Determination of Low Level Hydrocarbon Impurities in Propylene Using the Agilent 6820 Gas Chromatograph

Application

Petrochemical

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Abstract

A method for analyzing trace hydrocarbon impurities in propylene is described. The method employs an Agilent 6820 gas chromatography (GC) system configured with a gas sampling valve, split/splitless inlet, and flame ionization detector. The Agilent Cerity Networked Data System for Chemical QA/QC was used to control the 6820 GC and to provide data acquisition and data analysis. An Agilent HP-Al_2O_3 column was used for separation of the trace hydrocarbons. Impurity levels at 1 ppm were easily detected in propylene. This method does not determine all possible impurities such as CO, CO_2, H_2O, alcohols, nitrogen oxides, and carbonyl sulfide, or hydrocarbons larger than decane.

Introduction

High purity propylene is commonly used as the feedstock for production of polypropylene, and the quality of this monomer is critical to successful polymerization. The presence of trace amounts of certain hydrocarbon impurities can have deleterious effects on the catalyst. For example, acetylene can be adsorbed at the active center of the catalyst, resulting in catalyst deactivation. Dienes may reduce the rate of polymerization and adversely affect product quality. To maintain catalytic efficiency, most propylene processes require that alkyne and diene contaminants in the monomer be less than 10 ppm. The availability of a suitable method for the determination of impurities in propylene is critical to setting specifications, controlling internal quality, and doing development or research work.

Some propylene producers use their own standard method in which packed columns are used. It is difficult to detect trace level impurities by packed column. Presently, the American Society of Testing and Materials (ASTM) has published Method D2712 for the determination of trace hydrocarbon impurities in propylene streams [1]. In this method, an alumina porous layer open tubular (PLOT) column is used. The improved efficiency of the PLOT column provides better resolution and increases effective sensitivity.

Experimental

An Agilent 6820 GC system was used for this work. It was configured with a split/splitless capillary inlet and a flame ionization detector (FID). Gas samples were injected using an automatic gas sample valve that was heated to 80 °C. The sample loop volume was 0.25 mL. The gas sample valve was connected to the inlet using an aluminum-jacketed stainless steel tube that maintains the sample temperature during transfer from the sample loop. The configuration used for propylene analysis is shown in Figure 1 and the instrument conditions are given in Table 1.

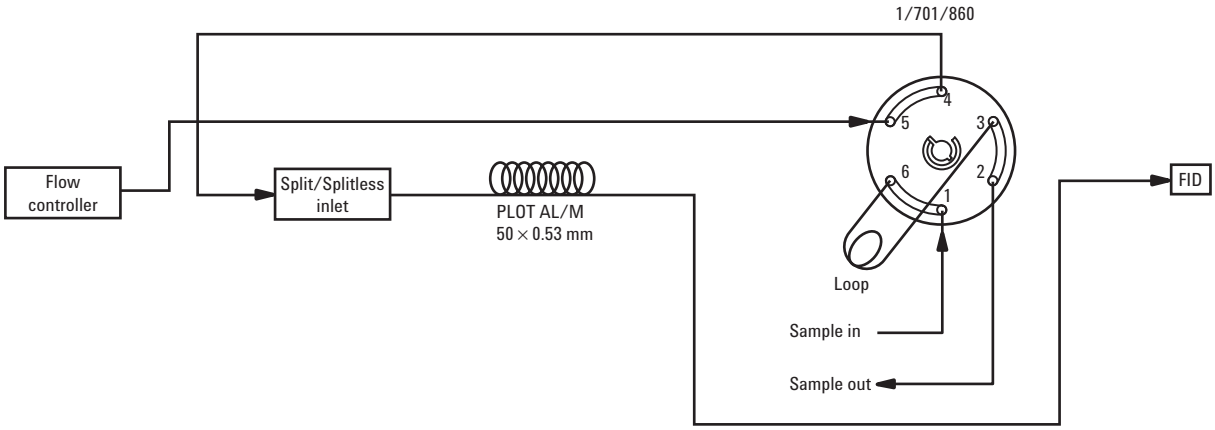

Figure 1. Configuration diagram.

