

Refinery Gas Analysis Using the Agilent 990 Micro GC

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Introduction

Refinery gas analysis (RGA) is a commonly used gas chromatography-based test method to characterize gases produced during crude oil refining including stack emission, flame, and reformat streams. Although the composition of the gases varies, they typically contain C₁ to C₅ paraffins, C₆+ paraffins, C₂ to C₅ olefins, and noncondensed gases.

The Agilent 990 Micro GC provides a fast RGA solution, which can significantly reduce the analysis time taken by a routine laboratory GC solution, for example, from 6 to 8 to 2 to 3 minutes.

Two types of RGA solutions have been previously developed based on the Agilent 490 Micro GC.^{1,2} One is a four-channel configuration, which analyzes permanent gas, except CO₂, on the molecular sieve channel, C₂ paraffins/olefins, carbon dioxide (CO₂), and hydrogen sulfide (H₂S) on the PoraPLOT U channel, C₃ to C₅ paraffins/olefins on an alumina channel, and C₆+ paraffins on the CP-Sil 5CB channel. The other RGA solution is three-channel configuration, whereby channels 1 and 2 are the same as the four-channel configuration. The third channel is an alumina channel with a backflush-to-detector (BF2D) option, which separates C₃ to C₅ paraffins/olefins and backflushes the C₆/C₆+ paraffins as a bundled peak to the detector for total C₆/C₆+ measurement. This study demonstrates two RGA approaches based on the 990 Micro GC for simulated refinery gas analysis.

Instrumentation

Channel 1

A 10 m, CP-Molesieve 5 Å channel with traditional backflush option (BF) for permanent gas analysis except CO₂. The RTS option is used for better long-term retention time stability.

Channel 2

A 10 m, CP-PoraPLOT U channel with traditional backflush option, for CO₂, C₂ paraffin/olefins, and H₂S analysis. The 990 Micro GC uses a proprietary metal deactivation technique to coat the surface of the sample flowpath including the sample inlet port and its connection tubing to each channel for better inertness, which is beneficial for detection of active components, such as H₂S, at low ppm levels with satisfactory signal-to-noise (S/N) values.

Channel 3 for four-channel solution

A 10 m CP-AL₂O₃/KCL channel with normal backflush option for analysis of C₃ to C₅ paraffins/olefins

Channel 3 for three-channel solution

A 10 m CP-AL₂O₃/KCL channel with backflush-to-detector option for analysis of C₃ to C₅ paraffins/olefins and bundled C₆/C₆+ paraffins

Channel 4

A 8 m CP-Sil 5CB straight channel for analysis of C₆ and C₆+ paraffins

Table 1. Configuration of two RGA solutions.

RGA Configuration 1	Compounds to be Analyzed	RGA Configuration 2	Compounds to be Analyzed
10 m, CP-Molesieve 5 Å, backflush (RTS)	Permanent gas except CO ₂	10 m, CP-Molesieve 5 Å, backflush (RTS)	Permanent gas except CO ₂
10 m CP-PoraPLOT U, backflush	CO ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , H ₂ S	10 m CP-PoraPLOT U, backflush	CO ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , H ₂ S
10 m CP-AL ₂ O ₃ /KCL, backflush	C ₃ -C ₅ paraffins and C ₃ -C ₅ olefins	10 m CP-AL ₂ O ₃ /KCL, backflush to detector	C ₃ -C ₅ paraffins and C ₃ -C ₅ olefins; total C ₆ /C ₆ + hydrocarbons
8 m, CP-Sil 5CB, straight	Detailed C ₆ and C ₆ + hydrocarbons		

Table 2. Analytical conditions for each channel.

Channel Type	10 m, CP-Molesieve 5 Å, (RTS) Backflush	10 m CP-PoraPLOT U, Backflush	10 m CP-AL ₂ O ₃ /KCL, Backflush	8 m, CP-Sil 5CB, Straight	10 m CP-AL ₂ O ₃ /KCL, Backflush to Detector
Carrier Gas	Argon	Helium	Helium	Helium	Helium
Injector Temperature	110 °C	110 °C	110 °C	110 °C	110 °C
Injection Time	40 ms	40 ms	40 ms	40 ms	40 ms
Column Head Pressure	200 kPa	150 kPa	100 kPa	200 kPa	300 kPa
Column Temperature	80 °C	100 °C	90 °C	150 °C	100 °C
Backflush Time	7 seconds	7.5 seconds	25 seconds	NA	4.5 seconds
Invert Signal	NA	NA	NA	NA	From 5 to 12 seconds

Table 3. Simulated refinery gas sample.

