Analysis of Trace Hydrocarbon Impurities in 1,3-Butadiene Using Rt®-Alumina BOND/MAPD Columns

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Identifying and quantifying trace hydrocarbon 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 compounds, but suffer from irreproducibility and poor sensitivity for more polar hydrocarbon impurities, like propadiene, acetylene, and methyl acetylene. New Rt®-Alumina BOND/MAPD PLOT columns feature a unique deactivation that improves response level and predictability for diene and acetylene hydrocarbons. In addition, these columns have a higher maximum temperature (up to 250°C) which extends the application range. Here, we demonstrate the utility of these columns for analyzing trace polar hydrocarbon impurities in 1,3-butadiene.

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 isobutylene 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; however, the determination of polar hydrocarbon impurities at trace levels can be quite challenging and is highly dependent on the deactivation of the alumina surface. Restek has recently developed a new line of alumina columns with a unique, high-performance deactivation. These columns—the Rt®-Alumina BOND/MAPD (fused silica) and MXT®-Alumina BOND/MAPD (metal) columns—are ideal for the analysis of polar hydrocarbons such as acetylene, methyl acetylene, and propadiene, and also perform well for generic light hydrocarbon analysis.

Excellent Resolution of Polar Hydrocarbons

The unique deactivation used in Rt®-Alumina BOND/MAPD PLOT columns produces high responses and consistent run-to-run results for the propadiene and acetylene impurities. As shown in the analysis of crude 1,3-butadiene before purification, this column provides excellent resolution for all the C4 contaminants, as well as propadiene and methyl acetylene *(Figure 1)*. In addition, another small impurity (1,2-butadiene), can be resolved from pentane and identified in this analysis. The new Rt®-Alumina BOND/MAPD column not only provides excellent separation of these analytes, but also elutes them with high response factors due to the inertness of the column. This makes light hydrocarbon purity methods more sensitive and accurate, allowing much tighter process control.

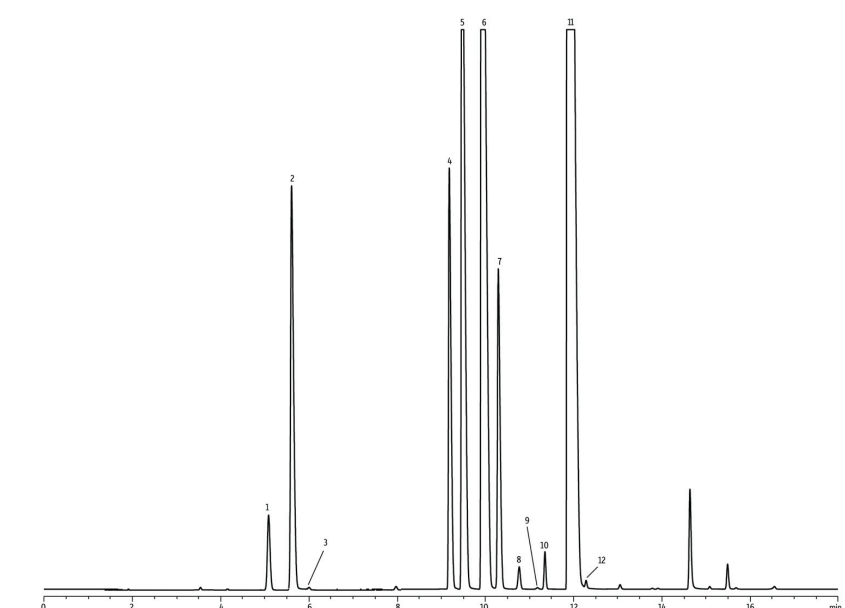

Figure 1. The optimized deactivation of Rt®-Alumina MAPD/BOND columns assures the separation of polar hydrocarbon impurities, such as propadiene and methyl acetylene, in 1,3-butadiene.

