



Agilent 7890 Series GC with Prefractionator for Reliable Analysis of Crude Butadiene and Mixed C₄ Streams

Application Note

Hydrocarbon processing industry

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Abstract

A previous application note [1] shows that an Agilent 7890 Series GC configured with a High Pressure Liquid Injector (HPLI) with post-column backflushing improves the analysis of the trace hydrocarbon impurities in monomer grade 1, 3-Butadiene. This application note uses a precolumn backflush system based on CFT (Capillary Flow Technology) to prevent polar compounds and heavier components present in crude butadiene and C₄ streams from entering the sensitive and expensive alumina PLOT column. In this way, the alumina column is protected and performance is maintained over many injections. The excellent separation of light hydrocarbons and improved retention time (RT) repeatability are also demonstrated.

Introduction

The crude mixed C₄ stream isolated from the steam cracking process is fed to butadiene extraction units, where butadiene is separated from the other C₄ s by extractive distillation. [2] There are several extraction distillation processes in use such as NMP (n-methylpyrrolidone)-based butadiene extraction, aqueous separation and ACN (acetonitrile) extraction. Most processes involve aqueous extractions. Before monomer-grade 1,3-Butadiene is produced, the crude 1,3-Butadiene stream contains entrained water, extraction solvent, and other impurities.



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A GS-Alumina column (50 m × 0.53 mm, 10.00 μm) was identified as an ideal column for trace impurity analysis in the previous application note [1]. However, the water presented in crude 1,3-butadiene will be absorbed by the Al₂O₃ surface, resulting in a retention time decrease. This can be avoided by heating the column at high temperature to remove the water after each run or several runs. This process is time consuming.

This application note uses pre-column backflushing to remove the water, polar solvent as well as higher molecular components before they enter the alumina column.

The pre-column backflushing system is based on a CFT device, the purged union which is controlled by an AUX EPC channel on the 7890 Series GC system. A polar HP-INNOWAX column is used as a pre-column to retain the water, polar solvents like ACN and higher molecular components such as the dimer. Once the light hydrocarbons are transferred to the alu-

mina column, a drop in the pressure at the inlet reverses flow through the pre-column, so that the polar and heavier components are backflushed through the split/splitless inlet (SSL)'s split vent. At the same time, the hydrocarbons are separated on the alumina column. Backflushing is complete by the end of the analytical run, so time savings are maximized.

Experimental

Figure 1 shows a diagram of the configuration. A 15 m × 0.53 mm, 1 μm HP-INNOWax is used as the pre-column (the first column) and a 50 m × 0.53 mm, 10.00 μm GS-Alumina as the analytical column (the second column). The sample is injected using a HPLI. An EPC flow (PCM B-1 in this example) controls the analytical column flow while a SSL controls pre-column flow.

