

Improved Gas Chromatograph Method for the Analysis of Trace Hydrocarbon Impurities in 1, 3-Butadiene

Application Note

Hydrocarbon processing industry

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Abstract

An improved gas chromatographic method based on an Agilent 7890 Series GC for the analysis of trace hydrocarbon impurities in monomer grade 1, 3-Butadiene has been developed. A High Pressure Liquid Injector (HPLI) allows sampling light petroleum without discrimination and provides high accuracy and precision. Post-column back-flushing eliminates the long bake-off time for late-eluting compounds such as the dimer, 4-vinylcyclohexene. It not only saves the analytical cycle significant time, but also improves the retention time (RT) repeatability. The performances of different types of PLOT Alumina columns are also discussed.

Introduction

1,3-Butadiene is an important petrochemical raw material. It is produced as a byproduct of the steam cracking process for the production of ethylene and other olefins. Most 1,3-Butadiene is used as a monomer in the production of synthetic rubber. The presence of trace hydrocarbon impurities especially propadiene and alkynes including propyne (also known as methyl acetylene) can interfere with catalytic polymerization. Therefore, identifying and quantifying trace hydrocarbon impurities in 1,3-Butadiene is critical to producing high quality synthetic rubber products.

ASTM standard method D 2593 uses packed columns for determination of hydrocarbon impurities in butadiene [1]. However, some C4 isomers cannot be separated by this method.



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Alumina PLOT columns are commonly used for light hydrocarbon separation. The determination of polar hydrocarbon impurities at trace levels can be challenging and is highly dependent on the deactivation of the alumina surface. Alumina with KCL deactivation modifies the Al₂O₃ surface making it less polar. This PLOT column is used in China's national standard method GBT-6017-2008 [2] and provides highly selective retention for both saturated and unsaturated light hydrocarbons, however, measurement of trace level propyne will be impacted by overloading of 1,3-Butadiene. Other challenges include a long bake-out time required for the high molecular weight impurities, primarily dimer (4-vinylcyclohexene), to elute. Also, RT repeatability is affected by sample residues.

In this application note, nonpolar Al₂O₃ surface HP-AL/KCL and more polar surface GS-Alumina columns were tested. Backflushing was used to remove the high molecular weight impurities including dimer to the detector so that the analytical cycle time was shortened and RT repeatability was improved. The dimer, which normally requires a second sample injection on an alternative column [3], can be possibly detected.

Experimental

Two configurations based on a 7890 Series GC are used in this study. Both configurations include an HPLI, a split/splitless inlet, and an FID. Configuration A did not use backflushing. Configuration B used a six-port valve with both ends of a PLOT GS-Alumina column connected (particle traps are recommended for both column sides). By switching the valve, the column flow can be reversed for backflushing the high molecular weight impurities to the detector. Figures 2 and 6 show the valve drawing for configuration A and B respectively.

Table 1 shows the typical GC conditions for impurities in 1,3-Butadiene analysis based on configuration B. Table 2 lists the gas standard mixtures used 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
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, to 105 °C hold 3 minutes at 5 °C/min, to 150 °C hold 3 minutes at 5 °C/min, to 180 °C hold 3 minutes at 30 °C/min
Column	GS-Alumina 50 m × 0.53 mm, 10.00 µm
Column flow (He)	7.5 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

Table 2. Standard Sample Information

Standard No. 1		Standard No. 2	
Compound	Amt [% w/w]	Compound	[ppm w/w]
Propane	1.8500e-2	<i>t</i> -2-Butene	120.000
Propylene	1.1230e-1	<i>c</i> -2-Butene	3400.000
<i>iso</i> -Butane	7.2690e-2	<i>n</i> -Pentane	50.000
Butane	6.2780e-2	1,2-Butadiene	370.000
Propadiene	8.5210e-2	1,3-Butadiene	Balance
<i>t</i> -2-Butene	9.7800e-2	Propyne	20.130
1-Butene	1.0410e-1	Vinyl acetylene	30.200
<i>iso</i> -Butylene	1.2890e-1	Ethyl acetylene	59.320
<i>c</i> -2-Butene	3.2740e-2		
<i>iso</i> -Pentane	3.0320e-3		
<i>n</i> -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		

Results and Discussion

Sample injection

Gas chromatographic sampling and representative analysis of highly volatile liquefied hydrocarbons with high precision and accuracy can be challenging. A unique sample injection device, HPLI, based on a unique needle interface and high pressure liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions without the danger of carryover. Various pressurized liquid samples have been tested on this device with high accuracy and precision in a previous application note [4]. The HPLI was selected as the best sample introduction device for this work.

