Fast Refinery Gas Analysis System Based on the Agilent 7890B GC System and G3507A Large Valve Oven Using Micropacked Columns

Application Note

Hydrocarbon Processing Industry

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Abstract

A three channel system on the Agilent 7890B GC System was used for the determination of refinery gases. Channel 1, using an FID and alumina PLOT column, was used for hydrocarbons from methane to C6+. Hydrogen was measured on Channel 3, where nitrogen was used for carrier. Permanent gases and hydrogen sulfide were measured on Channel 2 using the G3507A large valve oven (LVO) under isothermal conditions with helium carrier. Micropacked (1/16 in od, 1.00 mm id) were used for the permanent gas channel. Channels 1 and 3 were temperature programmed with their columns in the main 7890B GC System oven. Analysis time averaged approximately 8.5 minutes including a hydrogen sulfide determination.

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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 determination, over a wide concentration range, is also necessary. Finally, sulfur containing compounds such as hydrogen sulfide and carbonyl sulfide may also need to be measured.

The Refinery Gas Analyzer (RGA) system described here, with the exception of the PLOT column for hydrocarbon separation, is based on 1/16-inch micropacked columns in UltiMetal. Three 1/16-inch columns used for permanent gases and hydrogen sulfide separation are housed in the large valve oven (LVO) and held isothermal for the entire run. The columns are coiled around two 1 5/6-inch mandrels. 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 subjected to temperature programming. This phenomenon is avoided with the isothermal G3507A large valve oven.

Experimental

The column and valve configuration is shown in Figure 1. Seven columns are used with the system. Columns 1 through 3 are direct-heated, micropacked, and reside in the large valve oven coiled around two 1 5/8-inch mandrels for superior temperature stability. Columns 4 and 5 located in the 7890B main oven are 1/8-inch packed. Columns 6 and 7, also located in the main 7890B oven, are capillary 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.

Table 1.   System Parameters

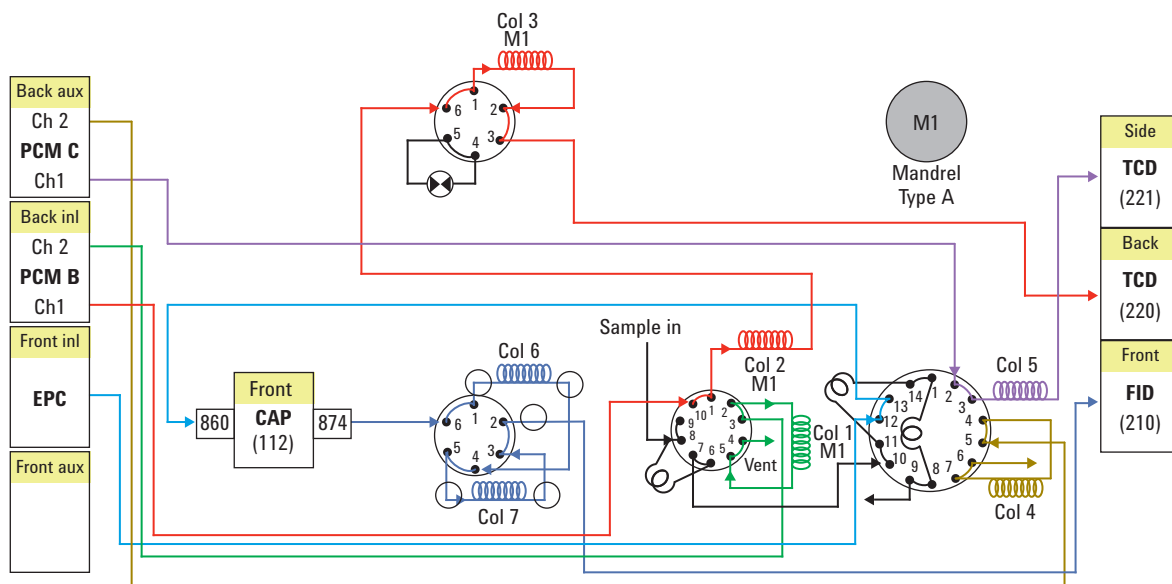|	
Split/splitless inlet	120 °C, helium carrier, 100 to 1 split
FID (front)	250 °C
TCD (rear)	260 °C, He carrier, Ref. 30 mL/min, makeup 2 mL/min
TCD (side)	250 °C, N_2 carrier, Ref. 45 mL/min, makeup 2 mL/min, neg. polarity
Main oven program	60 °C (1 minute) to 80 °C at 20 °C/min to 190 °C at 30 °C/min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

Figure 1.   System configuration. Columns 1, 2, and 3 are coiled around 1 5/8-inch mandrels.

