Trace Level Hydrocarbon Impurities in Ethylene and Propylene

Application

Gas Chromatography

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Abstract

An Agilent 6890 Series gas chromatography system was used to determine trace (low ppm) levels of hydrocarbon impurities in high-purity ethylene and propylene. The gas chromatograph (GC) was equipped with a heated gas sample valve, split/splitless inlet, and flame ionization detector (FID). An Agilent HP-PLOT Al_2O_3 column was used for separation of the trace hydrocarbons. Impurity levels below 10 ppm (mole) were easily detected in both ethylene and propylene.

Introduction

High-purity ethylene and propylene are commonly used as feedstocks for production of polyethylene, polypropylene, and other chemicals. Typically, these low molecular weight monomers are of very high purity (99.9+ percent). However, hydrocarbons, sulfur compounds, and other impurities in feed streams can cause such problems as reduced catalyst lifetime and changes to product quality. Process yields can also be adversely affected. Many impurities have been identified as potential contaminants (1,2).

Recently, ASTM has proposed several procedures to determine trace hydrocarbon impurities in both ethylene and propylene (3). These methods, currently in the investigation stage, use alumina porous layer open tubular (PLOT) columns. This application note describes the suggested Agilent configuration for such methods and illustrates resulting separations of both quantitative calibration blends and actual process samples. These proposed methods should be valuable in meeting commercial specifications.

Experimental

All experiments were performed on an 6890 Series gas chromatograph (GC) equipped with a split/splitless inlet and capillary optimized flame ionization detector (FID). All gas flows and pressures within the GC were controlled electronically. Gas sample injections were made using an automated sample valve placed in the 6890 valve oven (80 °C). The gas sample valve was interfaced to the capillary inlet using an aluminum tube (1/8-in.) that jacketed the stainless steel transfer line (option 860). The inlet was fitted with a split/splitless liner (part no. 19241-60540). All injections were made in the split mode.

A 50-m × 0.53-mm, HP-PLOT Al_2O_3 "M" column was used for separation. For ethylene analysis only, a 30-m × 0.53-mm, 5-µm HP-1 column was placed directly behind the HP-PLOT column. The two columns were joined using a glass press-fit connector.

The Agilent ChemStation was used to control the 6890 Series GC and to provide data acquisition and peak integration. The ChemStation was operated at a data acquisition rate of 10 Hz.

Standards for retention time and response factor calculation were obtained from DCG Partnership (Houston, Texas, USA 77061). Samples used for this work were obtained from commercial sources.

Table 1 lists the entire set of equipment and conditions.

Results and Discussion

Ethylene

The configuration used for ethylene analysis is found in figure 1.

The HP-PLOT Al_2O_3 column was used for hydrocarbon separation. The use of HP-PLOT Al_2O_3 columns for light hydrocarbon analyses has been previously described (4). These columns exhibit excellent separation characteristics for the C_1 through C_5 isomers.

The proposed method for ethylene specifies the use of a second nonpolar column placed after the HP-PLOT alumina column to improve the separation of impurity peaks eluting on the tail of ethylene. This nonpolar column gains importance for trace level analysis, where higher concentrations of ethylene (99.9 percent and higher) exhibit increased tailing. No attempt was made to compare separations without the nonpolar Agilent HP-1 column.

Table 1. Instrument Configuration and Operating Conditions

Item	Description
Gas Chromatograph	
G1540A	6890 Series GC
Option 112	Split/splitless inlet
Option 211	Capillary optimized FID
Option 701	6-port gas sample valve and automation
Option 751	Valve oven
Option 860	Valve to inlet interface
Column	● 50-m x 0.53-mm HP-PLOT Al_2O_3 "M" (part no. 19095P-M25) ● 30-m x 0.53-mm, 5-µm HP-1 (part no. 19091Z-236), used for ethylene analysis only
Data Acquisition	
G2070AA	Agilent ChemStation
Operating Parameters	
Injection port temperature	200 °C
Detector temperature	250 °C
Split ratio	10/1 to 50/1 depending on sample
FID conditions	30 mL/min hydrogen, 350 mL/min air, nitrogen make-up (25 mL/min column + makeup)
Temperature program	● Ethylene: 35 °C (2 min), 4 °C/min to 190 °C ● Propylene: 40 °C (2 min), 4 °C/min to 190 °C
Injection volume	● Ethylene: 0.5 mL ● Propylene: 0.25 mL
Column flow	● Ethylene: 6 mL/min constant flow (10 psi) ● Propylene: 3.5 mL/min constant flow (4 psi)
Valve temperature	80 °C