Column selection

Several types of Alumina PLOT columns with the deactivation of the Al_2O_3 surface are available. Alumina with KCL deactivation gives a relatively nonpolar Al_2O_3 surface. Alumina bond Na_2SO_4 produces a midpolar Al_2O_3 surface and GS-Alumina is the most polar Al_2O_3 surface with proprietary deactivation.

For impurity analysis, the affect of overloading must first be determined. Normally, overloading phenomena will produce asymmetric peak shapes with a significant tail. Alumina PLOT columns based on gas-solid chromatography show peak shape of an overloaded component that will sharply raise then

start to tail. In this case, with higher concentrations of 1,3-Butadiene, the peak elutes earlier and the peak tail remains the same as shown in Figure 1. Therefore, when injecting a large amount of 1,3-Butadiene, its peak may overlap the component which elutes just in front.

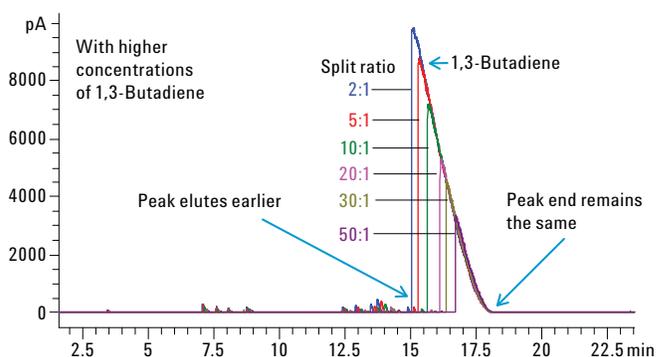


Figure 1. Impact of overloading on peak broadening on Alumina PLOT column.

To identify a suitable column for the impurities analysis, HP-AL/KCL (Alumina with KCL deactivation) and GS-Alumina columns were tested. Configuration A without backflushing was used for the experiments.