An Agilent 50 m × 0.53 mm PLOT Al_2O_3 "M" deactivated column was used. The sample was run in the split mode using an Agilent split liner (Agilent part number 19251-60540).

The Agilent Cerity NDS for Chemical QA/QC was used for instrument control, data acquisition, and data analysis. Data was acquired at 20 Hz.

Table 1. Instrument Conditions

Split/Splitless inlet	175 °C, Split mode, with 15:1 and ~4:1 Split ratio
Valve	Gas sample valve, 6-Port, option 701
Valve temperature	80 °C
Sample loop	0.25 mL
Column flow (He)	4 mL/min
Column	PLOT Al_2O_3 "M" 50 m × 0.53 mm × 0.25 µm (p/n: 19095P-M25)
Oven	40 °C for 2 min, 4 °C/min to 190 °C for 5 min
Detector	FID, 300 °C
H_2	35 mL/min
Air	350 mL/min
Makeup gas (N_2)	22 mL/min

A propylene standard mix (DCG Partnership I, LTD., Pearland, TX 77581) consisting of the components listed in Table 2 at the certified concentrations shown (mole fraction) was used.

Table 2. Propylene Sample Mix Component Concentrations

Compound	Concentrations (ppm)	Compound	Concentrations (ppm)
1. Methane	10	10 Acetylene	9.8
2. Ethane	27	11. *trans*-2-Butene	9.92
3. Ethylene	10	12. 1-Butene	9.89
4. Propane	3526	13. neo-Pentane	9.86
5. Cyclopropane	10	14. *iso*-Butylene	9.87
6. Propylene	Balance gas	15. *iso*-Pentane	9.83
7. *iso*-Butane	9.94	16. *cis*-2-Butene	9.91
8. n-Butane	9.85	17. n-Pentane	9.86
9. Propadiene	9.84	18. 1,3-Butadiene	9.96

A dynamic blending system (Figure 2) was used to quantitatively dilute the sample with helium.

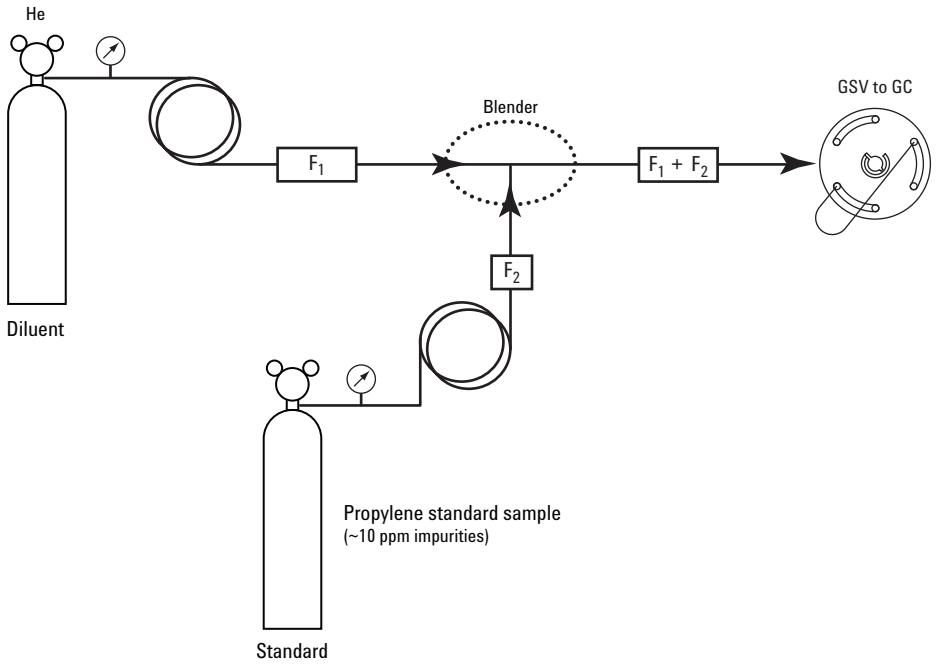

Figure 2. Dynamic blending scheme.