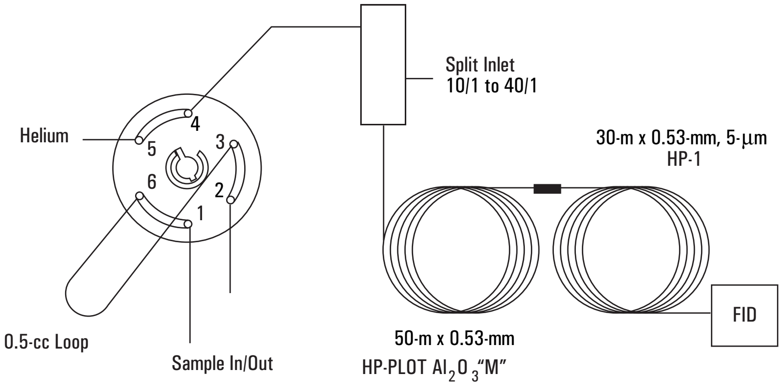


Figure 1. Valve drawing for impurities in ethylene.

Figure 2 shows the chromatogram of an ethylene calibration blend containing most of the major hydrocarbon impurities. This sample was analyzed at a split ratio of 10/1. The concentration of most components (except for ethane) ranges from 8 to 12 ppm (mole). For this analysis, baseline separation is achieved for all the impurities except for propane. Total analysis time is approximately 30 minutes. Because this separation is more than adequate, analysis time can be reduced by increasing the temperature program rate. Based upon conditions used for this analysis, most components can be detected at the 1-ppm level.

Chromatographic results for two process ethylene samples are given in figures 3 and 4. The sample presented in figure 3 contains only methane, ethane, and propylene as impurities. Less than 1-ppm methane was detected. The ethylene sample in figure 4 shows a high concentration of methane, with trace amounts of ethane, propane, and propylene.

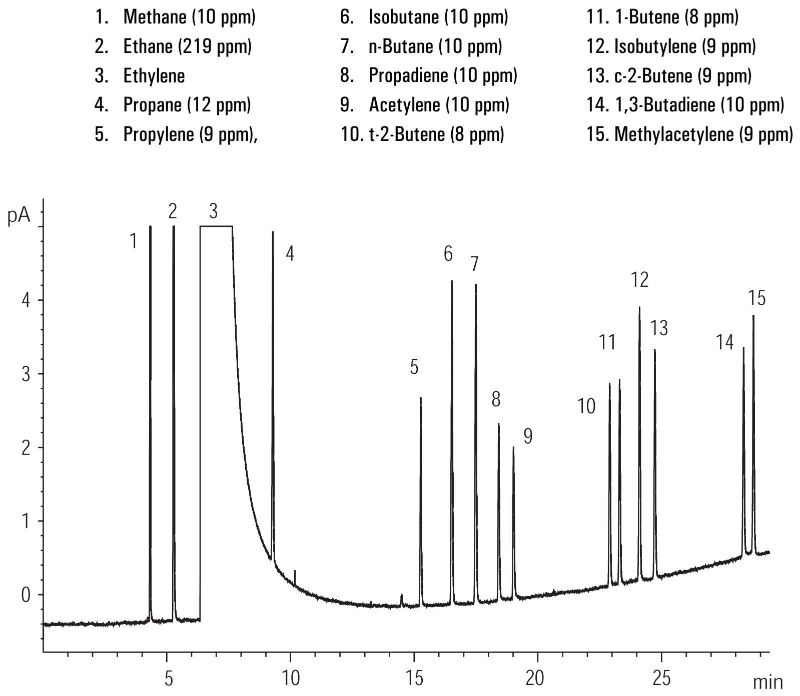


Figure 2. Chromatogram of ethylene calibration blend, split ratio 10/1.