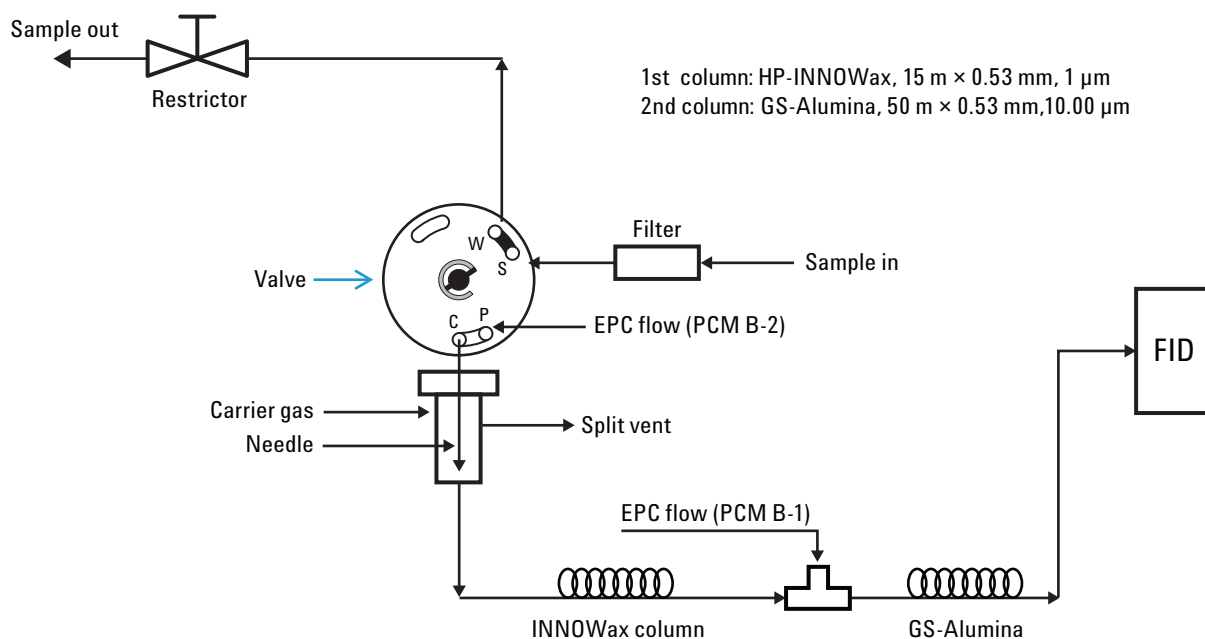


Figure 1. Diagram of the configuration.

The backflushing is triggered by programming a rapid pressure drop at the SSL to the pre-column. Defining the inlet and outlet sources for the columns is critical. The inlet to pre-column is the SSL and the outlet is PCM B-1. For the analytical column, the inlet is PCM B-1 and FID the outlet. The setup panes are shown in Figures 2A and 2B, respectively.

	Description
1	J&W 19095N-121: 240 °C: 15 m x 530 µm x 1 µm In: Front SS Inlet He Out: PCM B-1 He
2	Agilent 115-3552: 200 °C: 50 m x 530 µm x 15 µm In: PCM B-1 He Out: Front Detector FID
	Aux EPC 1 He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-2 He

Control Mode On

Flow: 4.9 mL/min
 Pressure: 10.469 psi
 Average Velocity: 24.983 cm/sec
 Holdup Time: 1.0007 min

(Initial): 0 min
He @ 60 °C Oven
Out: 9.159 psi
15 m x 530 µm x 1 µm

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
(Initial)		4.9	1.7	1.7
Ramp 1	100	-22	0	30
*				

Figure 2A. Pre-column setup pane. Backflushing starts at 1.7 minutes in this example.

	Description
1	J&W 19095N-121: 240 °C: 15 m x 530 µm x 1 µm In: Front SS Inlet He Out: PCM B-1 He
2	Agilent 115-3552: 200 °C: 50 m x 530 µm x 15 µm In: PCM B-1 He Out: Front Detector FID
	Aux EPC 1 He
	Aux EPC 2 He
	Aux EPC 3 He
	PCM B-2 He

Control Mode On

Flow: 6.5 mL/min
 Pressure: 9.159 psi
 Average Velocity: 46.135 cm/sec
 Holdup Time: 1.8063 min

(Initial): 0 min
He @ 60 °C Oven
Out: Ambient Pressure
50 m x 530 µm x 15 µm

	Rate mL/min per min	Value mL/min	Hold Time min	Run Time min
(Initial)		6.5	0	30
*				

Figure 2B. Analytical column flow set at 6.5 mL/min for the entire run.

To begin system setup, the pressure and flow sensors of the PCM and inlet must be zeroed [4]. This ensures correct control of the pressure at the inlet and purged union. This procedure is listed in the 7890A Series GC user guide. The alumina column must be calibrated as well, because the system relies on the fact that the current flows in the capillary columns which are dependent on the column dimensions. Experience has shown that the film thickness given for PLOT columns is an average and may not give the correct calculated flows in all cases. So it will need to find the equivalent film thickness for the GS-Alumina column according to following procedures:

1. Install the column to the GC inlet and detector.
2. Set the column pressure mode to constant pressure.
3. Set the oven temperature to 60 °C in this example, and column pressure to 9.8 psi in this example, which are used in the method.
4. Measure the column flow at the detector (ensure the detector gases are off). Note the amount of 8.2 mL/min in this example.
5. Enter the column length, labeled id, column pressure, oven temperature, and carrier gas type (He) into the appropriate fields of the flow calculator [3]. Figure 3 shows the sample exercise. Do not make any entry to the outlet flow field in the flow calculator.
6. In the flow calculator, adjust the column id until the calculated flow (Outlet Flow) is the same as the column flow measured, 8.2 mL/min. Figure 3 shows that, for this example, the effective id is 0.52 mm.