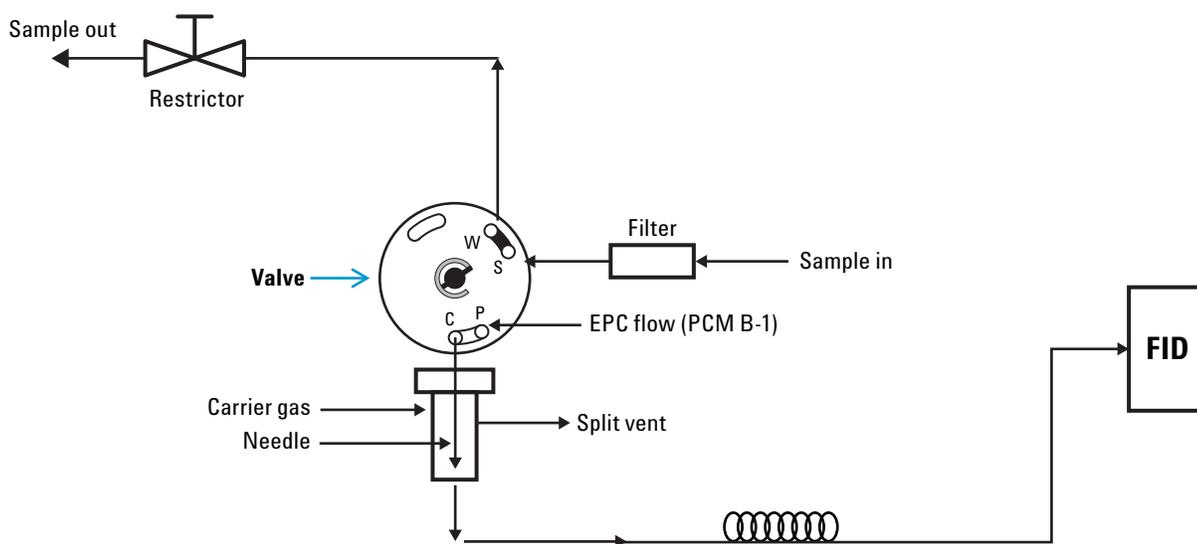
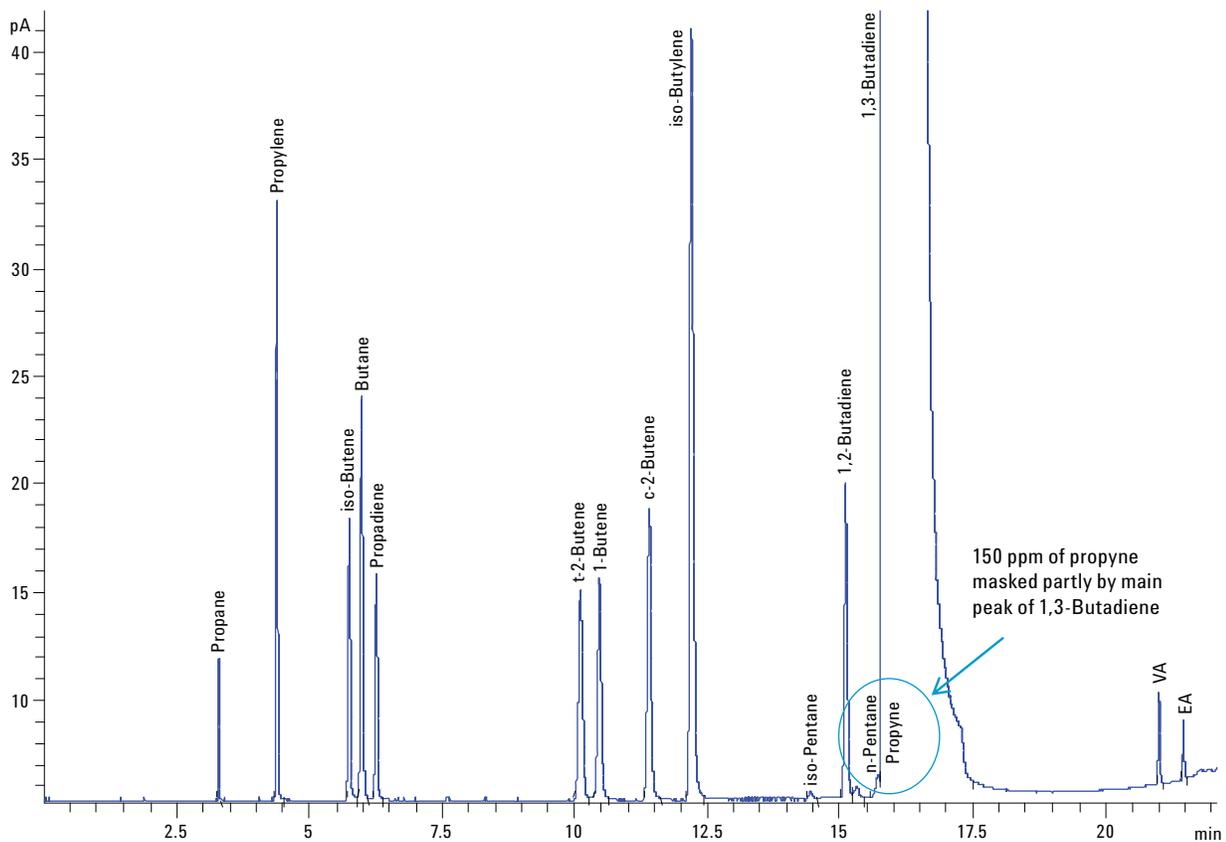


Figure 2. Configuration A – without backflush.

