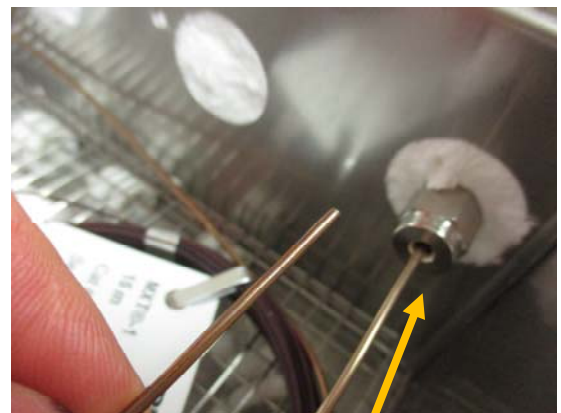
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In the chromatogram above, the ASD has been connected in series temporarily to the FID to show how the ASD only responds to the AROMATICS. The ASD exit tube is the same 1/16" size as the tube which normally goes to the FID so its easy to switch them. You can see how helpful it is to have a detector which is blind to most of the gasoline peaks. In normal operation the ASD would not be run in series with the FID. This was done just to illustrate the power of the ASD to detect just the benzene and toluene even in a sample containing many interfering peaks.



ASD exit tube connected to FID instead



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