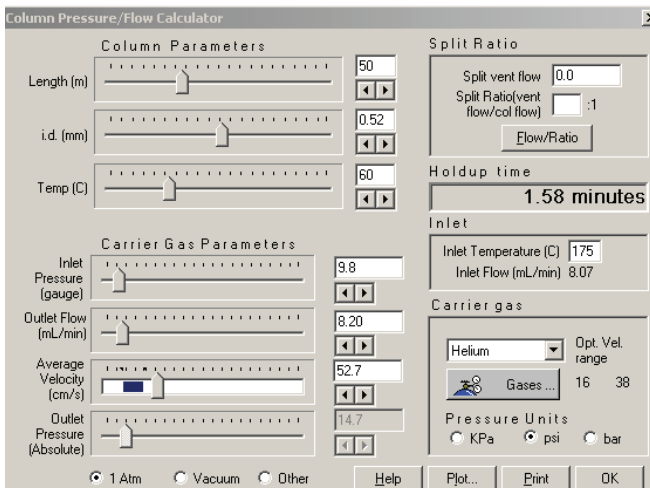


Figure 3. Alumina column calibration.

The internal diameter of a capillary column is the nominal internal tube diameter minus two times the film thickness. Therefore the equivalent film thickness for this column is: $(530 - 520)/2$

This gives an equivalent film thickness of 5 µm. Set the film thickness for column 2 to 5 µm.

Table 1 lists typical GC conditions, and Table 2 lists the gas standard mixtures used for method development. As a general rule, the pre-column flow should be set between 70% and 85% of the analytical column flow. [4] In this application note, the pre-column flow (4.9 mL/min) is set to approximately 75% of the analytical column flow. This is a good general rule to follow for method development.

Table 1. Typical GC Conditions for Impurities in 1,3-Butadiene Analysis Based on Configuration B with Backflushing

Gas chromatograph	Agilent 7890A Series GC System
Injection source	High Pressure Liquid Injector (HPLI)
Injection port	Split/splitless, 120 °C, split ratio: 20:1 (uses higher or lower split ratio according to the concentrations of hydrocarbons)
Sample size	0.5 µL (liquid)
EPC flow for HPLI	30 mL/min
Valve temperature	120 °C
Oven temperature program	60 °C hold 3 minutes, at 5 °C/min, to 105 °C hold 3 minutes at 5 °C/min, to 150 °C hold 3 minutes at 30 °C/min, to 180 °C hold 3 minutes
Column 1	INNOWax 15 m × 0.53 mm, 1 µm
Column 1 flow (He)	4.9 mL/min
Column 2	GS-Alumina 50 m × 0.53 mm, 10.00 µm
Column 2 flow (He)	6.5 mL/min, constant flow mode
FID	
Temperature	200 °C
H ₂ flow	40 mL/min
Air flow	400 mL/min
Make up (N ₂)	40 mL/min

Results and Discussion

Setup backflushing timing

The INNOWax pre-column retains water, polar solvent like ACN, and higher molecular components like dimer while the light hydrocarbons pass through quickly. Once hydrocarbons have migrated past the purged union, pressure at the inlet is dropped, flow reverses through the first column to backflush polar components while the analytical run continues in the second alumina column.