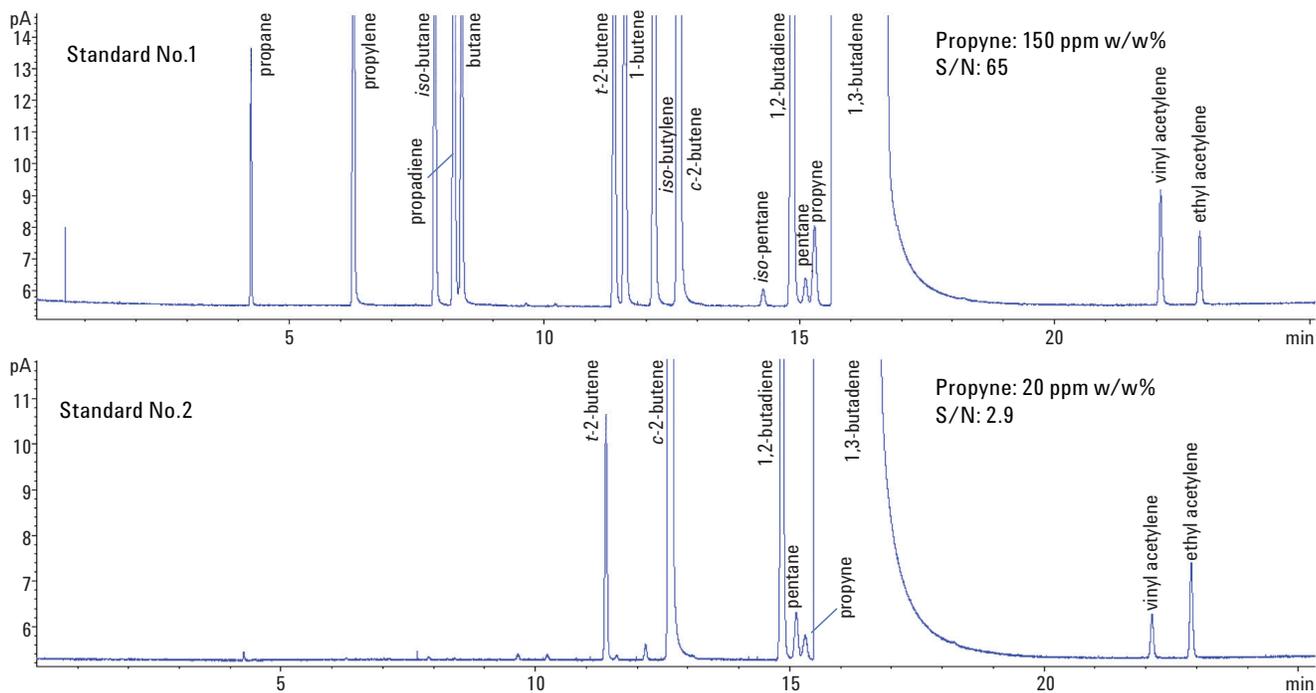
On the HP-AL/KCL column, propyne elutes just before 1,3-Butadiene. A 0.5- μ L solution of standard No.1 is injected by the HPLI at a split ratio of 200:1. Figure 3 shows that 150 ppm of propyne is masked partly by the main peak of 1,3-Butadiene. Reducing the sample size to 0.06 μ L with split ratio 10:1 allows propyne to be separated from 1,3 butadiene as shown in Figure 4. In this case, 20 ppm of propyne was detected with a signal-to-noise ratio of 2.9.



GC conditions

Column	HP-AL/KCL, 50 m, 0.53 mm, 15 μ m
Carrier gas	He: 4 mL/min
Sample size	0.5 μ L (liquid), EPC flow for HPLI: 15 mL/min
Inlet spit ratio	200:1
Oven	80 $^{\circ}$ C (hold 10 minutes), to 100 $^{\circ}$ C at 5 $^{\circ}$ C/min, to 110 $^{\circ}$ C at 3 $^{\circ}$ C/min, to 180 $^{\circ}$ C (hold 30 minutes) at 15 $^{\circ}$ C/min

Figure 3. Chromatograms on HP-AL/KCL column with the sample size of 0.5 μ L.