Diluted standard blend concentration is calculated by the following formula:

$C = C_o * F_2/(F_1+F_2)$

Where:
C: is diluted component concentration in ppm
C_o: original component concentration in standard blend in ppm
F_1: helium flow (mL/min)
F_2: propylene standard blend flow (mL/min)

Results and Discussion

Repeatability of 10 ppm Level Impurities in Propylene Analyses

Figure 3 shows the chromatogram from the undiluted sample. The PLOT AL_2O_3 column provides excellent separation for the C1 through C5 isomers [2]. The concentrations of most components are about 10 ppm. These trace level hydrocarbon impurities have a good FID response and are easily detected with baseline separation for most. Because the concentration of propylene is very high, some of the impurities such as *iso*-butane, n-butane, propadiene, and acetylene appear on the tail of the propylene peak. Even so, the Agilent 6820 GC system demonstrated very good repeatability, as shown in Table 3.

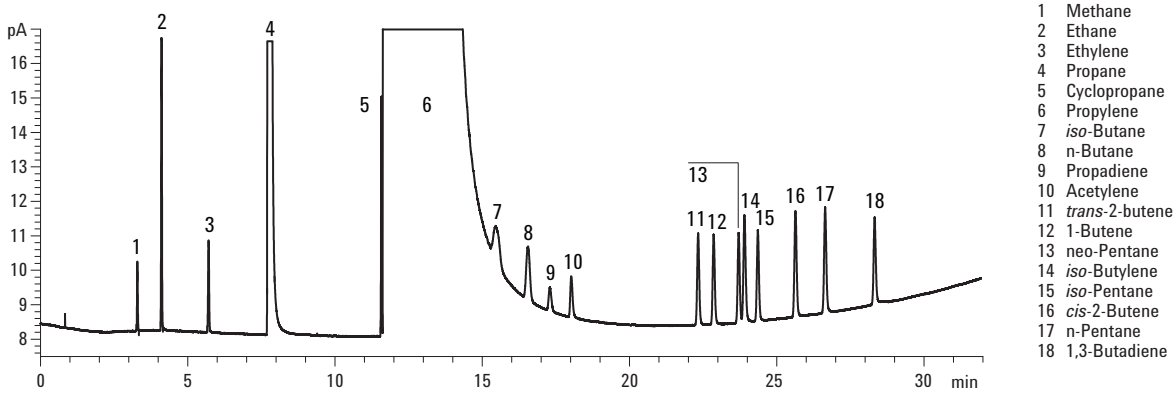

Figure 3. Propylene standard mix. Concentrations are given in Table 2. Split ratio: 15:1.

Table 3. System Repeatability of Three Propylene Standard Runs

Component	Amt1 (ppm)	Amt2 (ppm)	Amt3 (ppm)	Avg. (ppm)	RSD (%)
Methane	9.96	9.91	10.13	10.00	1.17
Ethane	26.95	26.78	27.27	27.00	0.92
Ethylene	10.21	9.90	9.90	10.00	1.76
Propane	3522	3503	3553	3526	0.73
Cyclopropane	9.99	9.95	10.07	10.00	0.61
Propylene	995642	988398	1004994	996344	0.84
iso-Butane	10.02	9.77	10.04	9.94	1.54
n-Butane	9.75	9.69	10.12	9.85	2.40
Propadiene	9.71	9.91	9.91	9.84	1.19
Acetylene	9.71	9.88	9.82	9.80	0.90
t-2-Butane	9.91	9.84	10.01	9.92	0.89
1-Butene	9.89	9.80	9.98	9.89	0.95
neo-Pentane	9.86	9.76	9.96	9.86	1.03
iso-Butylene	9.88	9.76	9.98	9.87	1.12
iso-Pentane	9.80	9.76	9.94	9.83	0.95
c-2-Butane	9.90	9.84	9.99	9.91	0.72
n-Pentane	9.84	9.76	9.98	9.86	1.16
1,3-Butadiene	9.97	9.87	10.04	9.96	0.85