The upper chromatogram in Figure 4 shows the separation on HP- INNOWax. 15 m × 0.53 mm, 1 µm, the experiments are based on the system shown in Figure 1, but the restrictor, uncoated deactivated fused silica tubing is used instead of GS-Alumina. The restrictor's length and diameter are chosen to have the same flow vs pressure characteristics as GS-Alumina 50 m × 0.53 mm, 10.00 µm. A sample of standard No.1 is spiked with water and methanol. In the chromatogram, the polar INNOWax column does not retain 1,3-Butadiene and other C₁-C₅ hydrocarbons and they elute as a group (the first group). However, any polar, compounds such as water and methanol are held on the INNOWax. Water elutes after methanol but is not seen on FID. Dimer elutes even later. This will give enough time for backflushing. The lower chromatogram in Figure 4 shows methanol and the dimer being backflushed with backflushing starting at 2 minutes.

Fine tuning of the backflush time is easily done by running a sequence of several methods with a slightly different backflush time. Standard No. 1 is used for the sequence on the system shown in Figure 1.

Table 2. Standard Sample Information

Standard No. 1

Compound	Amt [% w/w]
Propane	1.8500e-2
Propylene	1.1230e-1
iso-Butane	7.2690e-2
Butane	6.2780e-2
Propadiene	8.5210e-2
t-2-Butene	9.7800e-2
1-Butene	1.0410e-1
iso-Butylene	1.2890e-1
c-2-Butene	3.2740e-2
iso-Pentane	3.0320e-3
n-Pentane	5.0110e-3
1,2-Butadiene	1.1080e-1
1,3-Butadiene	Balance
Propyne	1.5150e-2
Vinyl acetylene	1.8590e-2
Ethyl acetylene	1.0430e-2

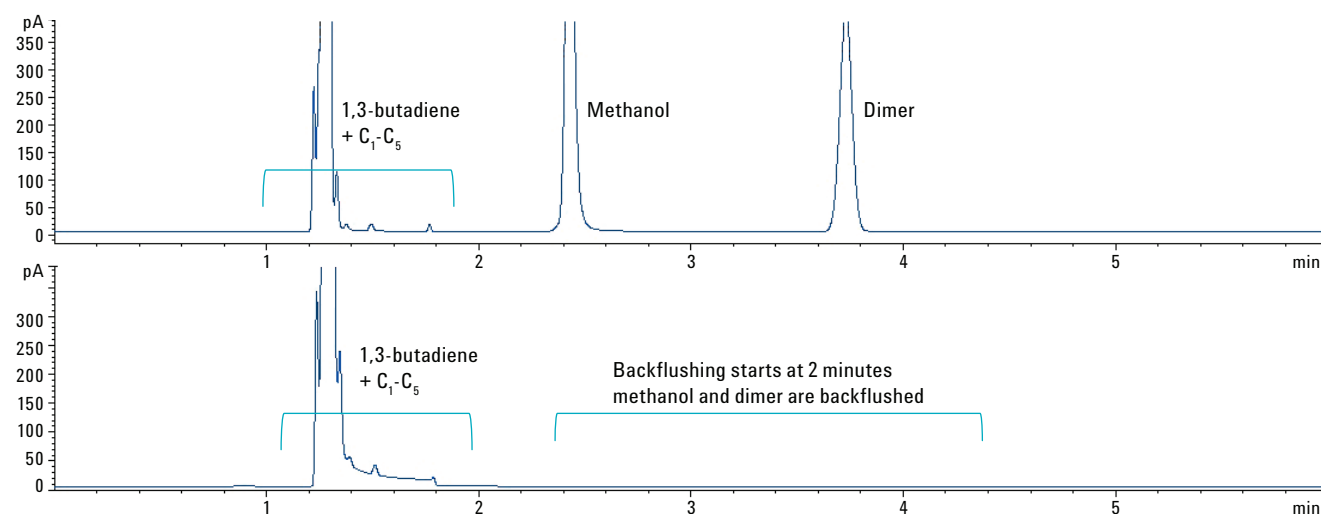


Figure 4. Separation on HP-INNOWax.

Set up a backflush time of 1.2 minutes, in this example, the last peak to appear in the chromatogram will be vinyl acetylene (VA), as VA elutes after EA on INNOWax column adjust backflush time in 0.1 minute increasing steps until the VA peak appears and the peak remains the same size (1.4 minutes) in this example as shown in Figure 5. 1.4 minutes plus 0.3 seconds to 0.6 seconds can be used as the backflush time which is 1.7 to 2.0 minutes for this study.