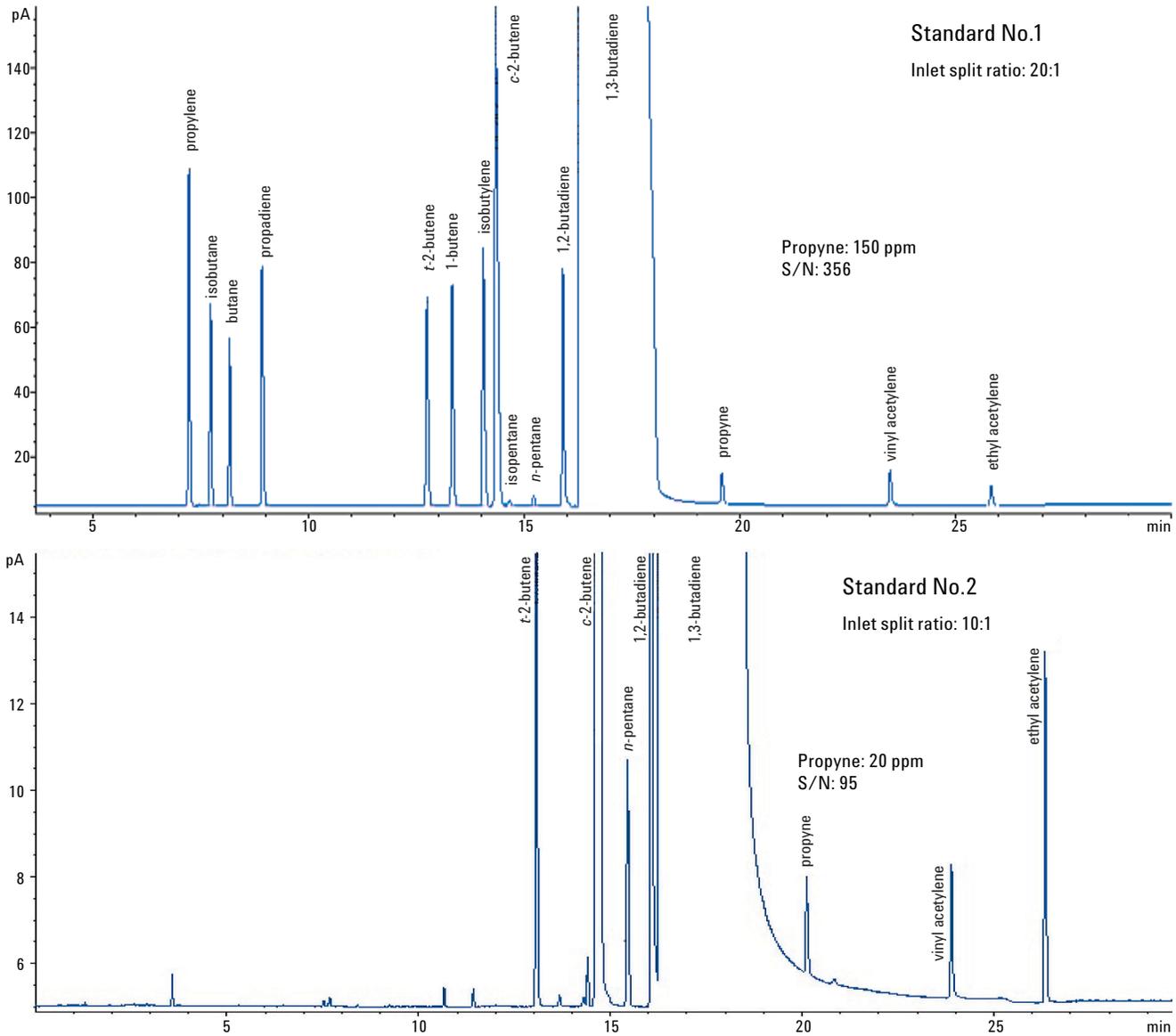
GC conditions

Column HP-AL/KCL, 50 m, 0.53 mm, 15 μ m
 Carrier gas He: 5.6 mL/min
 Sample size 0.06 μ L (liquid) , EPC flow for HPLI: 10 mL/min
 Inlet split ratio 10:1
 Oven program 60 $^{\circ}$ C (hold 3 minutes) to 105 $^{\circ}$ C (hold 4 minutes) at 5 $^{\circ}$ C/min to 150 $^{\circ}$ C at 5 $^{\circ}$ C/min, to 190 $^{\circ}$ C (hold 30 minutes) at 20 $^{\circ}$ C/min

Figure 4. Chromatograms on HP-AL/KCL column with sample size of 0.06 μ L.

On the GS-Alumina column propyne elutes after 1,3-Butadiene. The large amount of 1,3-Butadiene has less impact on propyne determination. As shown in Figure 5, a larger sample size of 0.5 μ L with a split ratio of 20:1 for standard No.1 and 10:1 for standard No. 2 are used. 20 ppm of

propyne can be separated from 1,3-Butadiene with a S/N of 95. In this case, levels lower than 20 ppm of propyne can be analyzed. Other hydrocarbon impurities including propadiene and 1,2-Butadiene which just elutes before 1,3-Butadiene are also well separated.



GC condition

Column GS-Alumina 50 m, 0.53 mm, 10.00 μ m
 Carrier gas He: 6.89 mL/min
 Sample size 0.5 μ L (liquid), EPC flow for HPLI: 30 mL/min
 Oven program 60 $^{\circ}$ C (hold 3 minutes) to 105 $^{\circ}$ C (hold 3 minutes) at 5 $^{\circ}$ C/min to 150 $^{\circ}$ C (hold 2 minutes) at 5 $^{\circ}$ C/min, to 180 $^{\circ}$ C (hold 35 minutes) at 30 $^{\circ}$ C/min

Figure 5. Chromatograms on GS-Alumina column with sample size of 0.5 μ L.

