Packed Column Refinery Gas Analysis System Based on the Agilent 7890B GC System and G3507A Large Valve Oven

Application Note

Hydrocarbon Processing Industry

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Abstract

A three-channel system on the Agilent 7890B GC System is used for the determination of refinery gases. Channel 1, using an FID and alumina PLOT column, is used for hydrocarbons from methane to C6+. Hydrogen is measured on Channel 3, where nitrogen is used as carrier. Permanent gases and hydrogen sulfide are measured on Channel 2 using the G3507A Large Valve Oven (LVO) under isothermal conditions with helium carrier. Channels 1 and 3 are temperature programmed while Channel 2 is isothermal with the temperature control independent from the main oven. Analysis time ranges from 15 to 18 minutes depending on the temperature of the G3507A LVO and valve timing.

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Introduction

Refinery gas analysis is an essential measurement in refinery operations. A detailed determination of hydrocarbons through C5 with C6 and higher (C6+), reported as a composite peak, is usually required. Along with hydrocarbons, permanent gases must be measured. Hydrogen over a wide concentration range is also necessary. Finally, sulfur-containing compounds such as hydrogen sulfide and carbonyl sulfide may also need determination.

The Refinery Gas Analyzer (RGA) system described, with the exception of the PLOT column for hydrocarbon separation, is based on 1/8-in packed columns. Three 1/8-in columns used for permanent gases and hydrogen sulfide separation are housed in the G3507A LVO and held isothermal for the entire run. This provides additional flexibility to fine tune separations and also provides stable oxygen measurement. Oxygen response on porous polymers is known to trend downward over time when these columns are subject to temperature programming. This phenomenon is avoided with the isothermal G3507A LVO.

Experimental

The column and valve configuration is shown in Figure 1. Seven columns are used in the system. Columns 1 through 5 are 1/8 in packed. Of these five packed columns, numbers 1 through 3 reside in the LVO coiled around a combination of 1 5/8-in and 1-in mandrels for superior temperature stability. A photo of the LVO with the cover removed is shown in Figure 2. Note the direct column heating with column-specific mandrels. Columns 6 and 7 are capillary located in the main 7890B GC oven and used for hydrocarbon separation up to C9. Samples containing hydrocarbons above C9 should not be injected on the system. The side mounted TCD is used exclusively for hydrogen determination using nitrogen as carrier. Flow sources are provided by two PCM's and a split/splitless inlet.

Selected system parameters are given in Table 1.

