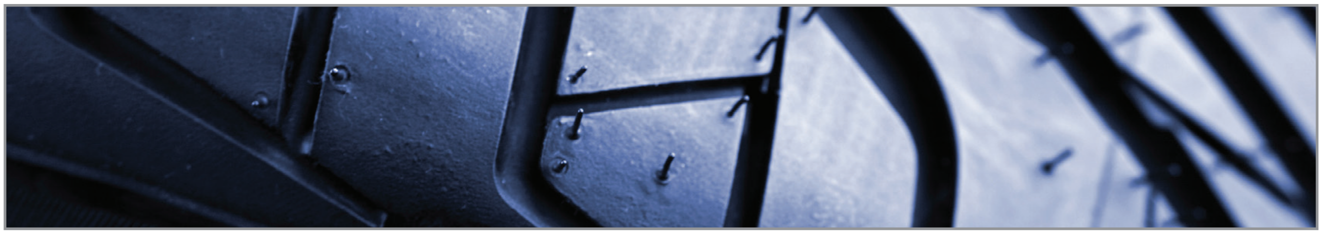

Petroleum & Petrochemical Applications

Analysis of Trace Hydrocarbon Impurities in 1,3-Butadiene

Using Optimized Rt®-Alumina BOND/MAPD PLOT Columns

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Abstract

Identifying and quantifying trace impurities in 1,3-butadiene is critical in producing high quality synthetic rubber products. Standard analytical methods employ alumina PLOT columns which yield good resolution for low molecular weight hydrocarbons, but suffer from irreproducibility and poor sensitivity for polar hydrocarbons. In this study, Rt®-Alumina BOND/MAPD PLOT columns were used to separate both common light polar contaminants, including methyl acetylene and propadiene, as well as 4-vinylcyclohexene, which is a high molecular weight impurity that normally requires a second test on an alternative column. By using an extended temperature program that employs the full thermal range of the column, 4-vinylcyclohexene, as well as all of the typical low molecular weight impurities in 1,3-butadiene, can be analyzed in a single test.

Introduction

1,3-butadiene is typically isolated from products of the naphtha steam cracking process. Prior to purification, 1,3-butadiene can be contaminated with significant amounts of isobutene as well as other C4 isomers. In addition to removing these C4 isomeric contaminants during purification, it is also important that 1,3-butadiene be free of propadiene and methyl acetylene, which can interfere with catalytic polymerization. Alumina PLOT columns are the most commonly used GC column for this application, but the determination of polar hydrocarbon impurities at trace levels can be quite challenging and is highly dependent on the deactivation of the alumina surface.

While alumina columns provide highly selective retention for both saturated and unsaturated volatile hydrocarbons, poor response and irreproducibility are often seen for polar compounds such as methyl acetylene and propadiene. Potassium chloride and sodium sulfate deactivations are commonly used to reduce the reactivity of the alumina adsorbent, but methyl acetylene/propadiene (MAPD) deactivations can be more effective for determining trace levels of these analytes. In this work, both crude and refined 1,3-butadiene samples were analyzed on an Rt®-Alumina BOND/MAPD PLOT column in order to evaluate column performance for both low and high molecular weight polar impurities. This column was selected for evaluation because, in addition to the specialized MAPD deactivation, it has a higher maximum operating temperature than other MAPD columns, which extends the application range to higher molecular weight impurities.

Experimental

Samples of crude 1,3-butadiene and refined 1,3-butadiene were analyzed using a 50 m x 0.53 mm ID x 10 µm Rt®-Alumina BOND/MAPD PLOT column (cat.# 19778) and an Agilent 5890 GC. 10 µL split injections were made using a 200 °C injector temperature and split flow of 100 mL/min. Helium carrier gas at 20 psi (140 kPa) was used. Different oven programs were used for analyzing crude and refined 1,3-butadiene. For the crude, the oven was held at 70 °C for 5 minutes and then brought up to 200 °C at 10 °C/min. For the refined product, the oven was held at 70 °C for 5 minutes and then brought up to 250 °C at 10 °C/min. and held there for 5 minutes. All samples were analyzed with an FID at 250 °C.

