# Analyze Hydrocarbon Impurities in 1,3-Butadiene with an Agilent J&W GS-Alumina PT Column

Application Note

Energy and Chemicals


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## Abstract

The typical method for analyzing hydrocarbon impurities in 1,3-butadiene was easily and successfully transferred from an Agilent J&W GS-Alumina column to an Agilent J&W GS-Alumina PT column of the same dimensions with two integrated particle traps. An Agilent 7890A gas chromatograph configured with a High Pressure Liquid Injector and column backflushing was used. The GS-Alumina PT column exhibited the same selectivity as the GS-Alumina column without integrated particle traps, and all compounds of interest were well separated. Furthermore, the GS-Alumina PT column with integrated dual-ended particle trapping technology can eliminate the risk of leakage or blockage at connectors, protect valves from particles that can shed from the PLOT column, and offer increased stability and reliability for valve-switching analysis. Excellent repeatability and stability were demonstrated.


## Introduction

1,3-Butadiene is a major petrochemical product and an important feedstock in the production of rubbers and plastics, such as styrene butadiene rubber and latex. The presence of trace hydrocarbon impurities in 1,3-butadiene, especially propadiene and alkynes including propyne (also known as methyl acetylene), can interfere with the catalytic polymerization needed to produce high quality synthetic rubber products. Therefore, identifying and quantifying trace hydrocarbon impurities in 1,3-butadiene is critical to producing high quality synthetic rubbers.

The Agilent J&W GS-Alumina column (50 m × 0.53 mm id) was identified as an ideal column for trace impurity analysis in a previous work [1]. Due to the presence of small amounts of 1,3-butadiene dimer (4-vinylcyclohexene) and other heavier impurities, it requires over 60 minutes at high temperature to bake these impurities out of the column. Otherwise, the residuals affect retention time repeatability in subsequent runs. Using backflushing with a GS-Alumina PLOT column can shorten the analytical cycle time and improve repeatability. However, conventional PLOT columns have the disadvantage that the stationary phase layer is not mechanically stable, and so the shedding of particles can plug or even damage column switching valves, and cause detector contamination. For these reasons, particle traps are recommended for both ends of a regular GS-Alumina column. However, connecting particle trap devices to the columns still presents a risk of leakage or blockage at the connectors. The GS-Alumina PT column, which includes integrated particle traps on both ends, is particularly well suited for this type of application. Alumina PLOT PT columns provide greater stability than conventional alumina PLOT columns [2,3].

In this work, the selectivity of the GS-Alumina PT column was compared with that of the popular GS-Alumina column. Repeatability and stability were also tested using backflushing with the GS-Alumina PT column to analyze impurities in 1,3-butadiene.

## Materials and Methods

The experiments were performed using an Agilent 7890A gas chromatograph equipped with a High Pressure Liquid Injector (HPLI), split/splitless inlet, and a flame ionization detector (FID). The configuration diagram is shown in Figure 1. This application was based on a six-port valve for backflushing heavier components. A GS-Alumina PT column was used for separation, with both ends connected with the six-port valve. By switching the valve, the column flow can be reversed for backflushing the high molecular weight impurities to the detector.

The gas standard mixtures used for method development are listed in Table 1.

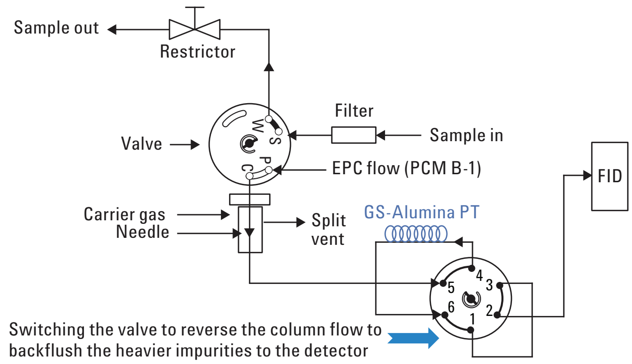


Figure 1. The configuration diagram.