Backflush improves the repeatability of retention times and saves analysis time

Without backflushing, water and polar compounds contained

in crude 1,3-butadiene will effect the performance of the alumina column and cause the bad RT repeatability and damage the sensitive stationary phase. Also, 1,3-butadiene is a reactive molecule which is typically stored with an inhibitor to prevent polymerization during storage. However, even in the presence of an inhibitor, small amounts of 1,3-Butadiene dimer (4-vinylcyclohexene) will be formed over the long term. This requires a long bake out time.

Figure 6 shows that the analytical cycle time is shortened significantly with backflushing. While without backflushing, an additional 36 minutes is required at 180 °C to allow the dimer to elute from the column.

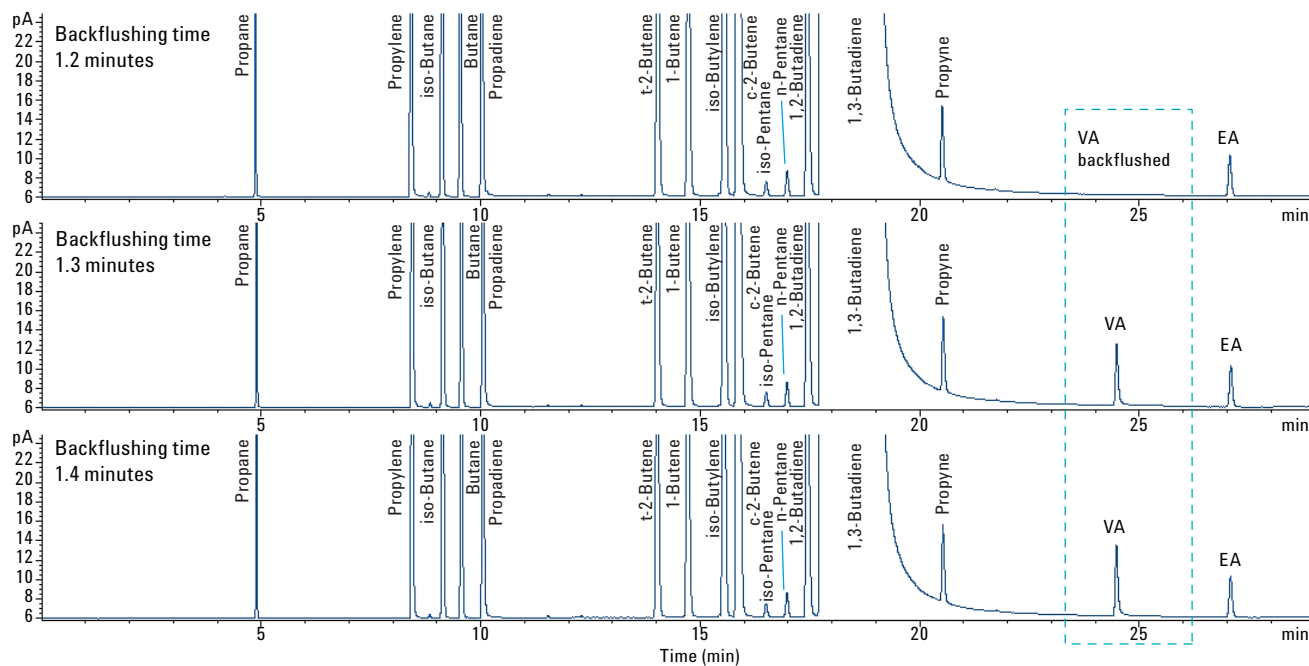


Figure 5. Set up a backflush time.