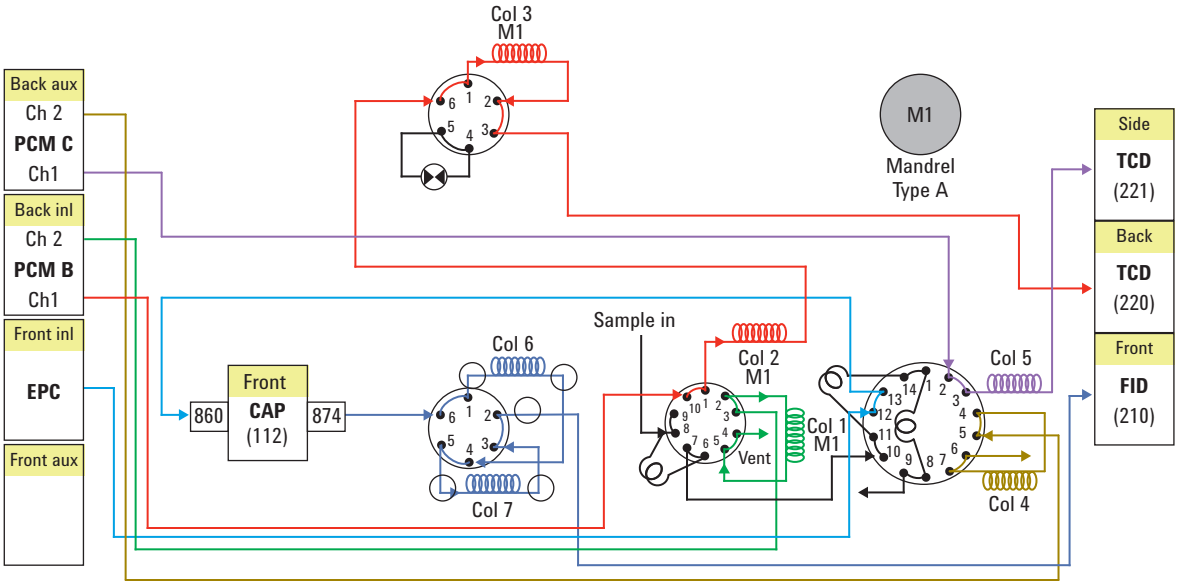

Figure 1. System valve diagram. Column 1 is coiled around a 1-inch mandrel, columns 2 and 3 are coiled around 1 5/8-inch mandrels.

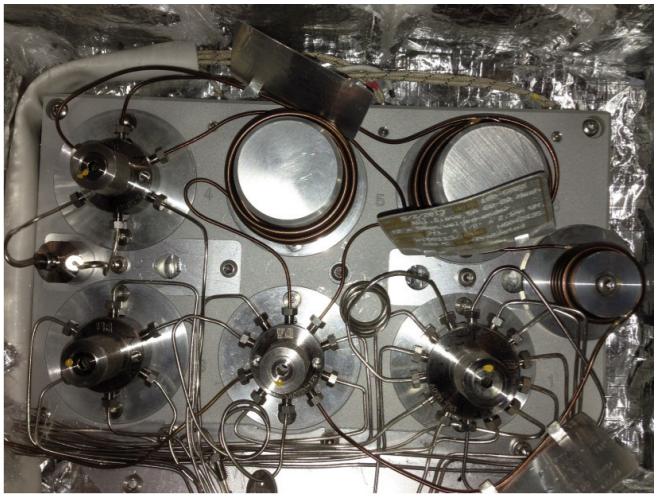

Figure 2. LVO with columns installed and cover removed. Columns 1,2, and 3 are shown.

Table 1. System Parameters

Split/splitless inlet	120 °C, helium carrier, 100 to 1 split
FID (front)	250 °C
TCD (rear)	260 °C, He carrier, ref. 30 mL/min, makeup 2 mL/min
TCD (side)	250 °C, N_2 carrier, ref. 45 mL/min, makeup 2 mL/min, neg. polarity
Main oven program	60 °C (1 minute) to 80 °C at 20 °C/min to 190 °C at 30 °C/min
Large valve oven	65 °C and 70 °C isothermal

Results and Discussion

Repeatability using a custom gas mix of some selected refinery gas components are given in Table 2, where the %RSD's are listed for retention times and areas with the LVO at 65 °C and 70 °C. The quantification range for typical RGA analytes is given in Table 3. If H_2S and COS need to be measured, the column tubing should be UltiMetal deactivated and the valve used should be made of Hastelloy C. Sample loops must also be UltiMetal.

Table 2. Retention Time (RT) and Area %RSD's for RGA Components at LVO Temperatures of 65 °C and 70 °C

Compound	Concentration (%)	RT 65 °C	RT 70 °C	Area 65 °C	Area 70 °C
C6+	0.06	0.026	0.022	0.35	0.31
Methane (FID)	4.99	0.009	0.011	0.19	0.12
Ethane (FID)	4.00	0.020	0.016	0.21	0.15
n-butane	0.30	0.103	0.038	0.23	0.16
t-2-butane	0.30	0.130	0.055	0.22	0.19
1-butene	0.30	0.130	0.056	0.34	0.26
n-pentane	0.10	0.082	0.034	0.29	0.22
Hydrogen	12.10	0.021	0.037	0.13	0.10
Oxygen	2.98	0.015	0.010	1.36	0.70
Nitrogen	balance	0.026	0.017	0.18	0.12
Carbon monoxide	1.52	0.044	0.023	0.16	0.12
Carbon dioxide	2.01	0.110	0.048	0.13	0.14
Methane (TCD)	4.99	0.031	0.020	0.25	0.13
Ethane (TCD)	4.00	0.099	0.055	0.22	0.14

