Optimized Determination of C_1–C_6 Impurities in Propylene and Ethylene Using HP-PLOT/Al_2O_3 Columns

Application Note
228-263

Columns and Supplies

Authors

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Abstract

Impurities in ethylene and propylene (light hydrocarbon gases C_1 to C_6) were analyzed using HP-PLOT/Al_2O_3 columns. In comparison with other commercially available alumina PLOT columns, the HP-PLOT columns showed better selectivity, increased capacity, and complete baseline separation. HP-PLOT column analyses were done using the 5890 Series II gas chromatograph with electronic pressure control and a flame ionization detector.

Introduction

Trace amounts of important impurities in high-purity hydrocarbon products, such as propylene and ethylene, are frequently masked by sample overload. Although standard commercially available PLOT columns[1,2] provide good separations for regular gas analysis, until now they have not been able to completely separate C_1 to C_6 impurities in high-purity propylene or ethylene with good resolution. This has limited the commercial application of alumina PLOT columns.

In comparison to these alumina PLOT columns, the HP-PLOT/Al_2O_3 columns showed baseline separations of all C_1 to C_6 hydrocarbon impurities. Improved selectivity for major components of C_1 to C_6 hydrocarbons was demonstrated including ethylene, propylene, acetylene, and 1,3-butadiene. In addition, in comparison to the other alumina/KCL and PLOT columns studied, the HP-PLOT/Al_2O_3 columns provided reliable, repeatable results from run to run and column to column.

Experimental

Four alumina PLOT columns were used in the analyses of hydrocarbon impurities in ethylene and propylene:

- HP-PLOT/Al_2O_3, S-deactivated, 50 m x 0.53 mm x 15 µm (part no. 19095P-S25)
- HP-PLOT/Al_2O_3, M-deactivated, 50 m x 0.53 mm x 15 µm (part no. 1905P-M25)
- Alumina/KCl, 50 m x 0.53 mm x 10 µm
- Brand X, 30 m x 0.53 mm

Gas chromatography analysis of C_1 to C_6 light hydrocarbon gases was done on a 5890 Series II gas chromatograph (GC) with electronic pressure control (EPC) and a flame ionization detector (FID). An Agilent 7673 automatic sampler was used to deliver 5 µl of gas samples under a split mode (split ratio 25–30:1). To simulate overloading conditions, manual or splitless injections with gas-tight syringes were used wherever appropriate. GC parameters are listed in **Table 1.**

Except **Figure 4**, where a C_1 to C_6 gas mixture was used, samples were prepared by spiking polymer-grade propylene (99.6% + purity) and ethylene (99.8% + purity) from Scott Specialty Gases Company with a hydrocarbons mix (Rusty Associates). The hydrocarbons mix contained 23 components of C_1 to C_6 hydrocarbon gases listed in **Table 2**.

Results and Discussion

Alumina PLOT columns have been frequently used to analyze C_1 to C_6 light hydrocarbon gases due to the unique retentive properties of aluminum oxide. However, trace amounts of critical impurities in high-purity products, such as polymer-grade propylene and ethylene, are difficult to quantify using alumina/KCl and Brand X alumina PLOT columns because these impurities are often masked by sample overload. Furthermore, the selectivity of these PLOT columns varies due to the variation in test conditions such as moisture and carrier gas flow.

Table 1. Experimental Conditions

Gas chromatograph:	Agilent 5890 Series II with EPC
Carrier:	He, constant flow
Oven:	TP1 = 35°C (2 min), 5°C/min to 100°C, 10°C/min to 180°C (5 min)
Injection:	Split/splitless inlet, inlet: 250°C
Detector:	FID (250°C)

Figure No.	Column Type	Carrier Flow	Oven Temperature	Injection Volume	Injection Mode (Split Ratio)
1A	Al_2O_3/KCl	He 35 cm/s	TP1	5 µl	0
1B	Al_2O_3/KCl	He 45 cm/s	TP1	5 µl	0
2A	Brand X	He 42 cm/s	TP1	0.5 cc	30:1
2B	Brand X	He 42 cm/s	100°C	5 µl	25:1
3A	HP "S"	He 35 cm/s	TP1	5 µl	0
3B	HP "M"	He 38 cm/s	TP1	5 µl	0
4	HP "S"	He 42 cm/s	TP1	1.5 cc	30:1

