Fast Refinery Gas Analysis Using the Agilent 490 Micro GC QUAD

Application Note

Energy & Fuels

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Introduction

There is a large variation in the composition and source of refinery gases. Therefore, the precise and accurate analysis of these gases is a significant challenge in today's refineries. Typical sources include fluid coking overheads, ethylene, propylene, fuel gas, stack gas, off gas, etc. The physical stream ranges from gas to highly pressurized gas or liquid.

Very fast refinery gas analysis (RGA) is possible with the portable Agilent 490 Micro GC QUAD. This note describes the use of the 490 Micro GC for RGA, with results obtained in about two minutes.

Instrumentation

490 Micro GC QUAD

- Channel 1: Agilent J&W CP- Molsieve with back flush
- Channel 2: Agilent J&W PoraPLOT U with back flush
- Channel 3: Aluminum oxide with back flush
- Channel 4: Agilent J&W CP-Sil 5 CB

The CP-Molsieve channel and the aluminum oxide channel are equipped with extra in line filters between the manifold and the column module to ensure moisture- and carbon-dioxide-free carrier gas. This enhances column lifetime and, most importantly, leads to stable retention times.

GC control and data handling software: Agilent chromatography software.

Materials and Reagents

Channel 1, equipped with a CP-Molsieve column, separates and analyzes the permanent gases except for carbon dioxide. Channel 2, with a PoraPLOT U column, separates and analyzes the C2 gases and hydrogen sulfide. The C3 and C4 hydrocarbons are analyzed on the third channel with an Al_2O_3 column. Finally, the higher hydrocarbons are analyzed on the fourth channel, with a CP-Sil 5 CB column.

Table 1. Peak identification and composition of gas standards

Gas Standard

Peak #	Component	Amt (%)
1	Hydrogen	
3	Oxygen	
4	Nitrogen	
5	Methane	Bal
6	Carbon monoxide	

Refinery Gas standard

Peak #	Component	Amt (%)	Peak #	Component	Amt (%)
2	Helium	Bal	15	Propadiene	0.62
4	Nitrogen	5.1	16	n-Butane	1.0
5	Methane	24.9	17	tr-2-Butylene	0.5
6	Carbon monoxide	1.0	18	1-Butylene	0.5
7	Carbon dioxide	0.5	19	iso-Butylene	1.01
8	Ethylene	24.9	20	cis-2-Butylene	0.5
9	Ethane	5.0	21	iso-Pentane	0.5
10	Acetylene	1.0	22	Methyl acetylene	1.0
11	Hydrogen sulfide	1.01	23	n-Pentane	0.2
12	Propane	5.0	24	1, 3-Butadiene	1.0
13	Propylene	5.0	25	n-Hexane	0.2
14	iso-Butane	0.5			

Conditions

Table 2. Chromatographic conditions

	Channel 1	Channel 2	Channel 3	Channel 4
	10 m CP-Molsieve	10 m PoraPLOT U	10 m Al2O3/KCL	8 m CP-Sil 5 CB
Injector Temp (°C)	110	110	110	110
Column Temp (°C)	80	100	100	80
Carrier Gas	Argon	Helium	Helium	Helium
Column Head Pressure (kPa)	150	205	70	205
Injection Time (ms)	40	10	10	100
Back Flush Time (s)	11	7.1	33	N/A

Results and Discussion

Figures 1 and 2 show chromatograms of the CP-Molsieve channel 1.