Table 3. Selected Detection Limit Guidelines

Compounds	Limit
Hydrocarbons	0.01 mol%
Hydrogen sulfide	500 ppm
Carbonyl sulfide	300 ppm
Hydrogen	0.01 mol%
O_2, N_2, CO, CO_2	0.01 mol%

A common problem often seen in temperature programmed permanent gas analysis channels in RGA and NGA configurations is the loss of oxygen response over time due to chemisorption of O_2 on porous polymers. This effect is not seen when the large volume oven is used due to its isothermal temperature control of all columns associated with permanent gas analysis. In Figure 3, a plot of oxygen area for a 60 plus run sequence is shown at a LVO temperature of 65 °C. While a small drop in oxygen response occurs initially, long term stability of peak area is excellent. The first few runs are not included so that initial system start-up effects are removed.

Figure 4 shows all three channels (FID, TCD1, and TCD2) of the refinery gas checkout sample (p/n 5190-0519). The LVO box was set to 70 °C. Total runtime was just under 18 minutes. Hydrocarbon identifications are shown in Figure 5 for the FID channel. A permanent gas channel (TCD1) separation using a test sample that is a subset of a full RGA mix showing hydrogen sulfide at 0.50% is shown in Figure 6. Finally, Figure 7 shows the permanent gas channel analysis with the large valve oven at 65 °C. Note that valve timing is for samples without H_2S. Total run time was 16 minutes.

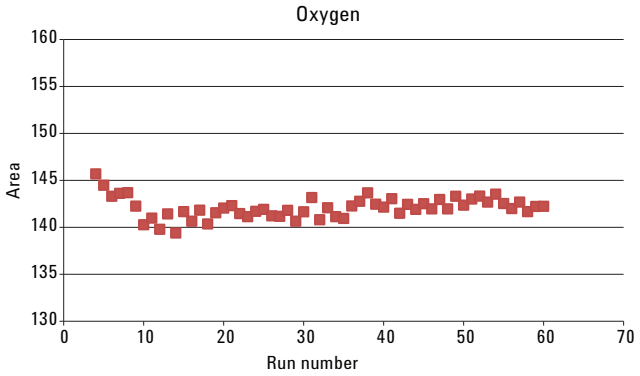

Figure 3. Oxygen analysis stability with the G3507A LVO at 65 °C.