In **Figure 1A,** cyclopropane (peak 5) was masked by the major analyte, propylene (peak 6), on the alumina KCl column. In this run, 1,3-butadiene (peak 17) coeluted with n-pentane (peak 16) as a result of 1,3-butadiene overload. When propylene was not overloaded (**Figure 1B**), cyclopropane was separated from propylene. However, acetylene (peak 10)

Table 2. Gas Mixture of C_1 to C_6

1. Methane	13. Isobutylene
2. Ethane	14. Cis-2-Butene
3. Ethylene	15. Isopentane
4. Propane	16. n-Pentane
5. Cyclopropane	17. 1,3-Butadiene
6. Propylene	18. Propyne
7. Isobutane	19. trans-2-Pentene
8. n-Butane	20. 2-Methyl-Butene
9. Propadiene	21. 1-Pentene
10. Acetylene	22. cis-Pentene
11. trans-2-Butene	23. Hexane
12. 1-Butene	

coeluted with isobutane (peak 7) as a result of increased carrier flow (**Figure 1B**).

For Brand X PLOT columns, masking and coelution problems also occurred. As shown in **Figure 2A**, the large tailing peak of propylene reduced the resolution of the propylene/isobutane pair, and isopentane (peak 15) coeluted with cis-butene (peak 14).

Additionally, overloaded ethylene (peak 3) distorted the propane peak (peak 4) and split the latter into two ghost peaks. However, these problems were not observed when overloading did not occur (**Figure 2B**).

Analysis of Impurities in Propylene

Figures 3A and **3B** are chromatograms of propylene sample analyzed using the HP-PLOT/Al_2O_3 columns, S-deactivated and M-deactivated, respectively. Trace amounts (60 ppm) of cyclopropane (peak 5) were separated from propylene (92% purity). Baseline separation was achieved for isobutane (peak 7) and propylene. All 23 components were well resolved in sharp symmetrical peaks within 24 minutes. Both Agilent PLOT columns exhibited excellent separation for acetylene (peak 10) from n-butane (peak 8), for isopentane (peak 15) from cis-2-butene (peak 14), and for n-pentane (peak 16) from 1,3-butadiene (peak 17).

Analysis of Impurities in Ethylene

Figure 4 shows the analysis of an ethylene sample using the HP-PLOT/Al_2O_3 S-deactivated column. The concentration of ethylene, based on peak area percentage, is 98.5%.

Within 24 minutes, all 22 impurities associated with ethylene were completely separated, including methane (peak 1), ethane (peak 2), and propane (peak 4). Distortion of the propane peak (**Figure 2A**) was not observed. In this run, 1.5 cc of sample was injected, demonstrating the large loading capacity of the HP-PLOT Al_2O_3 columns. Although not shown here, similar resolutions for ethylene impurities were also achieved using the M-deactivated HP-PLOT/Al_2O_3 column. Both Agilent alumina PLOT columns met all of the requirements for impurity analysis of polymer-grade ethylene.

Retention Index and Selectivity

Retention indexes (RI) are important indicators of column selectivity. **Table 3** lists the RIs of ethylene, propylene, and acetylene for the four alumina PLOT columns under evaluation.

Table 3. Retention Indexes

Column	RI (Ethylene)	RI (Propylene)	RI (Acetylene)
Alumina/KCl	248	349	372
HP "S"	248	361	418
HP "M"	254	369	407
Brand X	263.5	380	417

High RIs represent high affinity toward a specific "analyte." In the case of ethylene, the RI should be around 250 to minimize the impact of ethylene overload on the impurities eluting immediately after ethylene. The RI of ethylene for Brand X lies on the high end (263 verses 248 for HP "S" and the alumina/KCl). As a result, peak distortion of propane is likely to occur.