Column: Rt®-Alumina BOND/MAPD, 50m x 0.53mm ID x 10µm (cat.# 19778); Sample: crude 1,3-butadiene; Injection: 10µL, split, 200°C; Split vent flow rate: 100 mL/min.; Oven: 70°C (hold 5min.) to 200°C at 10°C/min.; Carrier gas: helium, (20psi, 140kPa); Detector: FID, 250°C; 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.

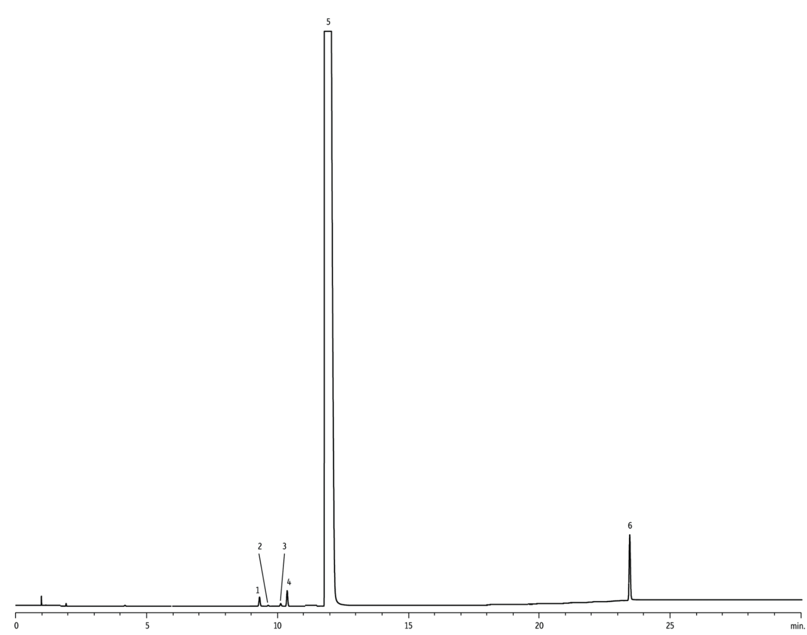

Figure 2. Rt®-Alumina MAPD/BOND columns extend the application range of alumina PLOT columns due to their higher temperature stability.

Column: Rt®-Alumina BOND/MAPD, 50m x 0.53mm ID x 10µm (cat.# 19778); Sample: refined 1, 3-butadiene; Injection: 10µL, split, 200°C; Split vent flow rate: 100mL/min.; Oven: 70°C (hold 5 min.) to 250°C at 10°C/min. (hold 5min.); Carrier gas: helium, (20psi, 140kPa); Detector: FID; Peaks: 1. trans-2-butene, 2. 1-butene, 3. isobutene, 4. cis-2-butene, 5. 1,3-butadiene, 6. 4-vinylcyclohexene.

Note that instrument conditions can affect the elution order and retention times of volatile hydrocarbons [1]. For example, when using higher flows, lower starting temperatures, or longer initial hold times, the components elute 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 impurity analyses.

Extended Application Range Includes High Molecular Weight Impurities

Typical alumina PLOT columns are problematic when analyzing higher molecular weight impurities, such as 4-vinylcyclohexene, due to the 200°C limitation in their maximum operating temperature. Such compounds elute very late and have poor peak shape. In contrast, the Rt®-Alumina BOND/MAPD column is specifically engineered with a maximum operating temperature of 250°C, which is 50°C higher than standard alumina PLOT columns. This extended temperature range allows for the analysis of higher molecular weight and higher boiling point compounds than can be achieved with standard alumina PLOT columns. Figure 2 shows the analysis of refined 1,3-butadiene. 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 one single test.

Summary

Restek's new Rt®-Alumina BOND/MAPD column is an ideal solution when performing purity testing for 1,3-butadiene. The column's superior resolution characteristics allow for the identification of all the critical contaminants found in crude 1,3-butadiene. The expanded operating temperature range also permits the analysis of refined 1,3-butadiene to ensure that the material is free from both low and high molecular weight contamination.

References

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

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