Peak no.	Compound	Concentration
1	Hydrogen	12.9%
2	Oxygen	0.098%
3	Nitrogen	Balance
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	1%
11	Propane	1.99%
12	Propylene	0.980%
13	Propadiene	1.01%
14	Isobutane	0.295%

Peak no.	Compound	Concentration
15	Butane	0.295%
16	<i>trans</i> -2-Butene	0.303%
17	1-Butene	0.295%
18	Isobutene	0.307%
19	<i>cis</i> -2-Butene	0.306%
20	Propyne	1.01%
21	Isopentane	0.104%
22	1,3-Butadiene	0.311%
23	Pentane	0.097%
24	<i>trans</i> -2-Pentene	0.098%
25	2-Methyl-butene	0.049%
26	1-Pentene	0.104%
27	<i>cis</i> -2-Pentene	0.094%
28	Hexane	0.024%

Figures 1A and 1B show the chromatograms of hydrogen, oxygen, nitrogen, methane, and carbon monoxide separated on a CP-Molesieve 5 Å column. When permanent gases, except CO₂, are carried to the molecular sieve column, the backflush function is automatically initiated at a preset backflush time to reverse the flow in the precolumn, and flush the heavier components out to vent. In this test, argon is the carrier gas for hydrogen determination. Carbon monoxide elutes within 100 seconds.

Figure 2 shows the chromatogram of carbon dioxide, ethylene, ethane, acetylene, and H₂S on the CP-PoraPLOT U column. The shape of the H₂S peak is symmetrical due to the inertness of the sample flowpath. H₂S elutes within 60 seconds.

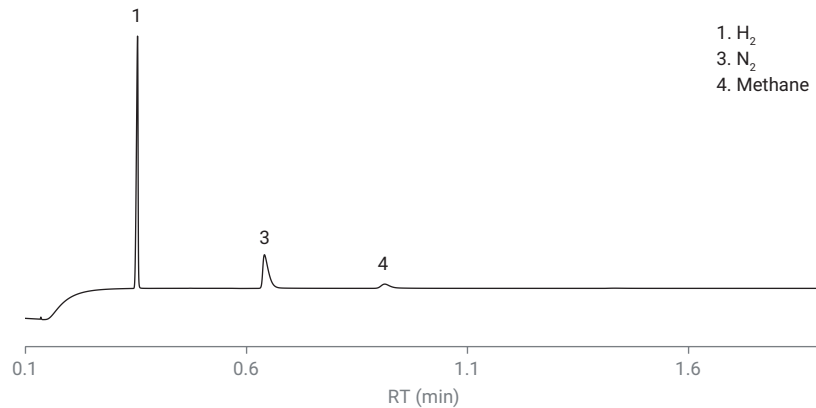


Figure 1A. Simulated RGA on the CP-Molesieve 5 Å column (channel 1).

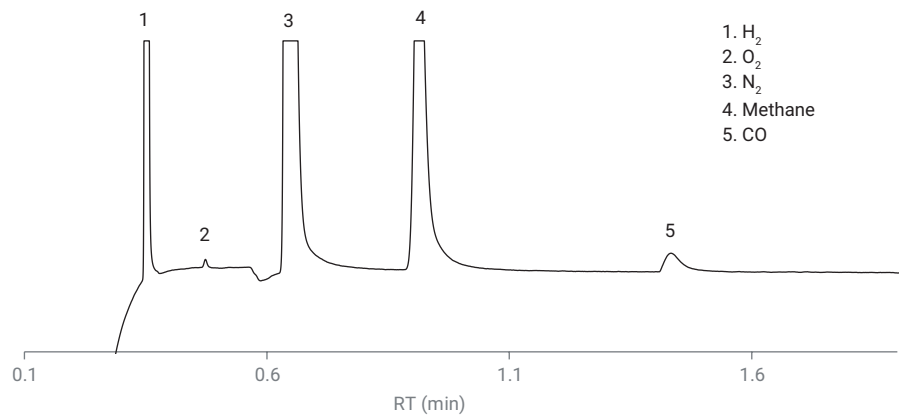


Figure 1B. Simulated RGA on the CP-Molesieve 5 Å column (channel 1) (chromatogram enlarged).