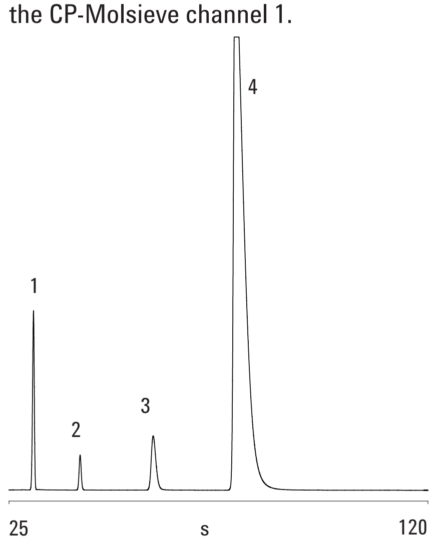

Figure 1. Standard gas on the CP-Molsieve column, channel 1

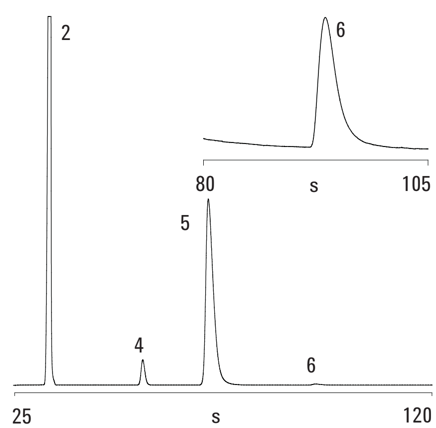

Figure 2. Refinery gas on the CP-Molsieve column, channel 1

Hydrogen or helium, oxygen, nitrogen methane and carbon monoxide were separated and analyzed. Later eluting components were back flushed to vent.

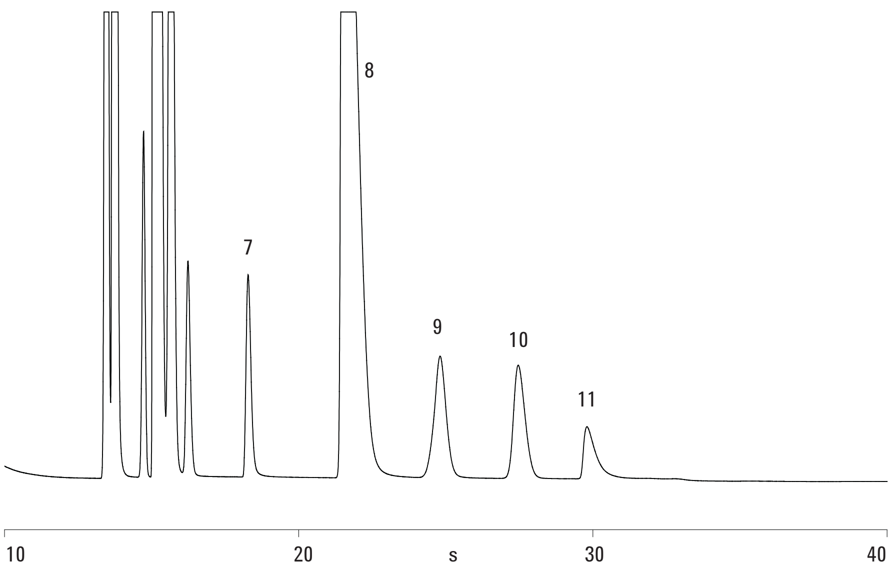

Figure 3. Refinery gas on the Agilent PoraPLOT U column, channel 2

On the PoraPLOT U channel (channel 2), the C2 hydrocarbons, hydrogen sulfide and carbon dioxide were separated and analyzed. The channel was equipped with a back flush, later eluting components to vent.