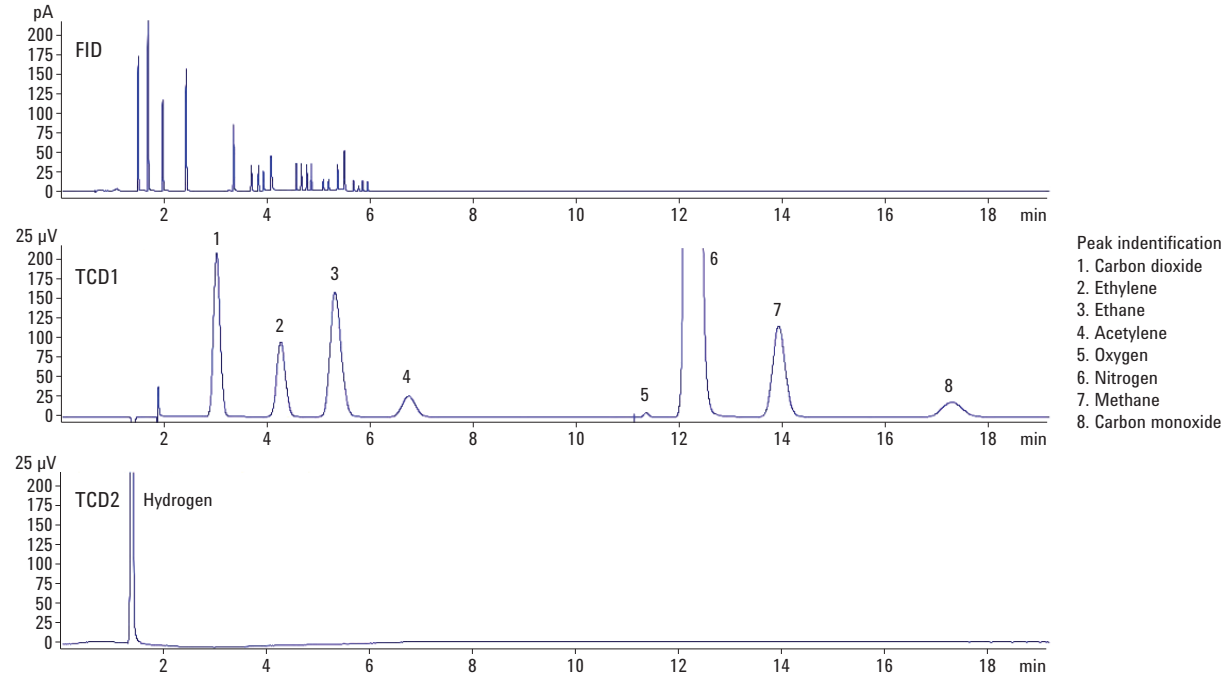

Figure 4. All three channels of the RGA analyzer. Sample is RGA checkout 5190-0519. Peak ID's for TCD1: 1. Carbon dioxide, 2. Ethylene. 3. Ethane, 4. Acetylene, 5. Oxygen, 6. Nitrogen, 7. Methane, 8. Carbon monoxide. TCD2: Hydrogen.

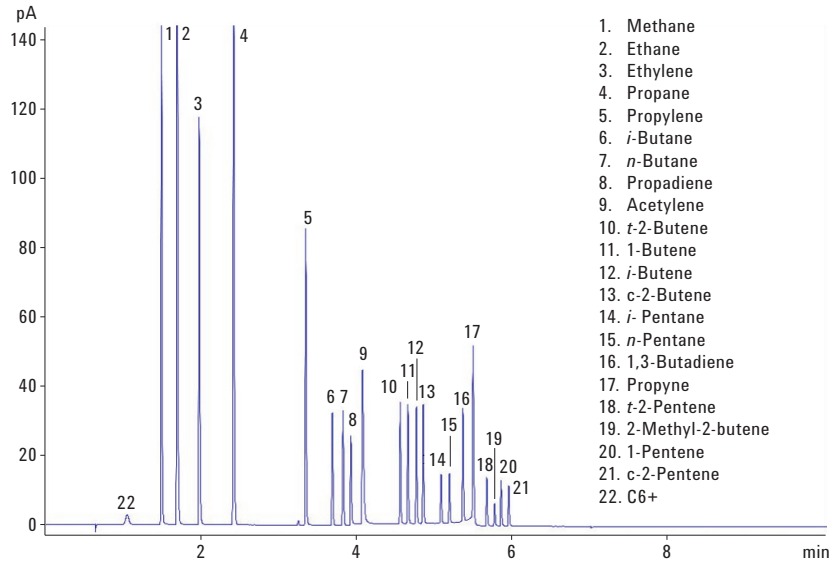

Figure 5. FID channel with hydrocarbon identifications. Sample is RGA checkout 5190-0519.