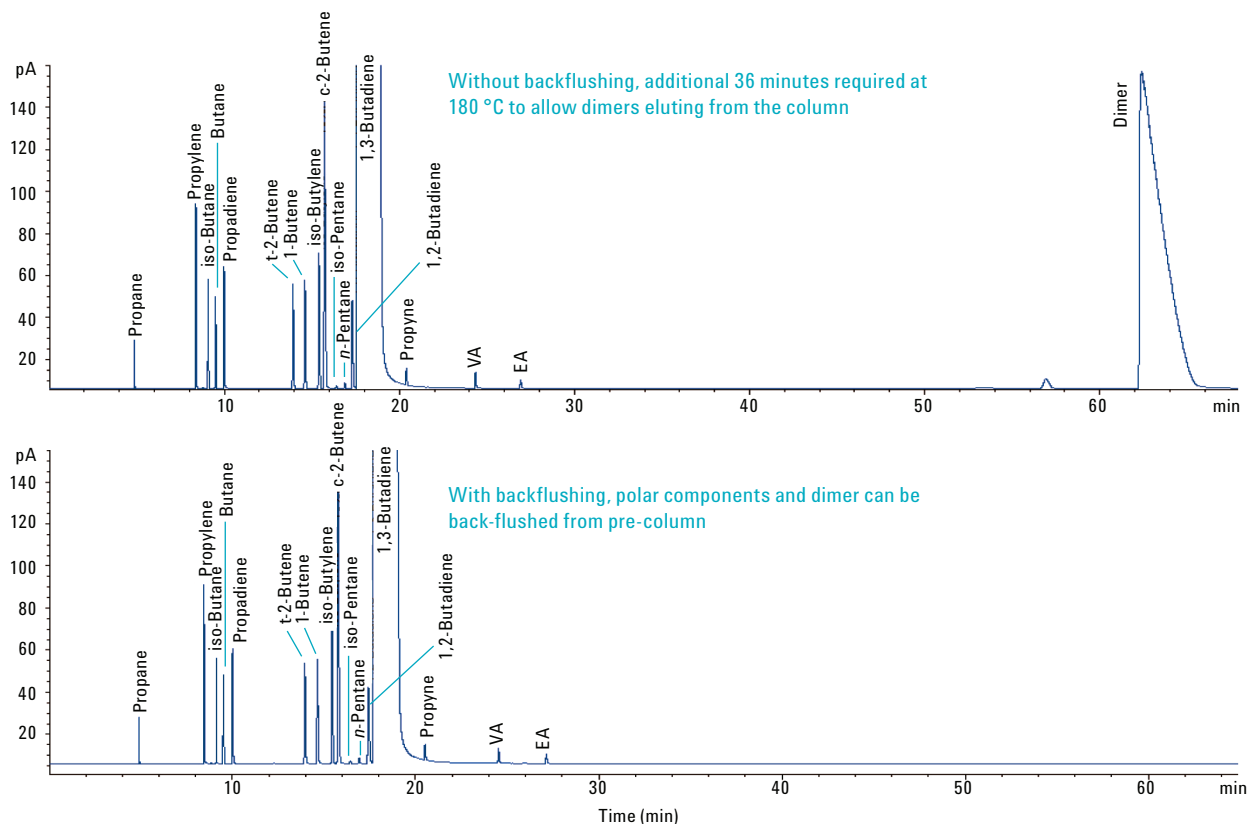


Figure 6. Chromatograms with and without backflushing.

Figure 7 shows a chromatogram for a sample, mixed C₄ from a petrochemical producer. The polar compounds including water and solvent as well as dimer are backflushed. In this experiment, the sample cylinder is pressured by 100 psig of nitrogen. Helium could also be used. The split ratio is 150:1 and the backflushing time is 1.9 minutes.