Post-column backflushing

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. Typically, alumina PLOT columns cannot be used to analyze the dimer and it requires over 30 minutes at high temperature to bake dimer and other heavier impurities out from the column. Otherwise, the residuals will affect RT repeatability in subsequent runs.

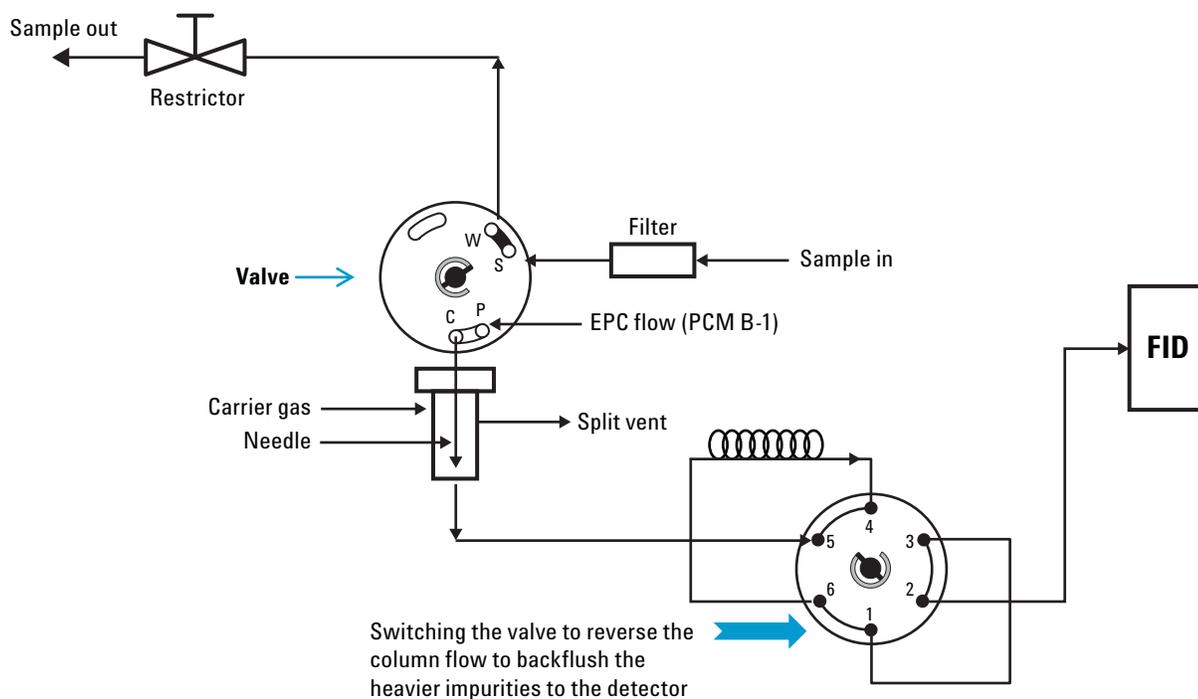
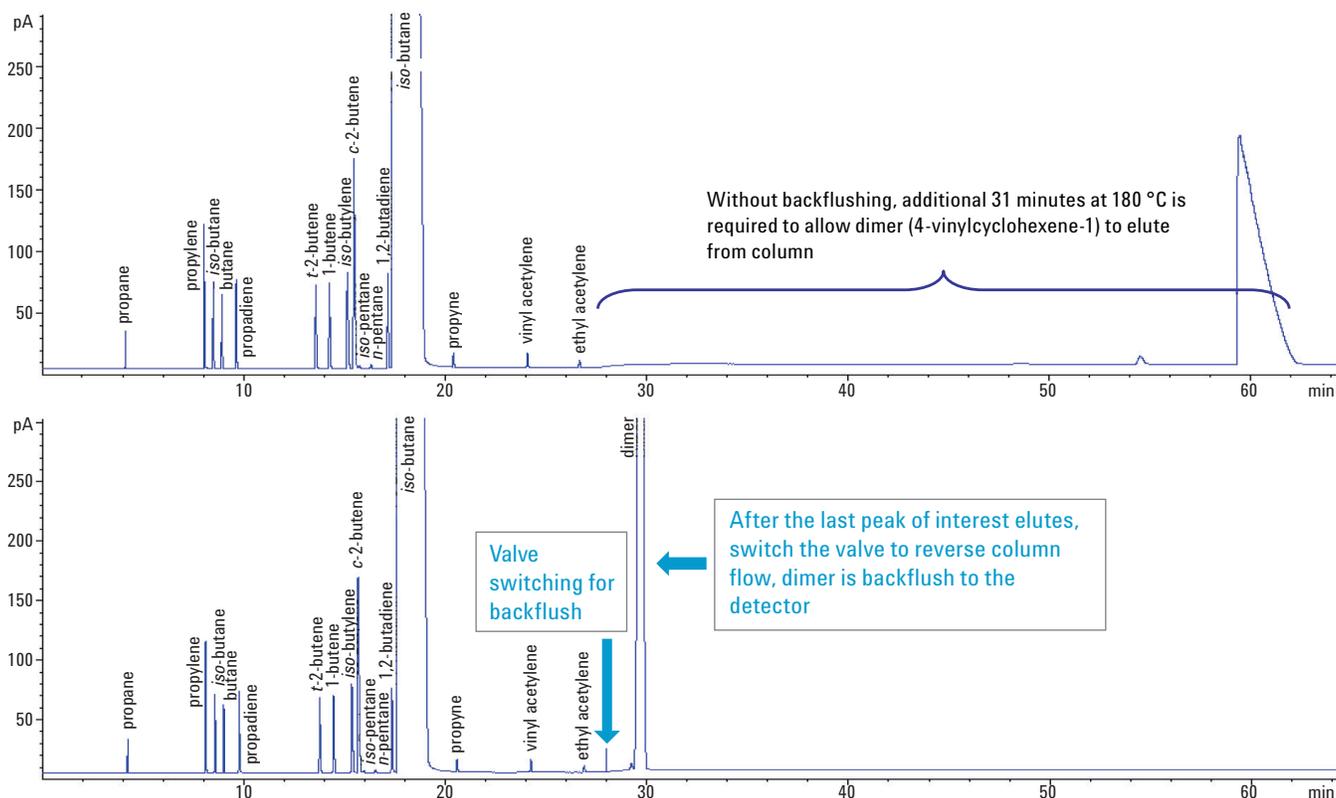


