Application Note

Agilent
Trusted Answers

Ultra-Fast Refinery Gas Analysis With a 490 Micro GC 3-Channel Configuration Equipped With a Backflush-to-Detector Option

Author

Jie Zhang
Agilent Technologies, Inc.

Introduction

Refinery gas is produced during the crude oil refinery process. It can be used as fuel gas or as feedstock for subsequent processing. The source of refinery gas and refinery process greatly varies, so therefore, does the composition of refinery gas. For optimization of refinery processes and to ensure product quality, it is crucial to know the composition of the refinery gas. The Agilent 490 Micro GC provides a fast and reliable analysis of refinery gas (RGA) composition.

The 490 Micro GC analyzer for RGA is a quad channel configuration:

- CP-Molsieve column for permanent gas analysis
- CP-PoraPLOT U channel for CO_2, ethylene, acetylene, ethane, and hydrogen sulfide (H_2S) analysis
- CP-Al_2O_3/KCl channel for analysis of light saturated and unsaturated hydrocarbons from C3 to C5
- CP-Sil 5CB channel for C6 and C6+ hydrocarbon analysis

This Application Note describes the RGA analysis results obtained with an alumina (Al_2O_3)channel featuring a backflush-to-detector (BF2D) configuration. During the analysis, C6 and C6+ components are trapped on the precolumn, allowing the targeted C3–C5 saturated and unsaturated hydrocarbons to enter the analytical column. Then, the flow through the precolumn is reversed while maintaining the foreflush over the analytical column. This results in C6/C6+ components being backflushed through a reference column to the thermal conductivity detector (TCD). The function of channel 3 and channel 4 in a traditional quad configuration can be replaced by one Al_2O_3 channel with a BF2D option, especially when the individual heavier hydrocarbon (≥C6) concentration results are not critical in RGA quality control and refinery process optimization.

Instrumentation: 3-channel configuration for RGA analysis

Channel 1: 10 m CP-Molsieve 5Å channel with traditional backflush configuration for permanent gas analysis except carbon dioxide (CO_2); RTS is an option for better long-term RT stability.

Channel 2: 10 m CP-PoraPLOT U channel with traditional backflush configuration, for CO_2, C2, and H_2S analysis. To ensure H_2S detection at ppm level, the complete sample flowpath of the 490 Micro GC from sample inlet to injector die is made inert by Ultimetal deactivation. (Application Note 5991-6241)[1]

Channel 3: 10 m CP-Al_2O_3/KCl channel with BF2D configuration, for C3 to C5 hydrocarbons and bundled C6/C6+ compounds analysis

Figure 1 is the chromatogram of hydrogen, oxygen, nitrogen, methane, and carbon monoxide separated on a CP-Molsieve 5Å column. This is a backflush channel, so the components eluting later than CO will be backflushed to the vent.

Sample

Peak no.	Compound	Concentration (mol/mol)
1	Hydrogen	12.9 %
2	Oxygen	0.098 %
3	Nitrogen	Bal
4	Methane	4.99 %
5	Carbon monoxide	0.989 %
6	Carbon dioxide	2.96 %
7	Ethylene	2.07 %
8	Ethane	3.94 %
9	Acetylene	1.06 %
10	Hydrogen sulfide	0.5 %
11	Propane	1.99 %
12	Propylene	0.980 %
13	Propadiene	1.01 %
14	*iso*-Butane	0.295 %

Peak no.	Compound	Concentration (mol/mol)
15	*n*-Butane	0.295 %
16	*trans*-2-Butene	0.303 %
17	1-Butene	0.295 %
18	*iso*-Butene	0.307 %
19	*cis*-2-Butene	0.306 %
20	Propyne	1.01 %
21	*iso*-Pentane	0.104 %
22	1,3-Butadiene	0.311 %
23	*n*-Pentane	0.097 %
24	*t*-2-Pentene	0.098 %
25	2-*m*-Butene; 1-Pentene	0.046 %; 0.104 %
26	*cis*-2-Pentene	0.094 %
27	*n*-Hexane	0.024 %

Table 1. Method for RGA analysis.