Full Dynamic Range Data

One of the advantages of the Agilent 6820 GC system is its ability to obtain full dynamic range data. The signal "range" setting is not required because the Cerity/ChemStation uses digital data that goes from the noise level all the way to 100% samples. Without this feature, the propylene peak would be flat at the top as soon as the range was exceeded, making accurate integration impossible. In many cases without digital signal processing, users would have to run the sample at two different ranges in order to quantitate both large and small peaks. The Agilent GC system with Cerity/ChemStation can simultaneously acquire both large and small peaks in one run without setting different ranges. This feature helps quantitate 100% and ppm compounds at the same time. Figures 4 and 5 separately illustrate scaling the small peaks and one large peak to demonstrate acquisition of ppm level peaks and high percent level peaks.

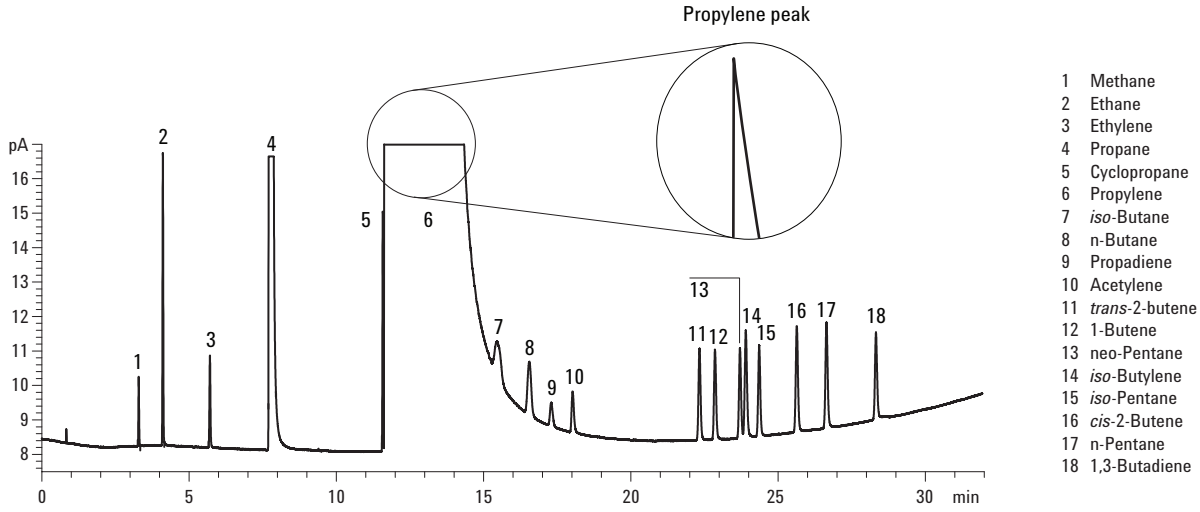

Figure 4. Propylene standard mix shown on small scale. Propylene peak looks flat due to graphic scaling.