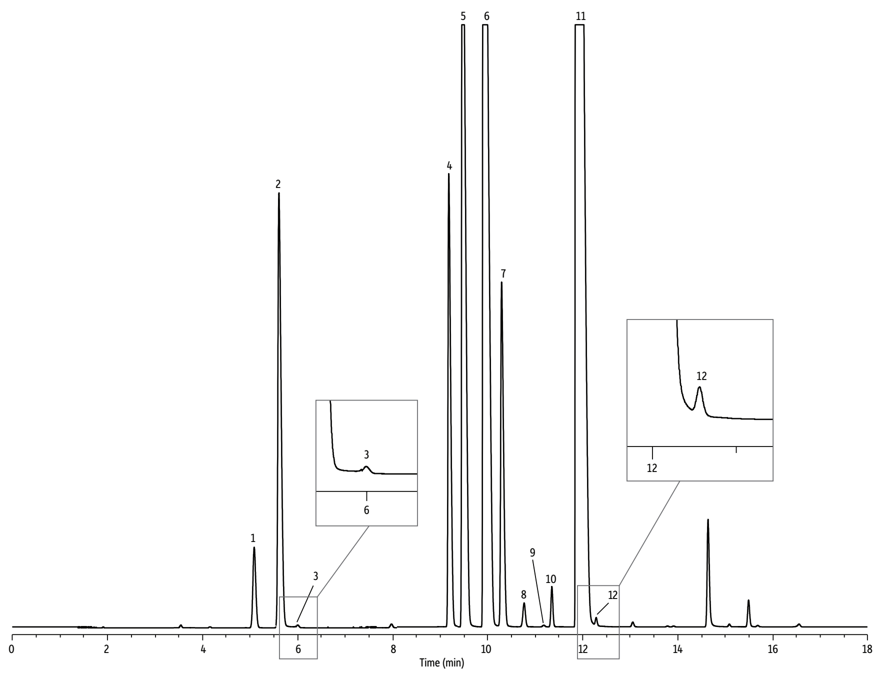
Results and Discussion

The Rt®-Alumina BOND/MAPD column used in this application provided excellent resolution and response for polar hydrocarbons in crude 1,3-butadiene (Figure 1). The column exhibited a high degree of inertness toward polar impurities and provided excellent resolution for all the C4 contaminants, as well as propadiene and methyl acetylene. In addition, another small impurity was resolved from pentane and identified as 1,2-butadiene in this analysis.

Figure 1 Analysis of crude 1,3-butadiene on an Rt®-Alumina MAPD/BOND PLOT column. Effective deactivation of the alumina results in good separation of polar hydrocarbon impurities, such as propadiene and methyl acetylene.

Peaks

1. Isobutane
2. *n*-Butane
3. Propadiene
4. *trans*-2-Butene
5. 1-Butene
6. Isobutene
7. *cis*-2-Butene
8. Isopentane
9. *n*-Pentane
10. 1,2-Butadiene
11. 1,3-Butadiene
12. Methyl acetylene



GC_PC1211

Column	Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19778)
Sample	Crude 1,3-butadiene
Injection	
Inj. Vol.:	10 µL split
Liner:	2.0 mm ID straight inlet liner (cat.# 20712)
Inj. Temp.:	200 °C
Split Vent Flow Rate:	100 mL/min.
Oven	
Oven Temp:	70 °C (hold 5 min.) to 200 °C at 10 °C/min. (hold 0 min.)
Carrier Gas	He, constant pressure (20 psi, 137.9 kPa)
Detector	FID @ 250 °C
Make-up Gas Flow Rate:	30 mL/min.
Make-up Gas Type:	N_2
Data Rate:	20 Hz
Instrument	HP5890 GC