Table 1. Standard mix gas.

| No. | Component | Concentration (% w/w) |
|---|---|---|
| 1 | Propane | 1.8500e-2 |
| 2 | Propylene | 1.1230e-1 |
| 3 | *iso*-Butane | 7.2690e-2 |
| 4 | Butane | 6.2780e-2 |
| 5 | Propadiene | 8.5210e-2 |
| 6 | *t*-2-Butene | 9.7800e-2 |
| 7 | 1-Butene | 1.0410e-1 |
| 8 | *iso*-Butylene | 1.2890e-1 |
| 9 | C-2-Butene | 3.2740e-2 |
| 10 | *iso*-Pentane | 3.0320e-3 |
| 11 | *n*-Pentane | 5.0110e-3 |
| 12 | 1,2-Butadiene | 1.1080e-1 |
| 13 | 1,3-Butadiene | Balance |
| 14 | Propyne | 1.5150e-2 |
| 15 | Vinyl acetylene | 1.8590e-2 |
| 16 | Ethyl acetylene | 1.0430e-2 |

### Conditions

| | |
|---|---|
| Column 1: | Agilent J&W GS-Alumina PT, 50 m × 0.53 mm, with two particle traps (p/n 115-3552PT) |
| Column 2: | Agilent J&W GS-Alumina, 50 m × 0.53 mm (p/n 115-3552) |
| Carrier: | Helium, constant flow mode, 7.5 mL/min (relocked during run) |
| Retention time locking: | Propylene at 7.907 min |
| Inlet: | Split/splitless, 120 °C, split ratio 20:1 |
| Oven: | 60 °C hold 3 min,<br>to 105 °C hold 3 min at 5 °C/min,<br>to 150 °C hold 4 min at 5 °C/min,<br>to 180 °C hold 5 min at 30 °C/min |
| Valve box temperature: | 120 °C |
| Injection source: | High Pressure Liquid Injector |
| EPC flow for HPLI: | 30 mL/min |
| Sample size: | 0.5 µL (liquid) |
| Instrument: | Agilent 7890A GC |
| Detector: | FID, 200 °C |

## Agilent supplies

- BTO nonstick 11 mm septa, 50/pk (p/n 5183-4757)
- Ultra Inert liner, universal (p/n 5190-2295)
- Universal column nut (p/n 5181-8830)
- Internal nut (p/n G2855-20530)
- Flexible Metal ferrule, 0.53 mm id (p/n G3188-27506)
- Flexible Metal ferrule, 0.25 mm id (p/n G3188-27501)
- Ultimate Plus Deactivated fused silica, 5 m × 0.25 mm (p/n CP802505), cut suitable length to connect six-port valve with FID
- Ultimate Plus Deactivated fused silica, 5 m × 0.53 mm (p/n CP805305), cut suitable length to connect 6-port valve with inlet

# Results and Discussion

## Selectivity

Alumina PLOT columns are commonly used for light hydrocarbon separation. Selectivity of the GS-Alumina column was very good for separating impurities in 1,3-butadiene in the previous work [1]. The GS-Alumina PT column provided equivalent performance to that of the GS-Alumina column, but with two integrated particle traps. By using a 50 m × 0.53 mm GS-Alumina PT column and retention time locking (RTL) technology, method transfer was completed quickly. As shown in Figure 2 and Figure 3, with or without backflushing, propyne can be well separated from 1,3 butadiene on both alumina columns. Resolution of 1,2-butadiene and 1,3-butadiene was about 4.25 on GS-Alumina, and about 4.38 on GS-Alumina PT. In summary, the selectivity of the GS-Alumina PT column was equal to that of the regular GS-Alumina column, therefore requiring minimal method adjustments and no further method revalidation. The results also indicate that other GS-Alumina column applications could be easily transferred to the GS-Alumina PT column.