The RIs for propylene should be greater than 350 to achieved baseline separations of both cyclopropane and isobutane from propylene. For the Al_2O_3/KCl column, the cyclopropane peak was masked by propylene because the RI for propylene is too close to 350. On the other hand,

Figure 1. Alumina/KCl PLOT column. (See Table 2 for peak identification.)

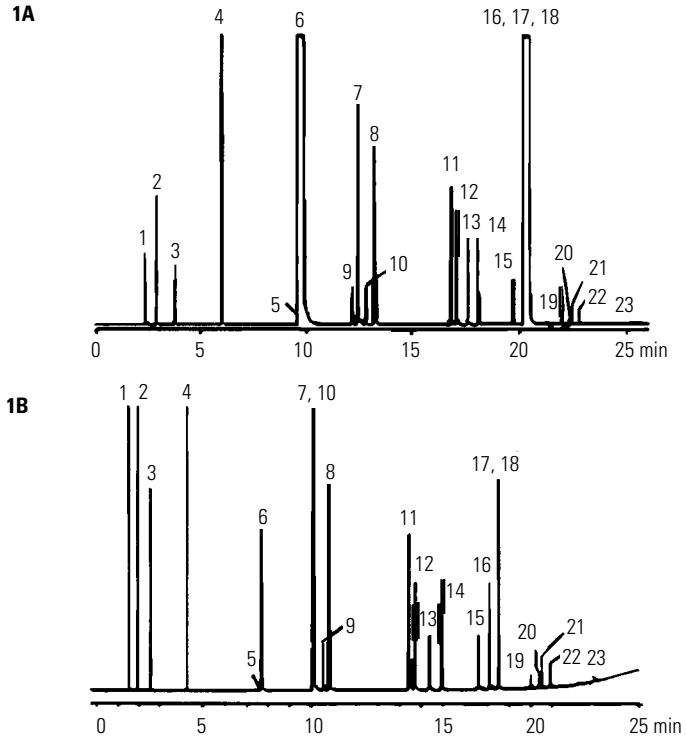
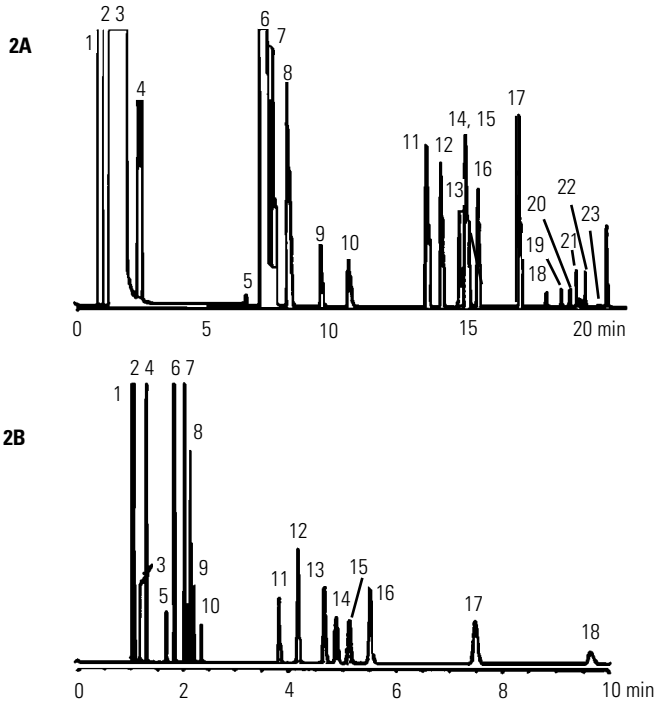


Figure 2. Brand X alumina PLOT column. (See Table 2 for peak identification.)



low resolution for the propylene/isobutane pair on the Brand X column can be attributed to its high RI for propylene (RI=380). Because the RIs of the HP-Al_2O_3/PLOT columns lie in between 350 and 380, excellent separations were achieved for the critical impurities, cyclopropane, and isobutane.