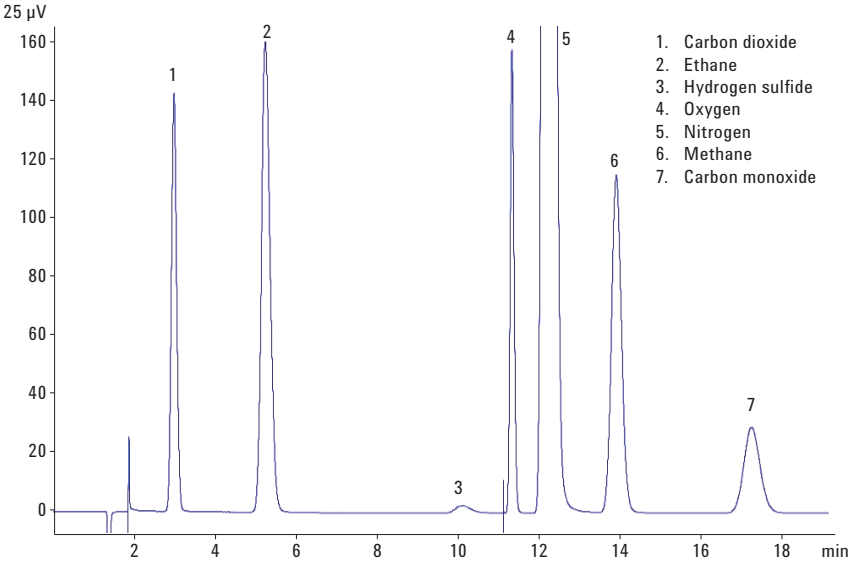

Figure 6. TCD1 channel with hydrogen sulfide. LVO at 70 °C.

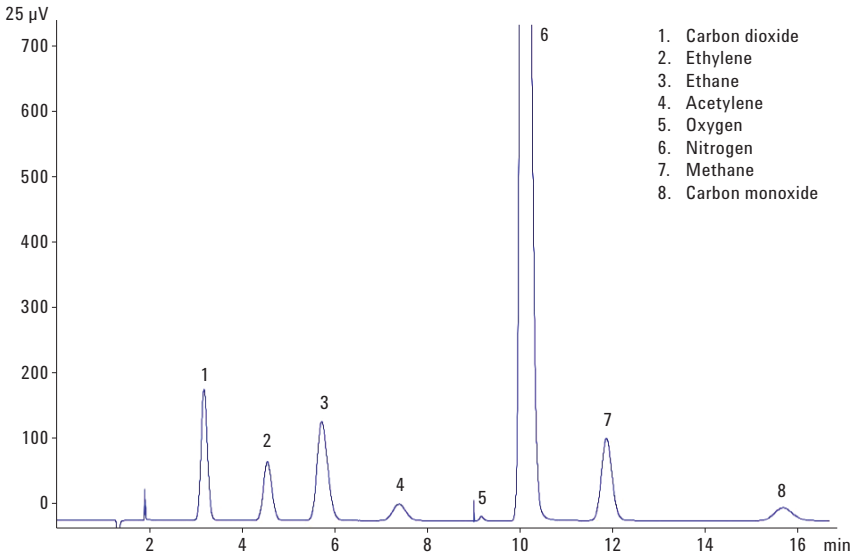

Figure 7. TCD1 channel with LVO at 65 °C. Sample is RGA checkout 5190-0519.

Conclusion

The G3507A Large Valve Oven was used to improve the performance and flexibility of a traditional packed column based Refinery Gas Analyzer. Stable oxygen response was seen due to the fact that the columns used for the permanent gas channel separation were held at a relatively low isothermal temperature. Hydrogen sulfide and carbonyl sulfide can also be analyzed with a longer run time by adjusting valve timing. Excellent %RSD's were achieved with the system for all typical components of RGA.

The large valve oven is thermally decoupled from the temperature programmed main Agilent 7890B GC System oven. This allows LVO isothermal temperature setting to be maintained when the main oven is programmed to 190 °C for the PLOT column separation.

The LVO can accommodate up to six heated valves. One valve position is lost for each large column mandrel used. Large mandrels can accept up to 15 ft of 1/8-in metal column. Valves supported include 4, 6, 10, and 14-port.

Ordering Information

When ordering this RGA system, specify:

G3445B #531 –Refinery Gas Analyzer with Large Valve Oven using Standard Packed Columns

For More Information

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