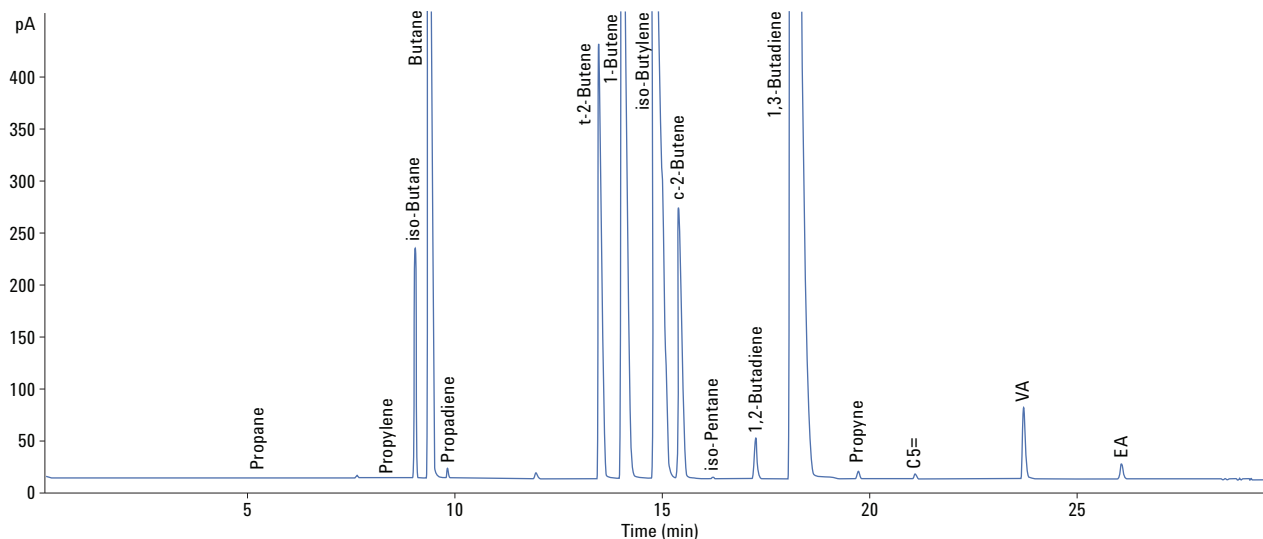


Figure 7. Plant sample, mixed C₄ stream analysis.

Figure 8 shows 20 consecutive injections of standard No.1. Figure 9 is a blank run after 50 sample runs with backflushing were completed. The blank run shows that the column was very clean after backflushing.

The performance of GS-Alumina is maintained over many injections since the HP-INNOWax column prevents polar oxygenates from damaging the sensitive stationary phase. Also, high molecular dimer is backflushed. So the RT repeatability is improved. Table 3 demonstrates the improved RT repeatability with backflushing.

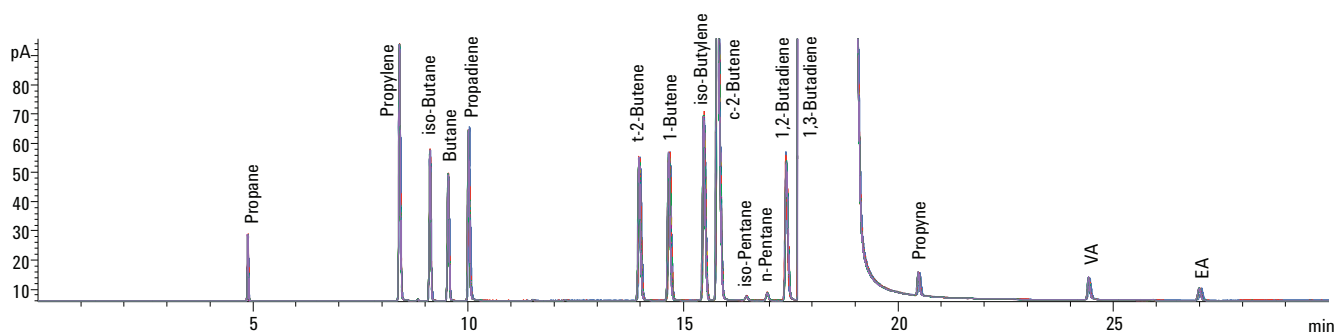


Figure 8. Overlays of 20-run with backflushing.