Figure 6. Configuration B - with backflushing.

The Configuration B uses a six-port valve with both ends of a PLOT GS-Alumina column connected. With this design, the column flow can be reversed by switching the valve after the last component of analytical interest elutes. In this way, the heavier impurities including dimer are back-flushed to the detector. The analytical cycle time is shortened significantly as shown in lower chromatogram in Figure 7. Also, this makes

it possible to analyze dimer. Without backflushing, it requires an additional 31 minutes at 180 °C to allow dimer to elute from the column as shown in upper chromatogram in Figure 7.

Since all the residuals are backflushed, the RT repeatability is improved. Table 3 demonstrates excellent repeatability.



GC conditions are listed in table 1

Sample Standard no.1

Figure 7. Chromatograms on GS-Alumina column with and without backflushing.

Table 3. Repeatability with Backflushing

Compounds	Area n=19			RT n=19		
	Average	STDEV	RSD%	Average	STDEV	RSD%
<i>t</i> -2-Butene	29.178	0.115	0.39	13.816	0.007	0.05
<i>c</i> -2-Butene	744.490	1.991	0.27	15.707	0.008	0.05
<i>n</i> -Pentane	11.029	0.034	0.31	16.561	0.008	0.05
1,2-Butadiene	76.324	0.232	0.30	17.408	0.007	0.04
1,3-Butadiene	211309.669	563.114	0.27	17.672	0.009	0.05
Propyne	4.346	0.033	0.77	20.597	0.006	0.03
VA	5.865	0.028	0.47	24.255	0.006	0.03
EA	13.501	0.045	0.33	26.878	0.009	0.03
Dimer	13772.325	33.166	0.24	29.771	0.018	0.06

Sample: Standard No.1

Mixed C4 from a petrochemical producer is also tested. The dimer is detected as a symmetric peak with other light hydrocarbon impurities as shown in figure 8. In the experiment, the sample cylinder is pressured by 100 psig of nitrogen. Helium could also be used.