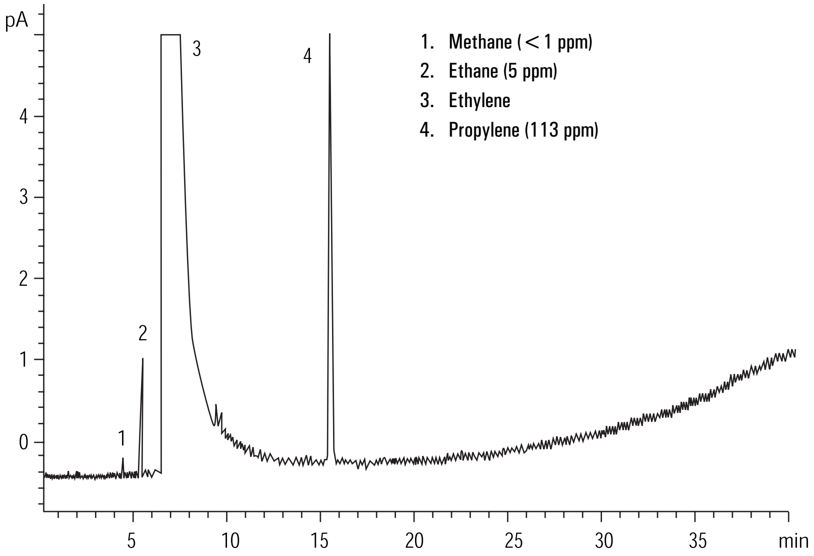


Figure 3. Chromatogram of process ethylene sample, split ratio 20/1.

Propylene

The configuration used for propylene analysis is illustrated in figure 5. This configuration is essentially the same as for ethylene, but without the HP-1 column. The sample volume was reduced to 0.25 mL. Propylene was sampled in the gas state.

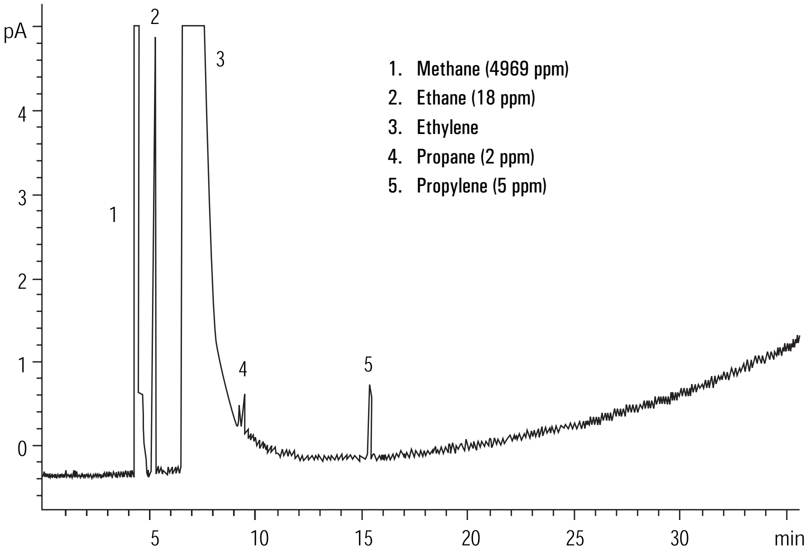


Figure 4. Chromatogram of process ethylene sample.

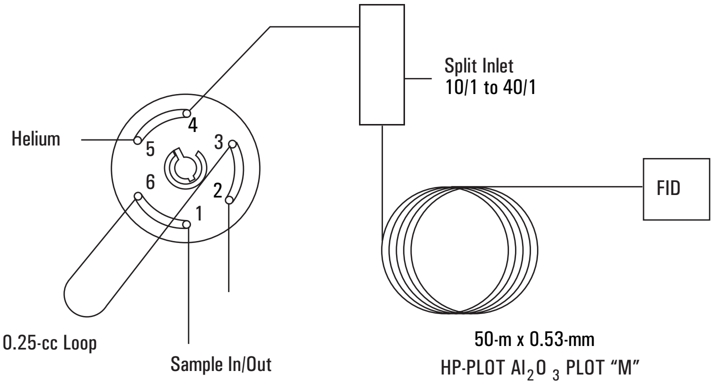


Figure 5. Valve drawing for impurities in propylene.