Channel type	10 m, MS5A, BF	10 m PPU, BF	10 m AL_2O_3, BF2D
Carrier gas	Argon	Helium	Helium
Injector temperature	110 °C	110 °C	110 °C
Injection time	40 ms	40 ms	40 ms
Column head pressure	150 kPa	150 kPa	300 kPa
Column temperature	80 °C	100 °C	90 °C
BF time	6.5 s	6.6 s	7 s

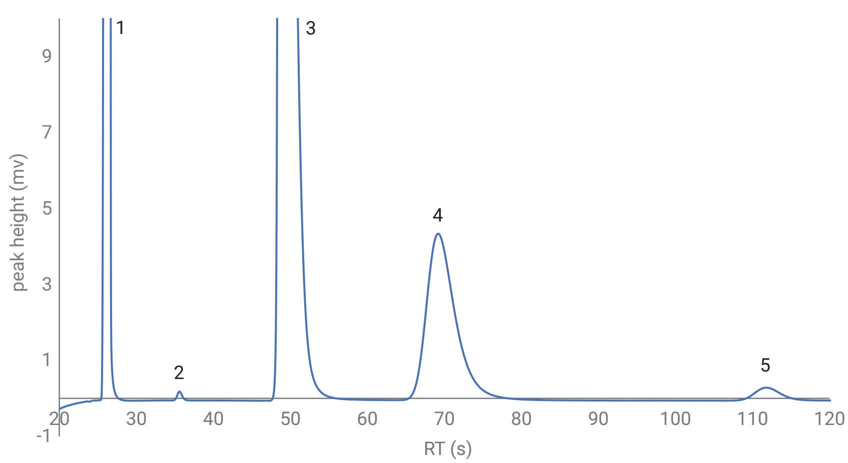

Figure 1. standard gas (simulated RGA) on MS5A channel.

Figure 2 is the chromatogram of carbon dioxide, ethylene, ethane, acetylene, and hydrogen sulfide.

Figure 3 is the chromatogram of C3–C5 saturated/unsaturated hydrocarbons and higher components on the Al_2O_3 channel. The C6+ hydrocarbons are backflushed through a reference column to the detector. The resulting negative peak can be inverted as a positive peak for quantitation. The total analysis time is less than 180 seconds.

An additional advantage is the improved resolution of *trans*-2-butylene and 1-butylene. It is much better than the traditional 10 m Al_2O_3 backflush channel because the precolumn has a different stationary phase and smaller id. As a result, the C3–C5 hydrocarbon peak width is much narrower when entering the Al_2O_3 column, enabling a much more efficient isomer resolution. With this type of backflush-to-detector channel, it is not necessary for the fourth channel to analyze the higher hydrocarbons. In addition, this setup prevents the C6/C6+ components from entering the Al_2O_3 column, efficiently protecting it from heavier components and the potential interference in subsequent analysis.

Table 2 lists the RT repeatability on the BF2D channel; RT RSD% is between 0.04 % and 0.09 %. This excellent repeatability guarantees accurate quantification results with high confidence.

Conclusion

The full compositional analysis of refinery gas, based on the CP-Al_2O_3/KCl backflush-to-detector channel is fast and reliable. The total analysis can be finished in three minutes, and the excellent RT repeatability is a guarantee for correct and reliable component identification and quantification. The 3-channel configuration of the RGA analyzer with BF2D is a good alternative to the traditional 4-channel configuration if speed and sample throughput is of critical importance.

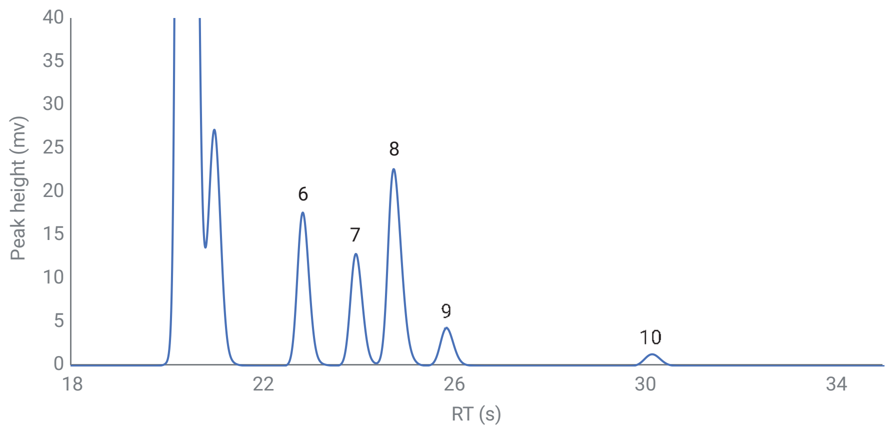

Figure 2. standard gas (simulated RGA) on PPU channel.

