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

Application

Petrochemical

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Abstract

A method for analyzing trace hydrocarbon impurities in ethylene 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 PLOT Al_2O_3 megabore column was used for separation of the trace hydrocarbons. Impurity levels at about 15 ppm were easily detected in ethylene. This method does not determine all possible impurities such as CO, CO_2, H_2O, alcohols, nitrogen oxides and carbonyl sulfide, nor hydrocarbons larger than decane.

Introduction

High purity ethylene is required as a feedstock for several manufacturing processes. The presence of trace amounts of certain hydrocarbon impurities can have deleterious effects on the catalysts used for conversion. For example, acetylene can be adsorbed at the active sites of the catalyst, resulting in catalyst deactivation. Dienes may reduce the rate of polymerization and adversely affect product quality. The availability of a suitable method for the determination of impurities in ethylene is critical to setting specifications, controlling internal quality, and performing development or research work.

It is difficult to detect trace level impurities by packed column. Presently, the American Society of Testing and Materials (ASTM) has published Method D6159 for the determination of trace hydrocarbon impurities in ethylene streams [1]. In this method, both an alumina porous layer open tubular (PLOT) column and a methyl silicone megabore column are used to improve the separation of methyl acetylene, *iso*-pentane, and n-pentane. In this application, an Agilent 50 m × 0.53 mm PLOT Al_2O_3 “M” deactivated column is used to provide resolution and effective sensitivity.

Experimental

An Agilent 6820 GC system was used for this work. Configured with a split/splitless capillary inlet and a flame ionization detector (FID), gas samples were injected using an automatic gas sample valve 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 ethylene analysis is shown in Figure 1.

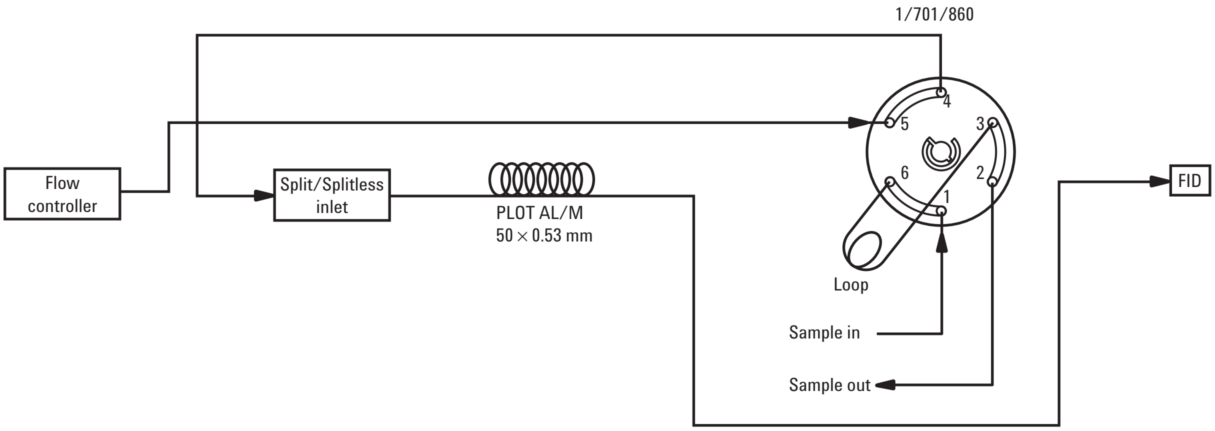

Figure 1. Configuration diagram.

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) and an Agilent advanced green septum (Agilent part number 5183-4759).

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 10:1 Split ratio
Valve	Gas sample valve, 6-Port, option 701
Valve temperature	80 °C
Sample loop	0.25 mL
Column flow (He)	6 mL/min
Column	PLOT Al_2O_3 "M" 50 m × 0.53 mm × 0.25 µm (p/n: 19095P-M25)
Oven	35 °C (2 min) with 4 °C/min to 140 °C (5 min)
Detector	FID, 300 °C
H_2	35 mL/min
Air	350 mL/min
Makeup gas (N_2)	19 mL/min

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

Table 2. Ethylene Sample Mix Components

Compound	Concentrations (ppm)	Compound	Concentrations (ppm)
1. Methane	998	9. *trans*-2-butene	997
2. Ethane	981	10. Butene-1	1000
3. Propane	999	11. *iso*-Butylene	983
4. Propylene	1001	12. c*is*-2-Butene	986
5. Acetylene	981	13. Propyne	1006
6. *iso*-Butane	978	14. 1,3-Butadiene	1003
7. Allene	1001	Ethylene	Balance
8. n-Butane	1000		