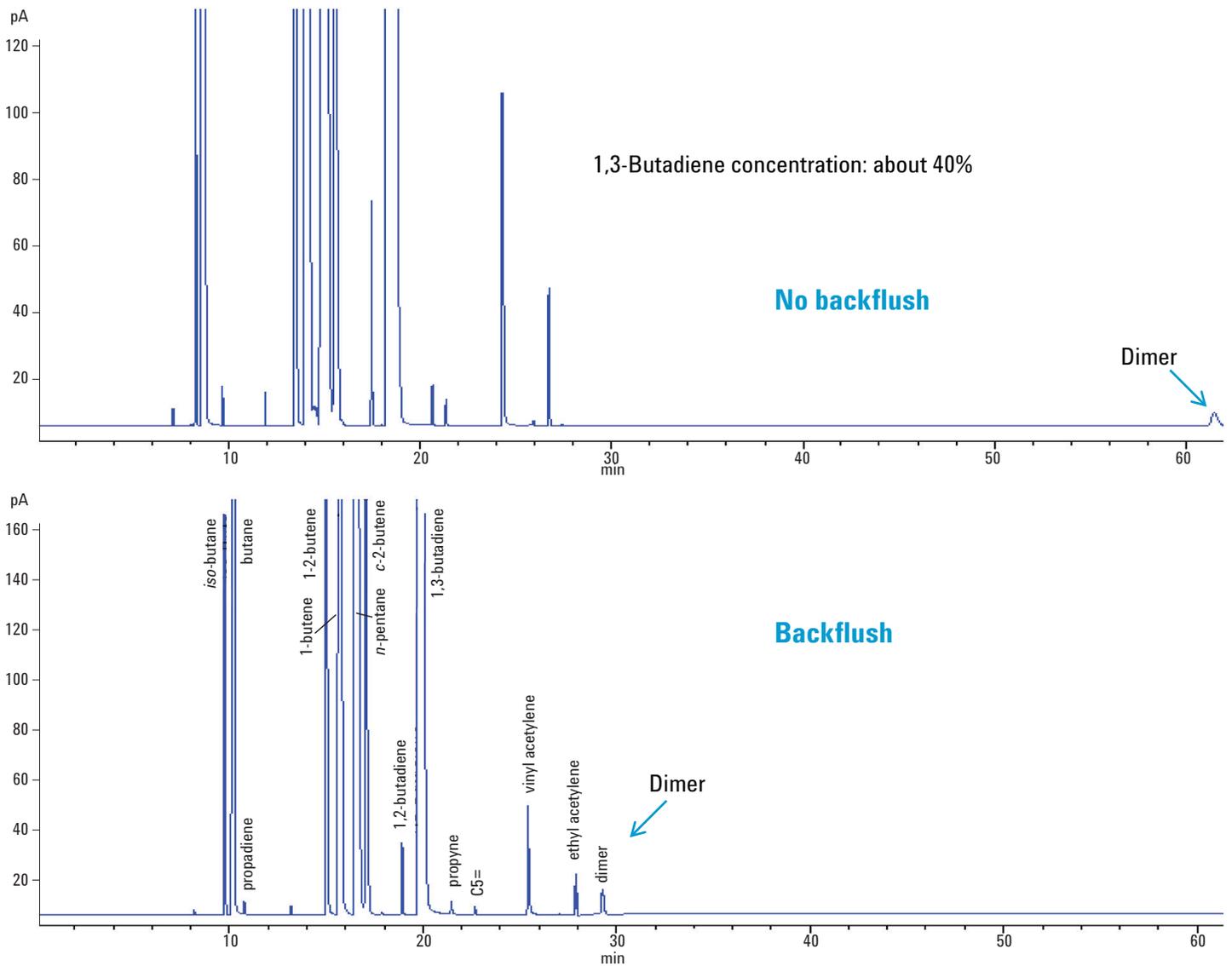


Figure 8. Plant sample, mixed C4 stream analysis with and without backflushing.

Conclusion

An Agilent 7890 Series GC configured with a High Pressure Liquid Injector (HPLI) with column backflushing mode improves the analysis of the trace hydrocarbon Impurities in 1,3-Butadiene. A GS-Alumina column (50 m × 0.53 mm, 10.00 µm) with 0.5 µL (liquid) sample size was identified as an ideal method for trace impurities analysis. The method has the following advantages:

- Low level hydrocarbon impurities including propyne in monomer grade 1,3-Butadiene can be analyzed
- The HPLI provides excellent peak area repeatability
- Post-column backflushing eliminates the long bake off time for late-eluting compounds including dimer and reduces the analytical cycle time significantly
- Backflushing improves the RT repeatability
 - The late-eluting compounds are eliminated
 - Baselines remain clean with no carryover
 - Peak positions remain stable

References

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