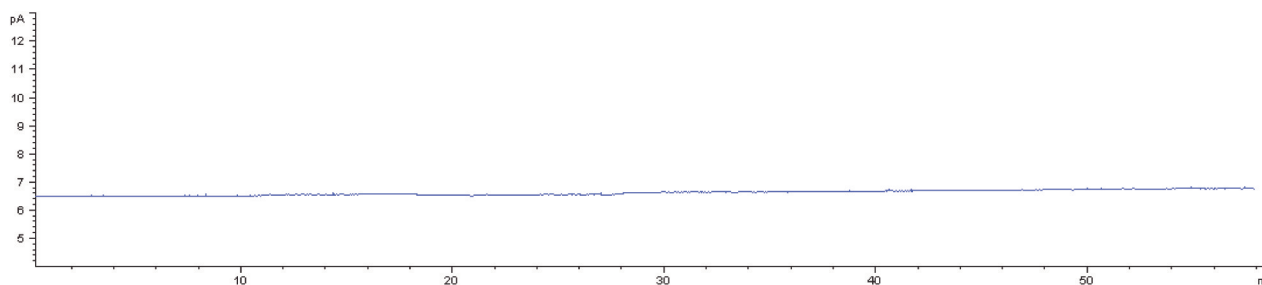


Figure 9. Blank run after the 50 runs with backflushing were completed.

Table 3. Improved RT Repeatability with Backflushing

Compounds	with Backflush			without Backflush*								
	Area n=20			RT n=20			Area n=20			RT n=20		
	Average	STDEV	RSD%	Average	STDEV	RSD%	Average	STDEV	RSD%	Average	STDEV	RSD%
Propane	35.640	0.237	0.67	4.875	0.001	0.03	36.122	0.28	0.78	4.839	0.004	0.07
Propylene	225.706	1.522	0.67	8.398	0.003	0.03	228.800	1.77	0.77	8.356	0.009	0.11
iso-Butane	142.680	0.973	0.68	9.106	0.003	0.04	144.792	1.17	0.81	9.056	0.008	0.09
Butane	122.406	0.845	0.69	9.532	0.003	0.03	124.262	1.01	0.81	9.482	0.009	0.09
Propadiene	166.380	2.033	1.22	10.003	0.006	0.06	167.013	1.55	0.93	9.966	0.011	0.11
t-2-Butene	192.217	1.351	0.70	13.971	0.008	0.06	195.179	1.56	0.80	13.912	0.016	0.11
1-Butene	210.954	1.459	0.69	14.661	0.010	0.07	214.122	1.72	0.80	14.593	0.017	0.12
iso-Butylene	266.110	1.861	0.70	15.475	0.008	0.05	270.141	2.16	0.80	15.398	0.016	0.11
c-2-Butene	678.610	4.804	0.71	15.787	0.007	0.04	689.040	5.48	0.79	15.710	0.016	0.10
iso-Pentane	5.899	0.049	0.83	16.467	0.002	0.01	5.992	0.06	1.01	16.388	0.014	0.09
n-Pentane	9.947	0.079	0.80	16.946	0.002	0.01	10.087	0.08	0.80	16.872	0.013	0.08
1,2-Butadiene	208.015	1.386	0.67	17.395	0.005	0.03	209.559	1.70	0.81	17.472	0.115	0.66
1,3-Butadiene	190,227.938	1,303.406	0.69	17.690	0.003	0.02	190,227.938	1,303.41	0.69	17.498	0.147	0.84
Propyne	30.442	0.323	1.06	20.460	0.009	0.04	30.266	0.31	1.01	20.456	0.019	0.10
Vinyl acetylene	30.149	0.272	0.90	24.415	0.007	0.03	30.149	0.27	0.90	24.405	0.019	0.08
Ethyl acetylene	20.264	0.181	0.89	26.995	0.012	0.04	20.487	0.20	0.98	26.996	0.030	0.11

*with additional 36 minutes at 180 °C

Conclusion

An Agilent 7890 Series GC system configured with a High Pressure Liquid Injector (HPLI) and a CFT purged union is used for reliable analysis of crude butadiene and mixed C₄ streams which contain polar components including water. The CFT purged union with precise and stable electronic pneumatic control enables midpoint backflushing to prevent polar components like water and heavier components like dimer which are present in mixed C₄ stream and crude butadiene from entering the sensitive and expensive alumina PLOT column. In this way, the alumina column is protected and performance is maintained over many injections. Excellent separations of light hydrocarbons and improved repeatability are also achieved.

References

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