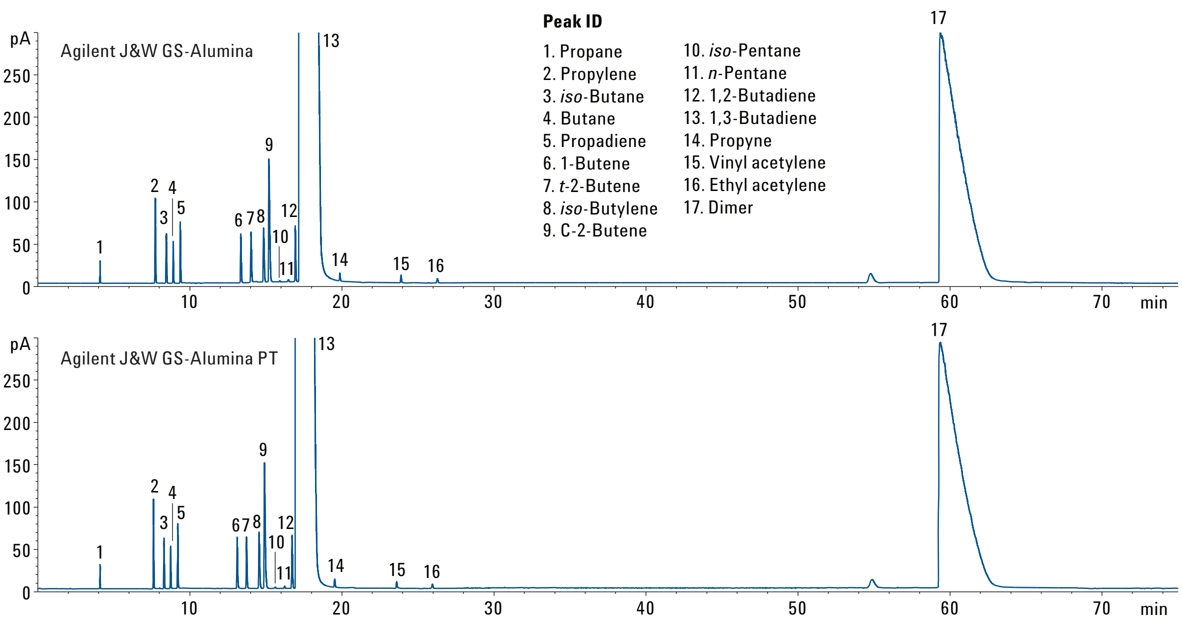


Figure 2. Overlay chromatograms of a standard gas mix on Agilent J&W GS-Alumina and Agilent J&W GS-Alumina PT columns, without backflushing.

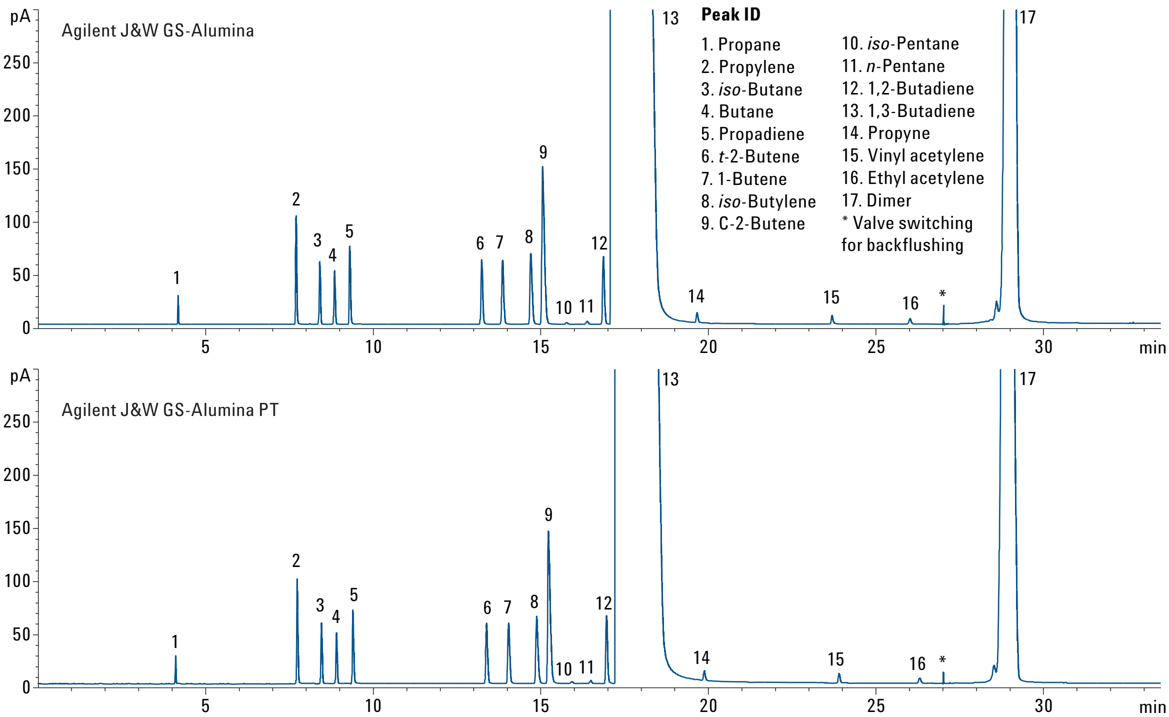


Figure 3. Overlay chromatograms of a standard gas mix on Agilent J&W GS-Alumina and Agilent J&W GS-Alumina PT columns, with backflushing.

## Integrated dual-ended particle trap technology

Both ends of the regular GS-Alumina column or GS-Alumina PT column were connected to a six-port valve. As shown in Figure 2, analysis time was more than 60 minutes without backflushing on both columns. The presence of dimer and other heavier impurities may contaminate the column and affect repeatability in subsequent runs. It can take more than 30 minutes at 180 °C to bake them out of the column.

One commonly used method to reduce cycle time or run time in GC analysis is to backflush late-eluting compounds from the column. Using the configuration design in this application, the column flow can be reversed by switching the valve to backflush the high molecular weight impurities to the detector after the last compound of interest elutes out of the column. The analysis time is shortened significantly (approximately 30 minutes) with backflushing, as shown in Figure 3 on both GS-Alumina and GS-Alumina PT columns.