Results and Discussion

Repeatability of some selected refinery gas components is given in Table 2 where the % RSD's are listed for retention times and component areas with the LVO at 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 valves used should be made of Hastelloy C. Sample loops must also be UltiMetal.

Table 2.   *Percent RSD's of RGA Compounds with the LVO at 70 °C Using a 50-Run Sequence*

Compound	Concentration (%)	RT (RSD)	Area(RSD)
C6+	0.06	0.027	0.28
Methane (FID)	4.99	0.006	0.14
Ethane (FID)	4.00	0.011	0.15
n-Butane	0.30	0.045	0.15
t-2-Butane	0.30	0.059	0.17
1-Butene	0.30	0.059	0.21
n-Pentane	0.10	0.038	0.20
Hydrogen	12.10	0.036	0.15
Oxygen	2.98	0.026	0.64
Nitrogen	balance	0.022	0.18
Carbon monoxide	1.52	0.035	0.15
Carbon dioxide	2.01	0.086	0.15
Methane (TCD)	4.99	0.031	0.16
Ethane (TCD)	4.00	0.09	0.16
Hydrogen sulfide	0.50	0.215	4.80

Table 3.   *Selected Compound MDL 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 Figures 2A and 2B, plots of oxygen area for 45-run sequences are shown at LVO temperatures of 70 °C and 75 °C, respectively. The first two runs are not included so that system start-up effects are removed. Stability of peak area is excellent at both temperatures.
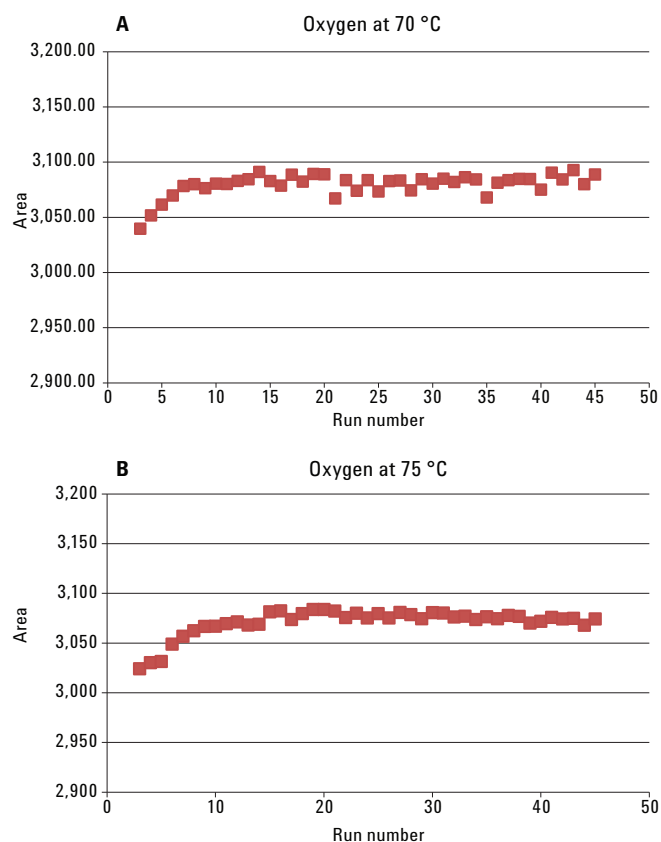

Figure 2.   *A) Oxygen response over a 45-run sequence with LVO at 70 °C. B) Oxygen response over a 45-run sequence with LVO at 75 °C.*