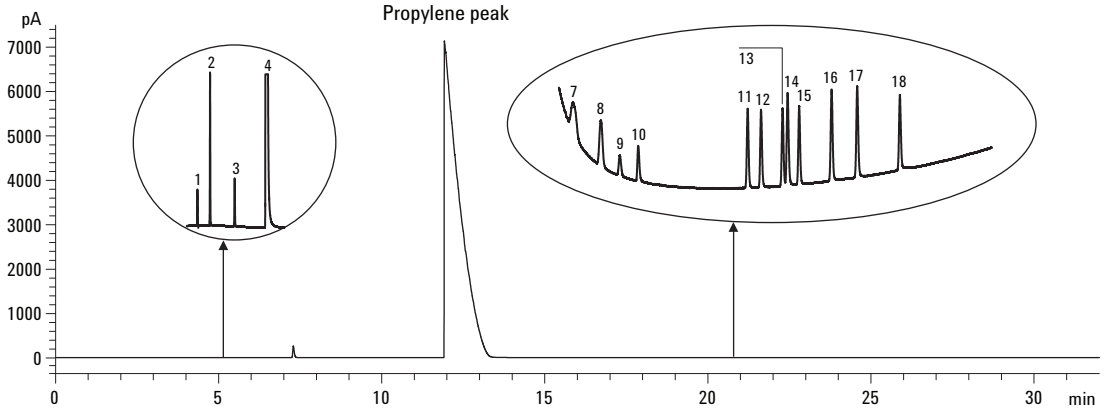

Figure 5. Propylene standard mix shown on high scale. Zooming in shows good resolution, identification, and integration.

Sensitive to 1 ppm Impurities

Figure 6 illustrates the chromatogram of less than 1 ppm impurities in propylene. The injected sample was prepared by a 10X dilution of the standard mix sample using helium; the impurities level decreased to 1 ppm as well as the 10:1 dilution of the propylene peak. In this analysis, the method was modified to use a split ratio of 4:1 instead of 15:1 in order to achieve the 1 ppm impurities detection. The sample presented in Figure 6 shows *iso*-butane, n-butane, propadiene, and acetylene clearly detected on the tail of the propylene peak. Other impurities show baseline separation with excellent signal to noise as well. This demonstrates the performance of the Agilent 6820 GC for sensitive and quantitative detection of 1 ppm hydrocarbon impurities in propylene.

Conclusions

The Agilent 6820 configured with a 6-port gas sampling valve interfaced directly to a split/splitless inlet was used to analyze trace hydrocarbon impurities in propylene with FID. Impurities below the 10 ppm mole % level can be easily quantitated. This system was able to detect 1 ppm level hydrocarbon impurities with excellent signal to noise. The Agilent 6820 system with Cerity can simultaneously acquire and quantitate both large concentrations (99 + mole %) and trace (low ppm) levels in a single run due to the use of a full dynamic range digital signal path. Manual range changes are not required. The feature of full dynamic range allows for accurate quantitation of near 100% propylene and ppm level compounds in one analysis. The system is simple and convenient to set up and use for routine QA/QC labs in the petrochemical and chemical industries.

References

1. ASTM Method D2712, “Standard Test Method for Hydrocarbon Traces in Propylene Concentrates By Gas Chromatography”.
2. Roger Firor, “Trace Level Hydrocarbon Impurities in Ethylene and Propylene,” Agilent Technologies, publication 5965-7824E www.agilent.com/chem

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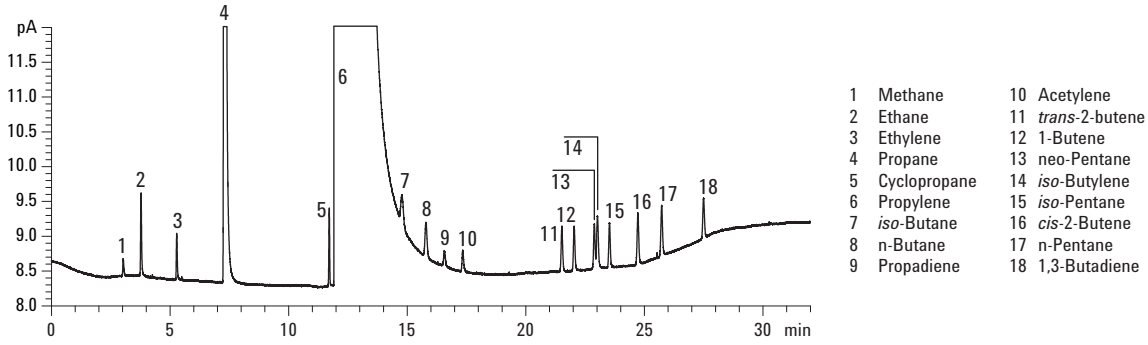

Figure 6. One ppm level impurities in the propylene standard mix.

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