For the quantitation of acetylene, the RI should be greater than 400. As shown in **Figure 1A** and **1B**, isobutane and acetylene coeluted on the alumina/KCl column because its RI for acetylene was below 400. Coelution of isobutane and acetylene was not observed for HP-Al_2O_3/PLOT and Brand X columns because their RIs for acetylene are greater than 400. Furthermore, acetylene is more sensitive to small variations in GC parameters (e.g., column temperature, column flow, and moisture in carrier gas) than impurities eluting near acetylene. As a result, coelution or change in elution order for acetylene and these impurities may occur if the column's RI for acetylene is not in the right range (slightly greater than 400).

The differences for selectivity of ethylene, propylene, and acetylene between the HP-PLOT/Al_2O_3 M- and S-deactivated columns are clearly represented by their RIs. Accordingly, the resolution of impurities in propylene for both these columns is slightly different.

Conclusion

The new HP-PLOT/Al_2O_3 columns showed excellent selectivity, sample loading capacity, and efficiency for the analysis of impurities in ethylene and propylene. Excellent resolution was achieved for impurities such as propane, cyclopropane, isobutane, and acetylene in ethylene and propylene.

Figure 3. HP-PLOT/Al_2O_3 columns. (See Table 2 for peak identification.)

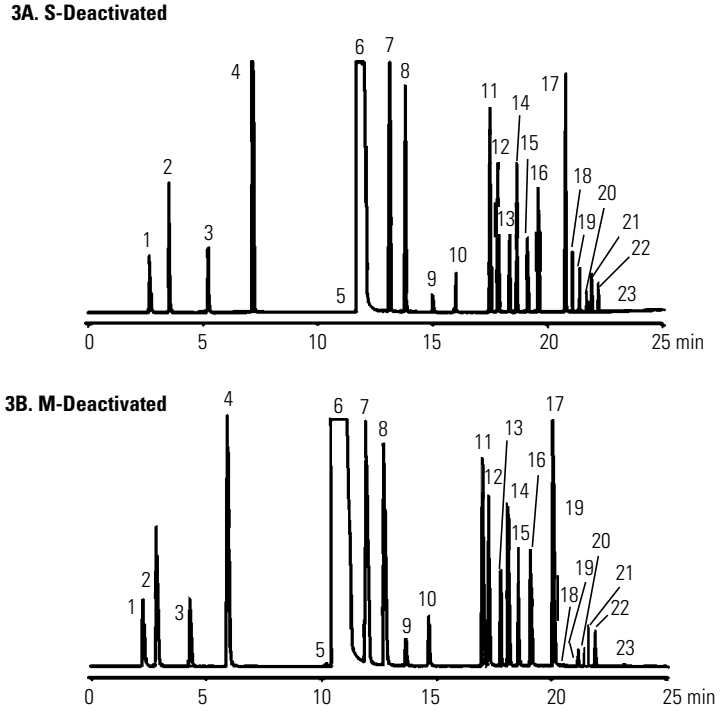
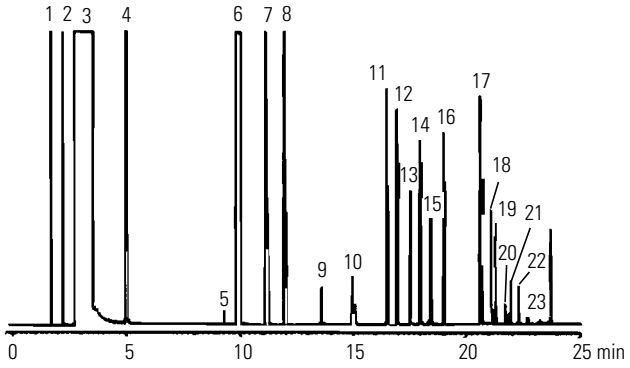


Figure 4. HP-PLOT/Al_2O_3 columns, S-deactivated. (See Table 2 for peak identification.)



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