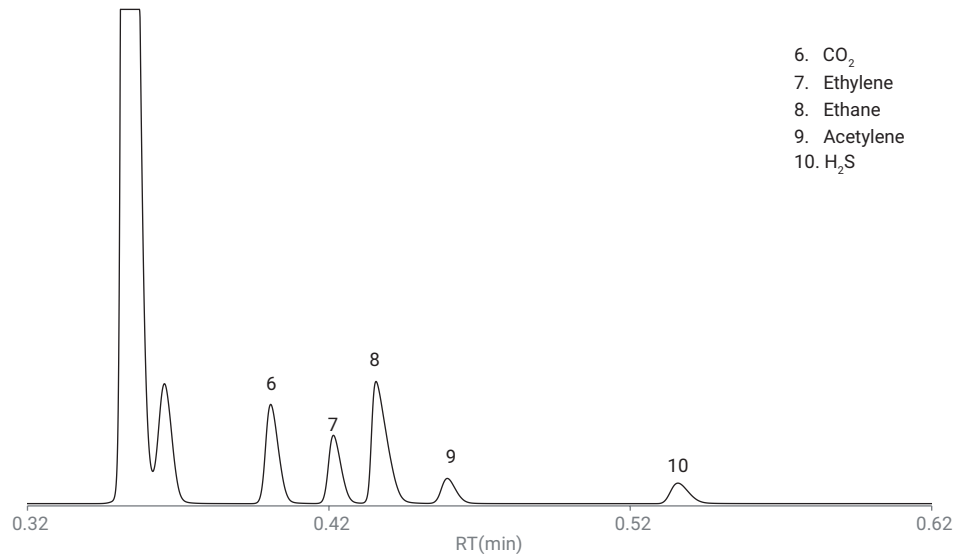


Figure 2. Simulated RGA on the CP-PoraPLOT U column (channel 2).

Figure 3 shows the chromatogram of C₃ to C₅ paraffins/olefins on the aluminum oxide column with the normal backflush option. C₆ and C₆+ paraffins are backflushed to vent before entering the alumina analytical column. The backflush time was optimized to ensure complete elution of C₅ paraffins/olefins without C₆/C₆+ paraffins penetrating the analytical column. *cis*-2-Pentene eluted before 180 seconds on this tested channel under the applied analytical conditions.

Figure 4 shows the chromatogram of simulated refinery gas on the 8 m, CP-Sil 5CB channel. This channel is for C₆ and C₆+ hydrocarbons analysis. Hexane was separated well from C₅ paraffins/olefins. The C₆ to C₉ hydrocarbon mixture was analyzed within 80 seconds.

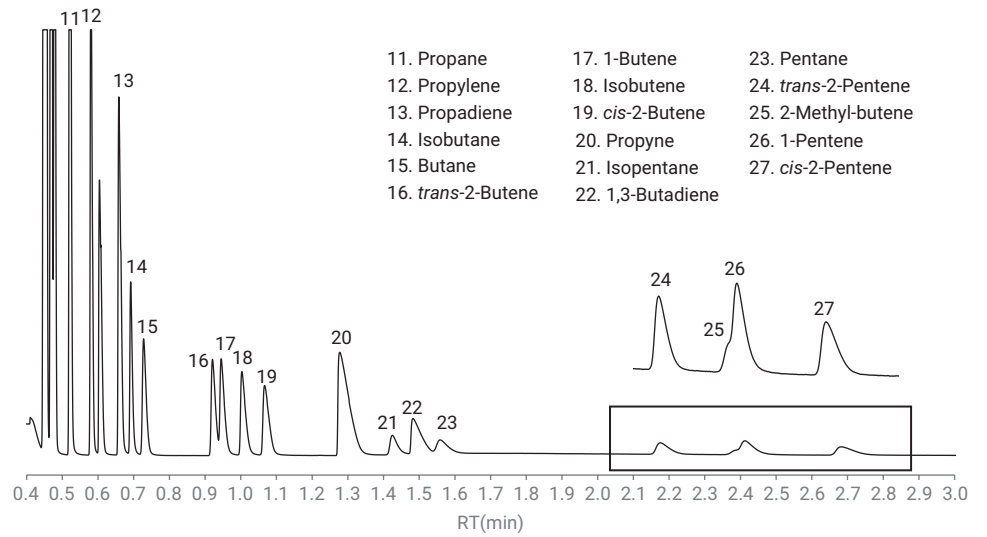


Figure 3. Refinery gas standard on CP-AL₂O₃/KCL column (normal BF option) (channel 3).