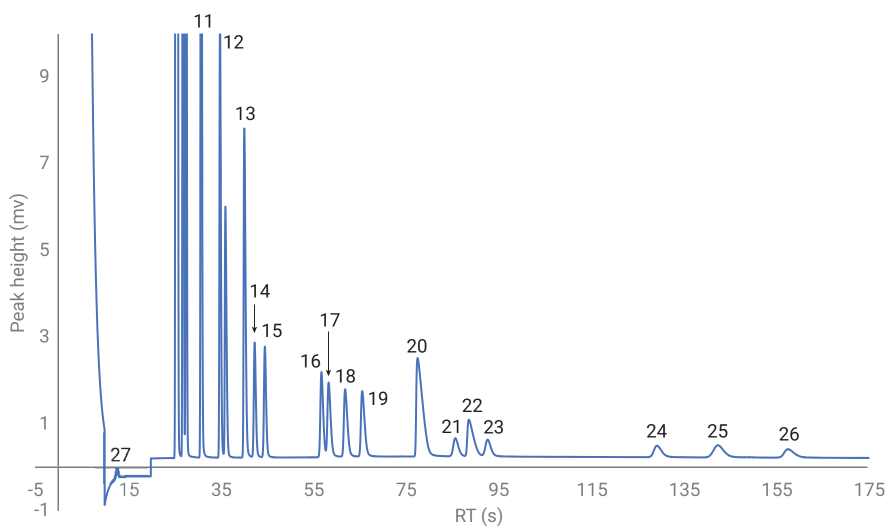

Figure 3. standard gas (simulated RGA) on Al_2O_3 BF2D channel.

Table 2. RT RSD% of representative compounds on the Al_2O_3 channel (30 injections).

Peak no.	Retention time (s)							
	27	16	17	18	19	24	25	26
Injection no.	C6+	*trans*-2-Butene	1-Butene	*iso*-Butene	*cis*-2-Butene	*t*-2-Pentene	2-*m*-Butene + 1-Pentene	*cis*-2-Pentene
1	12.48	56.97	58.43	62.60	66.51	129.24	142.77	157.60
2	12.48	56.99	58.45	62.62	66.54	129.30	142.83	157.67
3	12.48	56.98	58.45	62.61	66.53	129.29	142.80	157.67
4	12.49	57.00	58.47	62.63	66.56	129.35	142.86	157.75
5	12.48	57.00	58.46	62.63	66.56	129.34	142.88	157.71
6	12.48	57.03	58.50	62.67	66.60	129.44	143.02	157.87
7	12.49	57.03	58.49	62.67	66.59	129.43	142.98	157.82
8	12.49	57.02	58.49	62.67	66.59	129.42	142.96	157.83
9	12.48	57.04	58.51	62.69	66.61	129.47	143.05	157.94
10	12.49	57.03	58.50	62.68	66.60	129.41	142.96	157.82
11	12.49	57.04	58.51	62.69	66.61	129.47	143.02	157.91
12	12.49	57.07	58.54	62.72	66.65	129.51	143.13	157.96
13	12.49	57.04	58.51	62.68	66.61	129.44	143.00	157.92
14	12.49	57.04	58.51	62.69	66.61	129.45	143.00	157.86
15	12.49	57.05	58.52	62.70	66.63	129.51	143.10	157.96
16	12.48	57.06	58.53	62.71	66.64	129.53	143.08	157.97
17	12.48	57.06	58.53	62.71	66.64	129.54	143.18	158.03
18	12.48	57.08	58.56	62.74	66.67	129.57	143.18	158.08
19	12.48	57.08	58.55	62.73	66.66	129.59	143.19	158.05
20	12.49	57.08	58.56	62.74	66.67	129.60	143.20	158.08
21	12.48	57.09	58.57	62.75	66.68	129.65	143.25	158.14
22	12.48	57.07	58.54	62.72	66.65	129.57	143.19	158.04
23	12.48	57.07	58.55	62.73	66.66	129.63	143.20	158.09
24	12.48	57.07	58.55	62.73	66.66	129.59	143.20	158.06
25	12.48	57.05	58.52	62.70	66.63	129.51	143.12	157.98
26	12.48	57.07	58.54	62.72	66.65	129.56	143.13	158.02
27	12.49	57.06	58.53	62.71	66.63	129.51	143.10	157.96
28	12.49	57.04	58.51	62.69	66.62	129.49	143.03	157.91
29	12.48	57.06	58.53	62.71	66.64	129.51	143.04	157.94
30	12.48	57.05	58.52	62.70	66.62	129.46	143.04	157.88
Mean	12.48	57.04	58.51	62.69	66.62	129.48	143.05	157.92
%RSD	0.040 %	0.055 %	0.060 %	0.063 %	0.065 %	0.079 %	0.091 %	0.087 %

Reference

1. Fast refinery gas analysis using the Agilent 490 micro GC QUAD, *Agilent Technologies Application Note*, publication number 5991-6241.

www.agilent.com/chem

Printed in the USA, July 10, 2018
5994-0040EN

Agilent
Trusted Answers