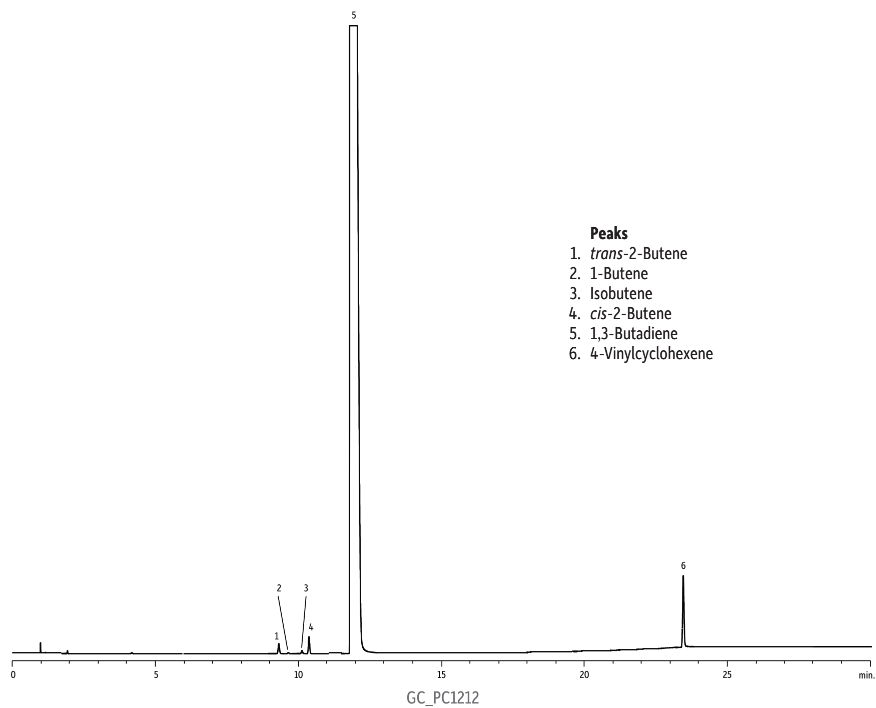
While the column provided good separation of all compounds under the conditions used here, it is important to note that instrument conditions can also affect the elution order and retention times of volatile hydrocarbons [1]. Using higher flows, lower starting temperatures, or longer initial hold times results in elution at lower temperatures which increases the separation of propadiene and acetylene from n-butane. Optimizing instrument parameters, in combination with using an Rt®-Alumina BOND/MAPD column, allows greater control of key separations during impurity analyses.

Since 1,3-butadiene is a reactive chemical and has a limited shelf life, it 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) form during long term storage. Typically, alumina PLOT columns cannot be used to analyze this and other heavier impurities due to limitations in their maximum operating temperature. However, the Rt®-Alumina BOND/MAPD column used here has a maximum operating temperature of 250 °C, which is 50 °C higher than standard alumina PLOT columns. As seen in Figure 2, this extended temperature range allows for the analysis of both trace amounts of the residual C4 impurities as well as higher molecular weight impurities, such as 4-vinylcyclohexene, in refined 1,3-butadiene.

Conclusions

The Rt®-Alumina BOND/MAPD column tested here performed well for the analysis of impurities in 1,3-butadiene. Due to the effectiveness of the column deactivation toward polar impurities, critical components, including propadiene and methyl acetylene, all were resolved and identified in the crude material. Also, the expanded operating temperature range permitted the analysis of 4-vinylcyclohexene, which usually has to be determined on a second column. The ability to analyze both low and high molecular weight contaminants in the same analysis should allow 1,3-butadiene purity testing to be done with greater laboratory efficiency for synthetic rubber production and other applications.

Figure 2 Analysis of refined 1,3-butadiene on an Rt®-Alumina MAPD/BOND PLOT column. Rt®-Alumina MAPD/BOND columns extend the application range of alumina PLOT columns due to their higher temperature stability.



Column Rt®-Alumina BOND/MAPD, 50 m, 0.53 mm ID, 10.0 µm (cat.# 19778)
Sample Refined 1,3-butadiene
Injection
Inj. Vol.: 10 µL split
Liner: 2.0 mm ID straight inlet liner (cat.# 20712)
Inj. Temp.: 200 °C
Split Vent Flow Rate: 100 mL/min.
Oven
Oven Temp: 70 °C (hold 5 min.) to 250 °C at 10 °C/min. (hold 5 min.)
Carrier Gas He, constant pressure (20 psi, 137.9 kPa)
Detector FID @ 250 °C
Make-up Gas Flow Rate: 30 mL/min.
Make-up Gas Type: N_2
Data Rate: 20 Hz
Instrument HP5890 GC

References

1. J. de Zeeuw, R. Morehead, T. Vezza, B. Bromps, *Chromatographic Behavior of Activated Alumina Adsorbents for the Analysis of Hydrocarbons*, American Laboratory (2011).