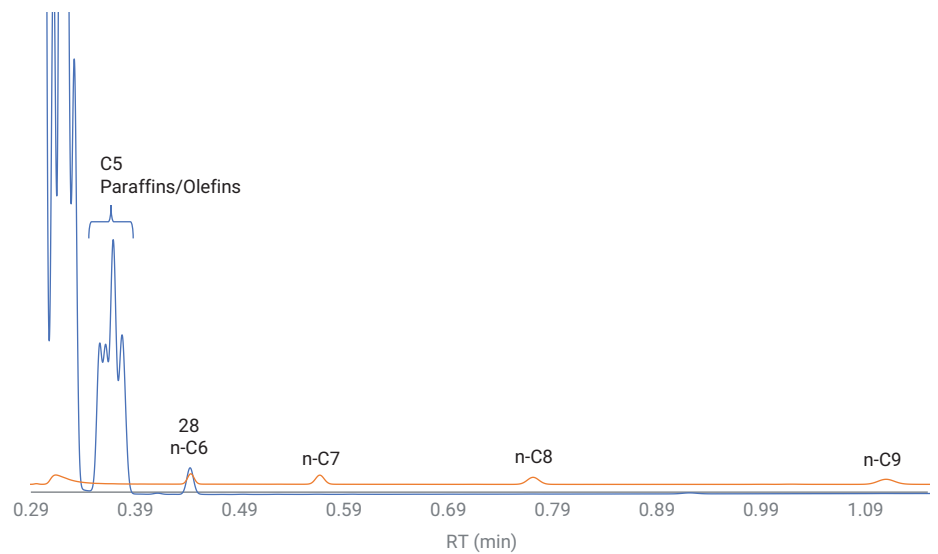


Figure 4. Refinery gas standard (blue trace) and hydrocarbons mixture of C₆ to C₉ (red trace) on a 8 m, CP-Sil 5CB column (channel 4).

Figure 5 shows the chromatogram of C₃ to C₅ paraffins/olefins and bundled C₆/C₆+ paraffins on the CP-AL₂O₃/KCL BF2D channel. The C₆/C₆+ paraffins are backflushed through a reference column to the detector. The resulting negative peak can be inverted as a positive peak (peak 28) for quantitation. The total analysis time on this test channel is less than 120 seconds.

Comparing Figure 3 and Figure 5, the separation of 2-methyl-butene/1-pentene on the CP-AL₂O₃/KCL BF2D channel is better than on the CP-AL₂O₃/KCL normal backflush option. The precolumn stationary phases are different between the two types of alumina column backflush options. In addition, the internal diameter of the precolumn in BF2D option is smaller, which helps generate the narrower C₃ to C₅ peaks when they enter the alumina analytical column, and thus the final resolution is better.

Due to the strong adsorption properties of the column coated with alumina, some compounds such as water or carbon dioxide, can accumulate on the column, leading to a change of retention time of analyzed compounds. This phenomenon is particularly seen during operation at low column temperatures (especially <100 °C). Therefore, it is recommended to activate the surface of the column at a higher temperature periodically³ for better RT stability.

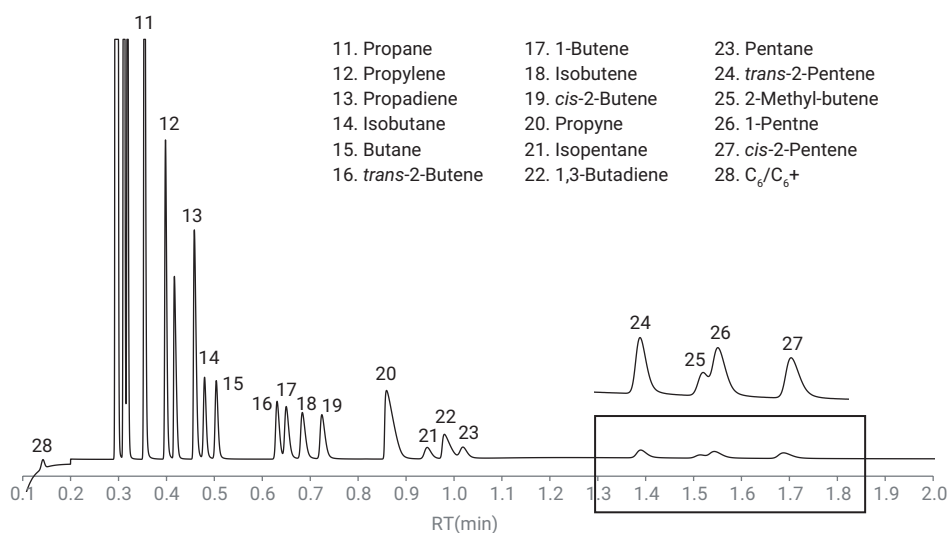


Figure 5. C₃ to C₅ paraffins/olefins on the CP-AL₂O₃/KCL column with backflush-to-detector option.

Conclusion

This study demonstrates fast refinery gas analysis based on the Agilent 990 Micro GC. Two types of RGA solutions are available. Both approaches can analyze permanent gas, H₂S, and C₂ to C₅ paraffins/olefins. For C₆+ paraffins, the three-channel configuration can provide the total amount. The four-channel configuration can give detailed information on individual C₆/C₆+ hydrocarbons. Choosing which one for refinery gas analysis depends on the sample composition and analysis requirements. If the individual heavier hydrocarbon (\geq C₆) concentration results are not critical in RGA quality control and refinery process optimization, the three-channel configuration is a good choice for faster refinery gas analysis. If detailed C₆+ hydrocarbon information is necessary, the four-channel configuration is the recommended solution.

References

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3. Poole, C. F., Ed.; Gas Chromatography, Chapter 5, Gas-Solid Chromatography, Elsevier Inc., 2012.

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