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

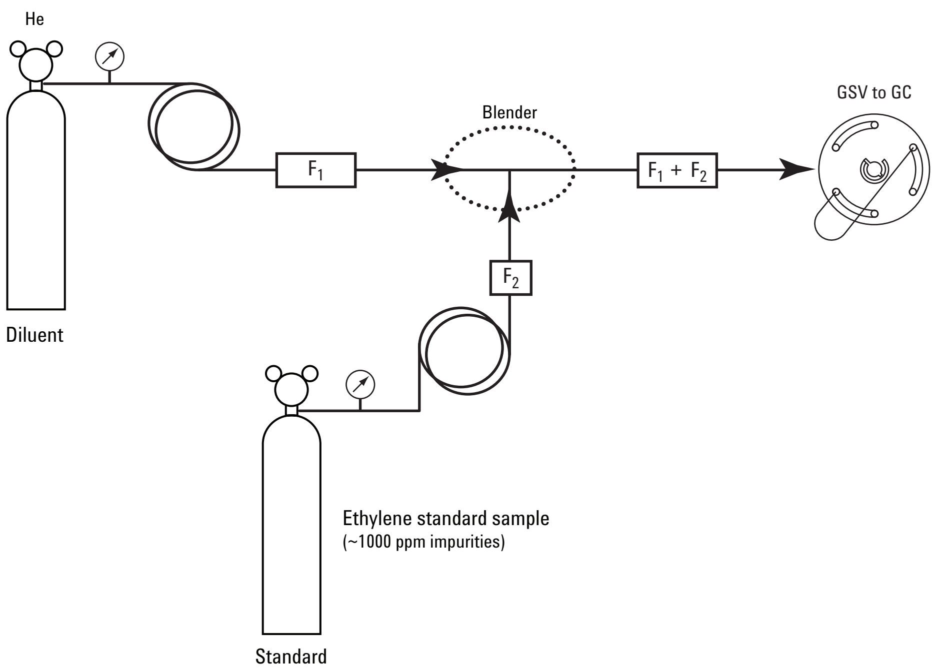

Figure 2. Dynamic blending scheme.

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 Trace Level Impurities in Ethylene Analyses

Figure 3 shows the chromatogram from the blended sample. The PLOT Al_2O_3 column exhibits excellent separation for the C1 through C4 isomers [2]. The concentrations of most components are about 16 ppm. These trace level hydrocarbon impurities have a good FID response and are easily detected with baseline separation for most. In this method, the hydrocarbon impurities are determined and the total impurities are used to determine the ethylene content. Even in the trace level impurities, the Agilent 6820 GC system demonstrated good repeatability, as shown in Table 3.

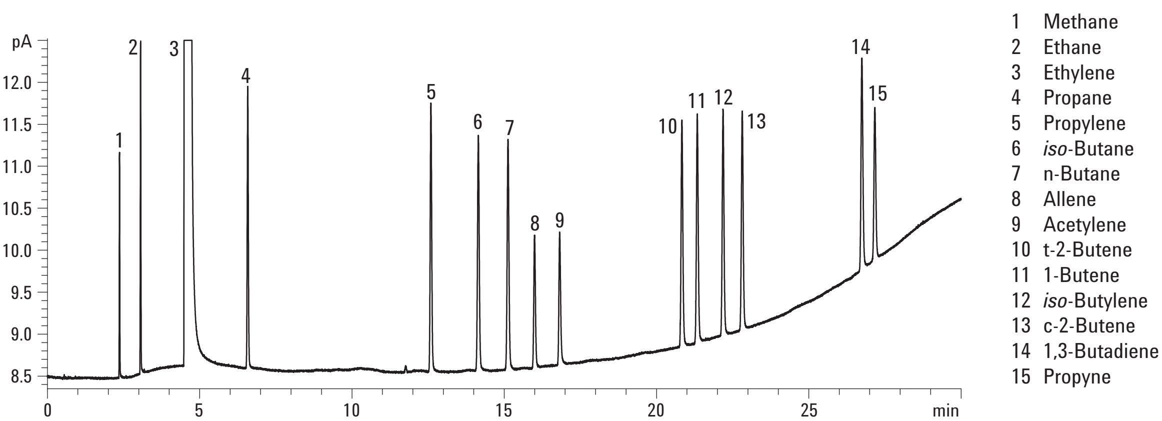

Figure 3. Sixteen ppm level impurities in the ethylene standard mix.

Table 3. System Repeatability of Three Runs for Diluted Ethylene Standard Mix

Component	Amt1	Amt2	Amt3	Avg.(ppmV)	RSD(%)	Repeatability criteria[1] (ASTM)
Methane	16.28	16.19	16.03	16.17	0.80	$0.02277 \times (ppmV^{0.6})$
Ethane	15.98	15.94	15.75	15.89	0.76	$0.03811 \times ppmV$
Propane	16.26	16.22	16.07	16.18	0.63	$0.03273 \times (ppmV +21.23)$
Propylene	16.45	15.98	16.22	16.22	1.46	$0.04780 \times ppmV^{1.15}$
Isobutane	15.97	16.02	15.69	15.89	1.10	$0.04370 \times ppmV^{1.07}$
n-Butane	15.98	15.96	15.59	15.84	1.37	$0.1156 \times ppmV^{0.85}$
Allene	16.38	16.32	15.95	16.22	1.42	$0.05091 \times (ppmV +0.7831)$
Acetylene	15.92	16.31	16.37	16.20	1.49	$0.1189 \times ppmV$ x 0.8
t-2-Butene	16.27	16.30	15.88	16.15	1.45	$0.063960 \times ppmV^{0.95}$
1-Butene	16.36	16.34	15.90	16.20	1.62	$0.03992 \times (ppmV +17.14)$
iso-Butylene	16.12	16.05	15.60	15.92	1.77	$0.1229 \times ppmV^{0.85}$
c-2-Butene	16.17	16.07	15.68	15.97	1.62	$0.08350 \times ppmV^{0.93}$
1,3-Butadiene	16.51	16.43	15.95	16.30	1.85	$0.07518 \times ppmV^{0.9}$
Propyne	16.34	16.22	16.18	16.25	0.52	$0.05205 \times ppmV^{1.1}$

[1]Ethylene repeatability (ASTM)-The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run and in the normal and correct operation of the test method, exceed the values in only 1 case in 20, where ppmV is the concentration of the component..

Conclusions

The Agilent 6820 gas chromatograph configured with a 6-port gas sampling valve interfaced directly to a split/splitless inlet was used to analyze trace hydrocarbon impurities in ethylene with FID. Impurities, about 15 ppm mole % level, can be easily quantitated and show good repeatability. 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 system is simple and convenient to set up and use for routine QA/QC lab in the petrochemical and chemical industries.

References

1. ASTM Method D6159, “Standard Test Method for Determination of Hydrocarbon Impurities in Ethylene 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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