The stationary phase layer of traditional PLOT columns is not mechanically stable, and can lead to particle shedding. In this application, the directions of column flow with backflushing and without backflushing are opposite. Therefore, particle traps are recommended on both ends of regular GS-Alumina columns through unions and associated fittings. However, the GS-Alumina PT column with integrated particle traps forms one continuous length of fused silica tubing, and is very suitable for this type of application. Connecting the GS-Alumina PT column with the valve is very convenient and presents no risk of leakage or blockage at the connectors.

## Repeatability and stability

To evaluate the performance of the GS-Alumina PT columns, 250 injections were made of the standard gas mix to demonstrate stability and repeatability. As shown in Table 2, the average peak area for 250 injections of the standard gas mix revealed low standard deviation, and had relative standard deviations (RSDs) below 2.0% over 8 days of analyses. Good reproducibility of retention times can be achieved, and RSD obtained from 250 replicate analyses of standard gas mix was found to be below 0.4%. Better intra-day reproducibility of peak area and retention time was obtained with RSD below 0.8% and 0.09%, respectively. This showed that excellent repeatability and long-term precision was achieved using the Agilent J&W PLOT PT columns. No signal spikes related to particle shedding were observed in the 250 injections.

Table 2. Repeatability data of a standard gas mix.

| | Area n = 250 | | | RT n = 250 | | |
|---|---|---|---|---|---|---|
| Compounds | Average | St dev | RSD % | Average | St dev | RSD % |
| Propane | 45.885 | 0.295 | 0.64 | 4.273 | 0.026 | 0.40 |
| Propylene | 291.085 | 1.748 | 0.60 | 7.954 | 0.034 | 0.32 |
| *iso*-Butane | 183.047 | 1.043 | 0.57 | 8.629 | 0.035 | 0.40 |
| Butane | 157.376 | 1.030 | 0.65 | 9.072 | 0.035 | 0.39 |
| Propadiene | 205.681 | 2.677 | 1.30 | 9.608 | 0.036 | 0.38 |
| *t*-2-Butene | 249.895 | 2.739 | 1.10 | 13.651 | 0.048 | 0.35 |
| 1-Butene | 273.663 | 2.924 | 1.07 | 14.334 | 0.053 | 0.37 |
| *iso*-Butylene | 341.648 | 3.611 | 1.06 | 15.223 | 0.059 | 0.39 |
| C-2-Butene | 887.267 | 9.683 | 1.09 | 15.564 | 0.057 | 0.37 |
| *iso*-Pentane | 7.743 | 0.169 | 1.58 | 16.213 | 0.056 | 0.34 |
| *n*-Pentane | 13.215 | 0.257 | 1.84 | 16.800 | 0.054 | 0.32 |
| 1,2-Butadiene | 266.048 | 3.843 | 1.44 | 17.314 | 0.054 | 0.31 |
| 1,3-Butadiene | 244,603.871 | 2,512.404 | 1.03 | 17.473 | 0.059 | 0.33 |
| Propyne | 39.731 | 1.016 | 1.92 | 20.247 | 0.050 | 0.25 |
| Vinyl acetylene | 34.825 | 0.428 | 1.23 | 24.192 | 0.058 | 0.24 |
| Ethyl acetylene | 25.345 | 0.451 | 1.78 | 26.755 | 0.087 | 0.33 |

The results indicate that high molecular weight impurities were backflushed effectively, demonstrating that Agilent J&W PLOT PT columns with integrated dual-ended particle trap technology can prevent particle shedding, protect column-switching valves, and offer increased stability and reliability for valve analysis.

## Conclusions

An Agilent 7890A gas chromatograph configured with an Agilent J&W GS-Alumina PT column with backflushing improved the analysis of hydrocarbon impurities in 1,3-butadiene.

With equivalent selectivity, a typical GS-Alumina column method was reproduced successfully on the GS-Alumina PT column, with minimal method adjustment and without the need for additional method revalidation. Due to integrated dual-ended particle trap technology that avoids the need for external particle traps, which have the risk of leakage or blockage at the connectors, the GS-Alumina PT column exhibits excellent repeatability and stability for 250 injections of a standard gas mix. The unique stabilization technology of the PT column also removes concerns of performing valve-switching GC analysis with PLOT columns, for more confident day-to-day operation.

## References


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2. Anon. *Protect your GC system from PLOT column phase shedding*; Agilent Technologies, Inc. Brochure, publication number 5991-1174EN, **2012**.
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