A chromatogram representing the trace hydrocarbon impurities in propylene is shown in figure 6. This sample was analyzed at a split ratio of 20/1. The concentration of most impurities range from 8 to 20 ppm. Ethylene is present at a higher concentration level. Most of the impurities in the sample are well separated using the conditions described in table 1. Cyclopropane elutes just before propylene and is baseline separated under these conditions. Several of the C_4 hydrocarbons elute on the tail of the high-purity propylene. This affects the lower limit of detection for these peaks, compared to those components that are baseline separated. The remainder of the C_4 and C_5 impurities are well separated.

1. Methane
2. Ethane (10 ppm)
3. Ethylene (50 ppm)
4. Propane
5. Cyclopropane (10 ppm)
6. Propylene
7. Isobutane (10 ppm)
8. n-Butane (7 ppm)
9. Propadiene
10. Acetylene
11. t-2-Butene (10 ppm)
12. 1-Butene
13. neo-Pentane
14. Isobutylene (9 ppm)
15. Isopentane
16. c-2-Butene (9 ppm)
17. n-Pentane (10 ppm)
18. 1,3-Butadiene (9 ppm)

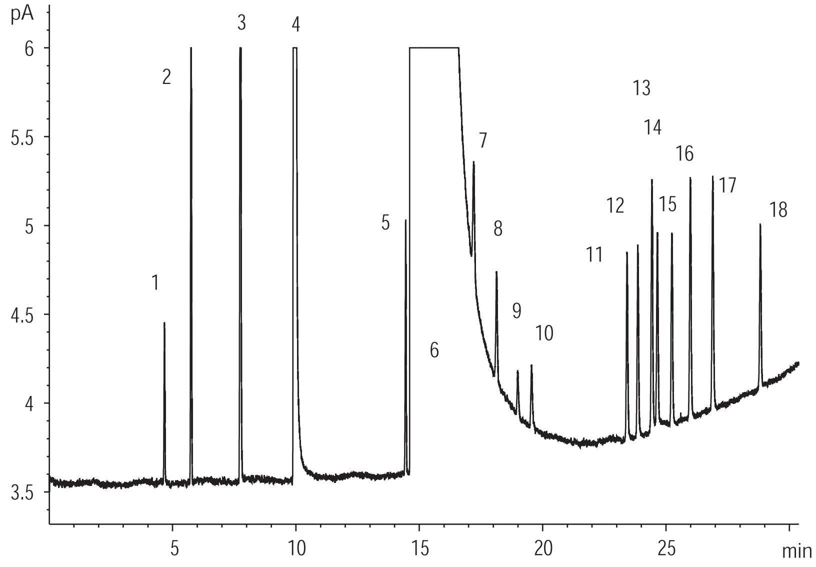


Figure 6. Chromatogram of propylene calibration standard.

For comparison, figure 7 shows the analysis of a second calibration blend containing a higher level of impurities (50 to 1000 ppm).

Figure 8 presents the chromatographic results for a high-purity propylene process sample. This sample contains only ethane and propane impurities.

Summary

This application note describes two methods for analyzing trace hydrocarbon impurities in ethylene and propylene. These methods use a gas sample valve with split injection, an Agilent HP-PLOT Al_2O_3 and HP-1 (for ethylene only) column, and an FID. Impurities below the 10-ppm mole level can be easily quantitated using these methods. For some impurities, especially those that are well separated from the large ethylene or propylene peaks, detection limits were estimated to be about 1 ppm.