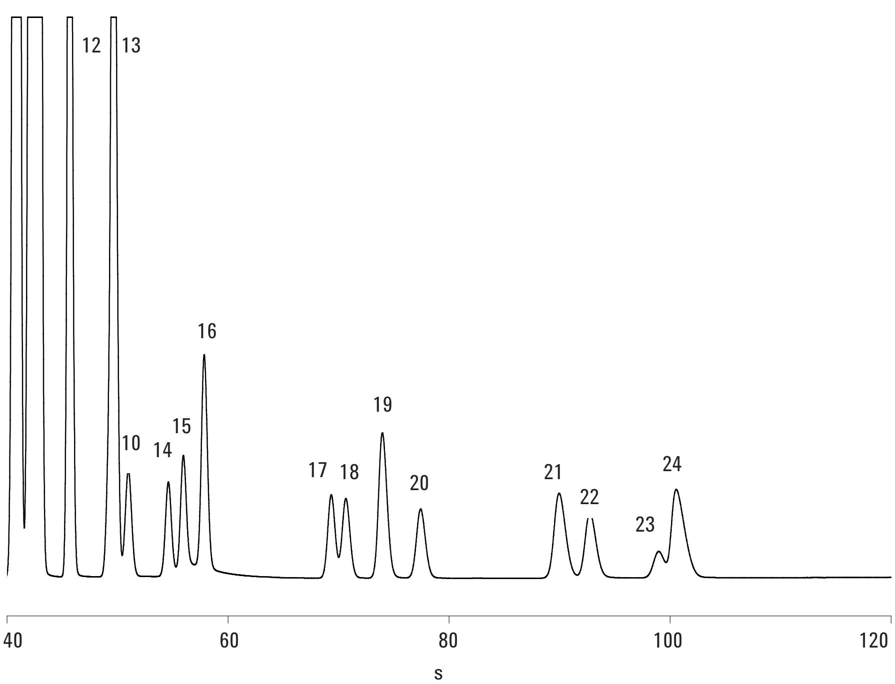

Figure 4. Refinery gas on the aluminum oxide column, channel 3

On channel 2 the C3 and C4 saturated and unsaturated hydrocarbons were separated and analyzed. This channel was also equipped with back flush in order to prevent the later eluting hydrocarbons from entering the analytical column. This prevented the later eluting components from interfering with the next analysis causing "ghost" peaks and/or baseline drift and higher noise. Furthermore, this channel was equipped with extra filters in the carrier gas lines, effectively protecting the analytical column from traces of moisture and carbon dioxide that could influence the chromatographic properties of the stationary phase in the long term.

Stable retention times are key factors for good chromatographic results. Repeatability results derived from Table 3 and Figure 5 for retention times are superb with RSDs around 0.1% and no drift.