Figure 3 shows the FID channel using the alumina PLOT column for separation of the refinery gas checkout sample (p/n 5190-0519). A permanent gas channel (TCD1) separation showing hydrogen sulfide at 0.50% is shown in Figure 4. Run time was just over 8 minutes with the large valve oven set to 70 °C.
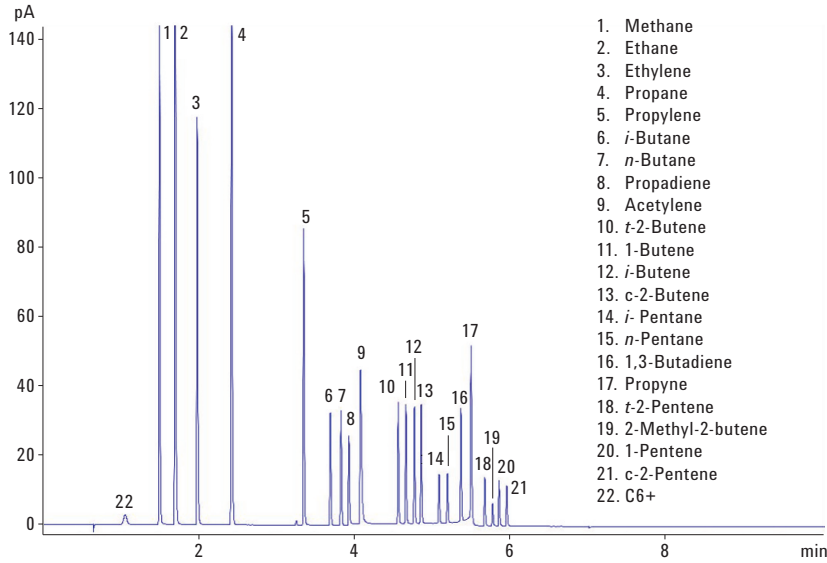

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Propylene
6. *i*-Butane
7. *n*-Butane
8. Propadiene
9. Acetylene
10. *t*-2-Butene
11. 1-Butene
12. *i*-Butene
13. c-2-Butene
14. *i*- Pentane
15. *n*-Pentane
16. 1,3-Butadiene
17. Propyne
18. *t*-2-Pentene
19. 2-Methyl-2-butene
20. 1-Pentene
21. c-2-Pentene
22. C6+

Figure 3.   *FID channel with compound identifications. RGA checkout sample 5190-0519.*

1. Carbon dioxide
2. Ethane
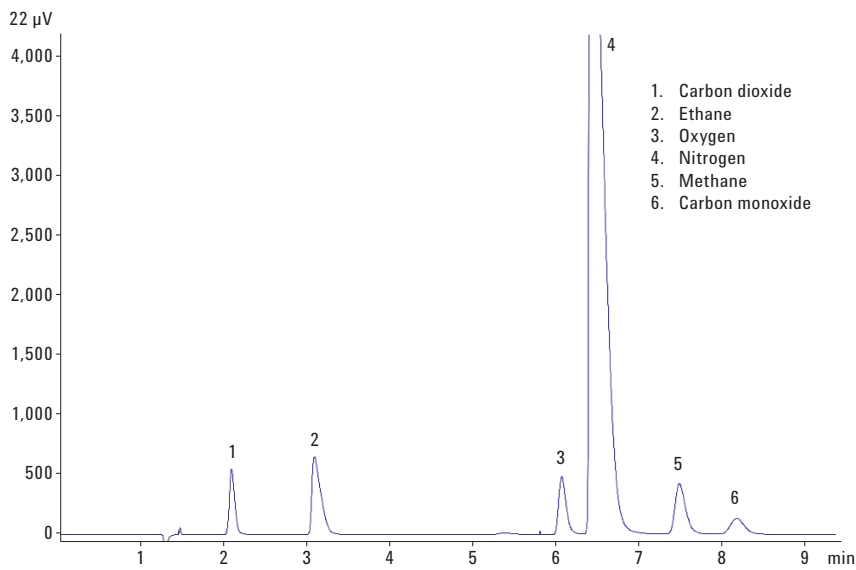3. Oxygen
4. Nitrogen
5. Methane
6. Carbon monoxide

Figure 4.   *Permanent gas channel (TCD1) with LVO at 70 °C. Minor column overloading from high concentration components such as nitrogen will cause some peak asymmetry but will not affect quantitation.*

Conclusion

The G3507A large valve oven was used to improve the performance and flexibility of a traditional packed column based Refinery Gas Analyzer. Temperature control of the LVO was completely independent of the main 7890B oven. Micropacked columns offered a good balance between speed and capacity. This system could perform a complete RGA analysis in 8 minutes. The system will perform well for typical RGA compound concentration ranges. Results will vary if hydrocarbon streams with extreme component concentration ranges (high or low) are injected. Stable oxygen response was seen due to the fact that the micropacked columns used for the permanent gas channel separation were held at a relatively low (less than 80 °C) isothermal temperature. Hydrogen sulfide and carbonyl sulfide were also 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 LVO was thermally decoupled from the temperature programmed main 7890B oven so that the isothermal temperature setpoint was maintained when the main oven was programmed to 190 °C.

The LVO can accommodate up to 6 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#532 – Fast Refinery Gas Analyzer with Large Valve Oven using Micropacked Columns

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

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