1. Methane
2. Ethane
3. Ethylene
4. Propane (988 ppm)
5. Cyclopropane (100 ppm)
6. Propylene
7. Isobutane (129 ppm)
8. n-Butane
9. Propadiene (62 ppm)
10. Acetylene (48 ppm)
11. t-2-Butene
12. 1-Butene
13. Isobutylene
15. Isopentane
16. c-2-Butene
17. 1,3-Butadiene
18. Methylacetylene (100 ppm)

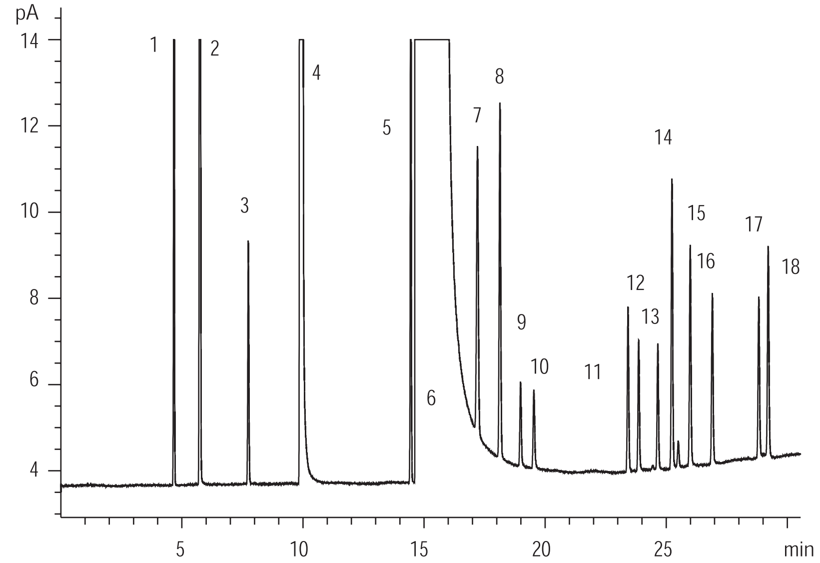
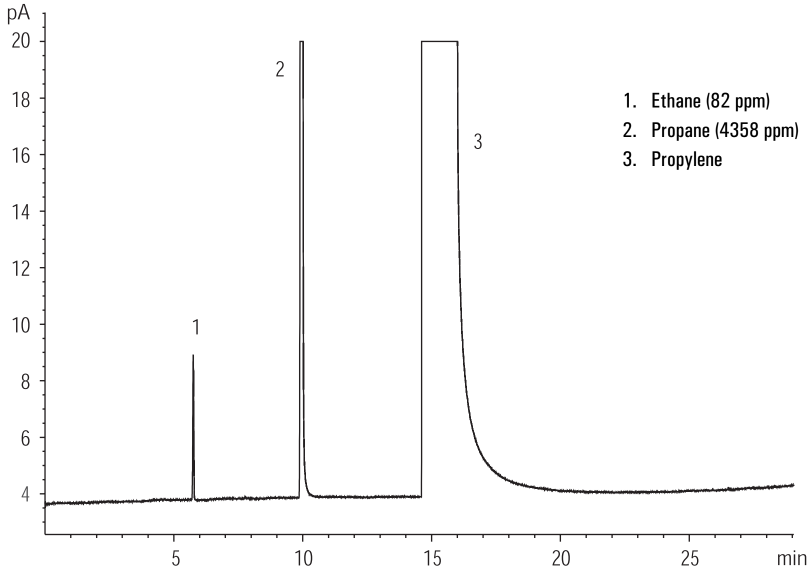


Figure 7. Chromatogram of propylene calibration blend containing higher levels of impurities.



1. Ethane (82 ppm)
2. Propane (4358 ppm)
3. Propylene

Figure 8. Chromatogram of process propylene sample.

References

1. ASTM Method D 5325, "Standard Guide for the Analysis of Ethylene Product," Annual Book of Standards, Volume 5, ASTM,
   100 Bar Harbor Drive,
   West Conshohocken, PA 19428
   USA.

2. ASTM Method D 5273, "Standard Guide for the Analysis of Propylene Concentrates," Annual Book of Standards, Volume 5, ASTM,
   100 Bar Harbor Drive,
   West Conshohocken, PA 19428
   USA.

3. Proposed methods for hydrocarbon impurities in ethylene and propylene by gas chromatography are being investigated under ASTM committee D-2, subcommittee D.

4. "Optimized Determination of C_1–C_6 Impurities in Propylene and Ethylene Using HP-PLOT/Al_2O_3 Columns," Agilent Technologies, Inc. Publication (43) 5062-8417E, March 1994.

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