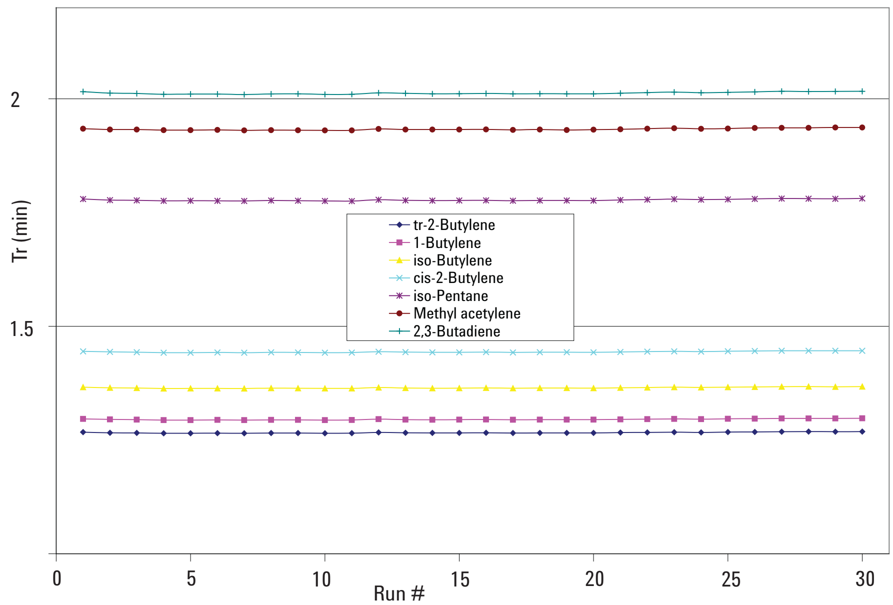

Figure 5. Repeatability figures for the aluminum oxide channel, channel 3

Table 3. Repeatability figures for the aluminum oxide channel

Run #	Tr (min) tr-2-Butylene	Tr (min) 1-Butylene	Tr (min) iso-Butylene	Tr (min) cis-2-Butylene	Tr (min) iso-Pentane	Tr (min) Methyl acetylene	Tr (min) 2, 3-Butadiene
1	1.2672	1.2963	1.366	1.4447	1.7797	1.934	2.0155
2	1.266	1.2952	1.3647	1.4437	1.7772	1.9322	2.0122
3	1.2657	1.2948	1.3643	1.443	1.7768	1.9323	2.0115
4	1.2647	1.2938	1.3632	1.442	1.7755	1.931	2.0097
5	1.2647	1.2937	1.3633	1.442	1.7758	1.931	2.0102
6	1.265	1.2942	1.3633	1.4423	1.7757	1.9315	2.0102
7	1.2648	1.2938	1.3632	1.442	1.7753	1.9303	2.0092
8	1.2653	1.2943	1.364	1.4427	1.7763	1.931	2.0105
9	1.2653	1.2943	1.3638	1.4423	1.776	1.9308	2.0108
10	1.2647	1.2938	1.3633	1.442	1.7753	1.9305	2.0095
11	1.265	1.294	1.3633	1.4422	1.7752	1.9303	2.0098
12	1.2667	1.2958	1.3653	1.444	1.778	1.9337	2.0128
13	1.2658	1.2948	1.3643	1.4432	1.7768	1.9322	2.0117
14	1.2655	1.2945	1.3638	1.4427	1.7762	1.9322	2.0108
15	1.2655	1.2947	1.364	1.4428	1.7763	1.9322	2.011
16	1.2658	1.295	1.3645	1.4432	1.7768	1.9325	2.0115
17	1.2653	1.2945	1.3638	1.4425	1.776	1.9315	2.0107
18	1.2657	1.2948	1.3642	1.443	1.7765	1.9322	2.011
19	1.2657	1.2947	1.3642	1.443	1.7765	1.9312	2.0108
20	1.2655	1.2947	1.364	1.4428	1.7762	1.932	2.0108
21	1.2663	1.2953	1.3648	1.4435	1.7775	1.9328	2.012
22	1.2667	1.2958	1.3653	1.4443	1.7782	1.934	2.0133
23	1.2672	1.2963	1.366	1.4448	1.7793	1.9353	2.0145
24	1.2667	1.2958	1.3655	1.4443	1.7782	1.9338	2.013
25	1.2675	1.2967	1.3662	1.445	1.7788	1.9343	2.0138
26	1.2678	1.2968	1.3667	1.4455	1.7798	1.9357	2.015
27	1.2683	1.2975	1.367	1.446	1.7807	1.936	2.0162
28	1.2685	1.2975	1.3673	1.4462	1.7803	1.936	2.0158
29	1.2682	1.2973	1.3668	1.446	1.7802	1.9367	2.016
30	1.2685	1.2977	1.3673	1.4462	1.781	1.9367	2.0163
Average	1.2662	1.2953	1.3648	1.4436	1.7774	1.9329	2.0122
Std Dev	0.0012	0.0012	0.0013	0.0014	0.0018	0.0020	0.0022
Rsd %	0.10%	0.09%	0.10%	0.10%	0.10%	0.10%	0.11%

Table 4. Reproducibility figures

Day	tr-2-Butylene	1-Butylene	iso-Butylene	cis-2-Butylene	iso-Pentane	Methyl acetylene	2, 3-Butadiene
1	1.2695	1.2988	1.3687	1.4481	1.7849	1.9406	2.0216
2	1.2678	1.2970	1.3668	1.4458	1.7815	1.9370	2.0173
3	1.2668	1.2958	1.3654	1.4443	1.7787	1.9339	2.0137
4	1.2665	1.2956	1.3652	1.4439	1.7781	1.9333	2.0130
8	1.2697	1.2989	1.3689	1.4483	1.7854	1.9405	2.0222
9	1.2681	1.2973	1.3671	1.4462	1.7821	1.9367	2.0180
10	1.2667	1.2957	1.3655	1.4443	1.7785	1.9345	2.0139
Average	1.2679	1.2970	1.3668	1.4458	1.7813	1.9366	2.0171
St. dev.	0.0013	0.0014	0.0015	0.0018	0.0031	0.0030	0.0037
RSD	0.10%	0.11%	0.11%	0.13%	0.17%	0.15%	0.19%

Table 4 and Figure 6 show the effects over several days. RSDs are only slightly higher when compared to the "results-per-day", which is to be expected. However, the results are very good, demonstrating the suitability of the Al_2O_3 channel for this type of analysis.

RSDs below 0.2% are shown in Table 4. During the ten day laboratory experiments no drift in retention times were observed, as can be seen in Figure 6.

Figure 6 shows no drift in retention time of components analyzed on the Al_2O_3 channel over ten days.

Figure 7 shows a chromatogram of refinery gas on the CP-Sil 5 CB channel. In this case the higher hydrocarbons C5+ were analyzed.

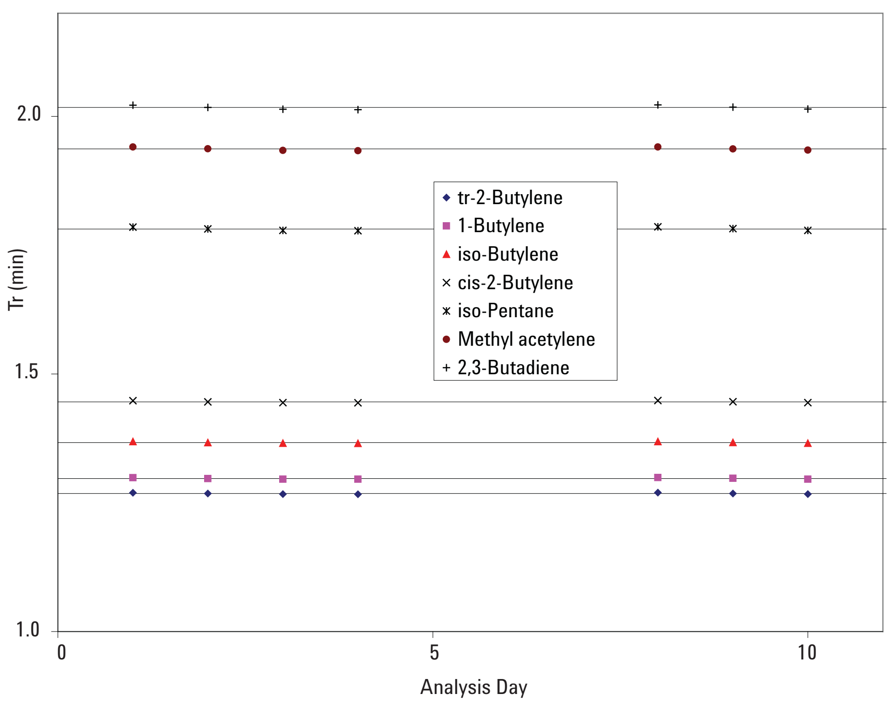

Figure 6. Reproducibility of the aluminum oxide channel, channel 3

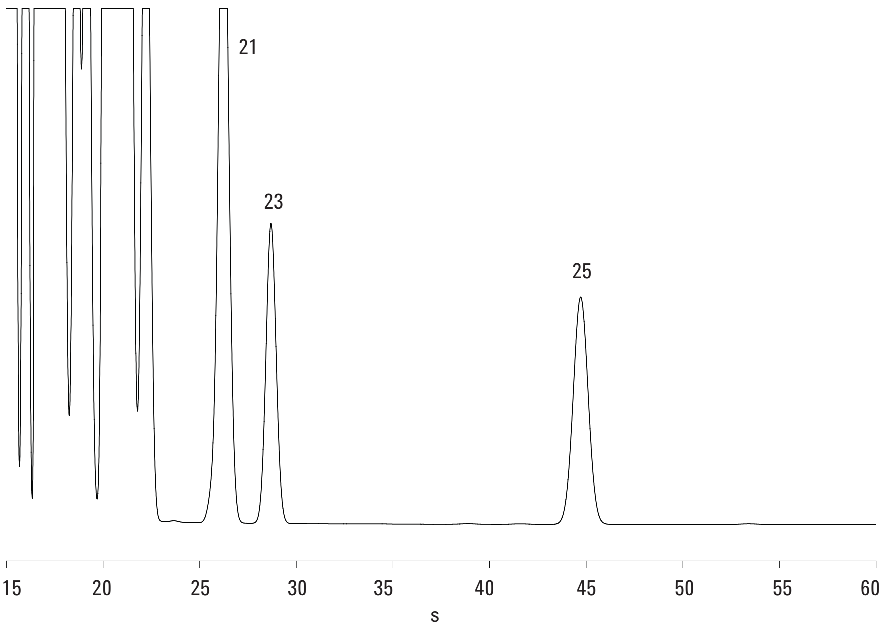

Figure 7. Refinery gas on the Agilent CP-Sil 5 CB column, channel 4

Conclusion

The Agilent 490 Micro GC QUAD was successfully used for the analysis of refinery gas. The permanent gases helium, hydrogen, oxygen, nitrogen, methane and carbon monoxide were analyzed on the CP-Molsieve channel. The C2 hydrocarbons, carbon dioxide and hydrogen sulfide were analyzed on the second channel equipped with a PoraPLOT U column. On the third channel, with an aluminum oxide column, the C3 and C4 hydrocarbons were analyzed. This channel was equipped with extra in line filters to ensure moisture and carbon-dioxide-free carrier gas. This significantly enhanced column lifetime and ensured long-term stable retention times. Finally, the fourth channel, equipped with a CP-Sil 5 CB column, analyzed the C5+ hydrocarbons.

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