

Analysis of Impurities in Ethylene

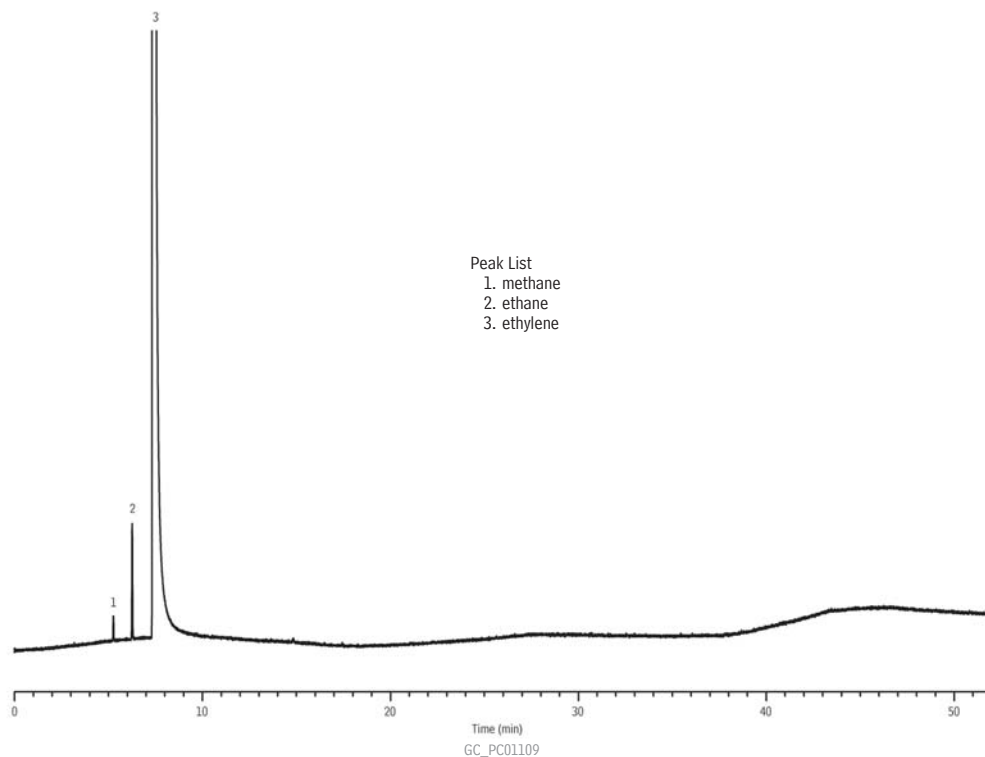
by ASTM D6159-97

Ethylene is one of the highest volume chemicals produced in the world, with global production exceeding 100 million metric tons annually. Ethylene is primarily used in the manufacture of polyethylene, ethylene oxide, and ethylene dichloride, as well as many other lower volume products. Most of these production processes use various catalysts to improve product quality and process yield. Impurities in ethylene can damage the catalysts, resulting in significant replacement costs, reduced product quality, process downtime, and decreased yield.

Ethylene is typically manufactured through the use of steam cracking. In this process, gaseous or light liquid hydrocarbons are combined with steam and heated to 750–950°C in a pyrolysis furnace. Numerous free radical reactions are initiated and larger hydrocarbons are converted (cracked) into smaller hydrocarbons. The high temperatures used in steam cracking promote the formation of unsaturated or olefinic compounds like ethylene. Ethylene feedstocks must be tested to ensure that only high purity ethylene is delivered for subsequent chemical processing.

Testing typically follows ASTM D6159-97, a GC/FID method which employs a two-column configuration consisting of an alumina PLOT column with KCl deactivation (50m x 0.53mm ID) coupled to a methyl silicone column (30m x 0.53mm ID x 5.0µm df).

Figure 1 Methane and ethane are well resolved in high purity ethylene samples.



Column: Rt®-Alumina BOND/KCl, 50m, 0.53mm ID, 10.0µm (cat.# 19760) in series with Rtx®-1, 30m, 0.53mm ID, 5.0µm (cat.# 10179), connected using a Universal Press-Tight® Connector (cat.# 20401)

Sample: ethylene

Inj.: 1µL split, 60mL/min. split vent flow rate
2mm splitless liner (cat.# 20712)

Inj. temp.: 200°C

Carrier gas: helium, constant pressure (8.0psi, 55.2kPa)

Linear velocity: 25.4cm/sec. @ 35°C

Oven temp.: 35°C (hold 2 min.) to 190°C @ 4°C/min. (hold 15 min.)
(conditions as per ASTM D6159-97)

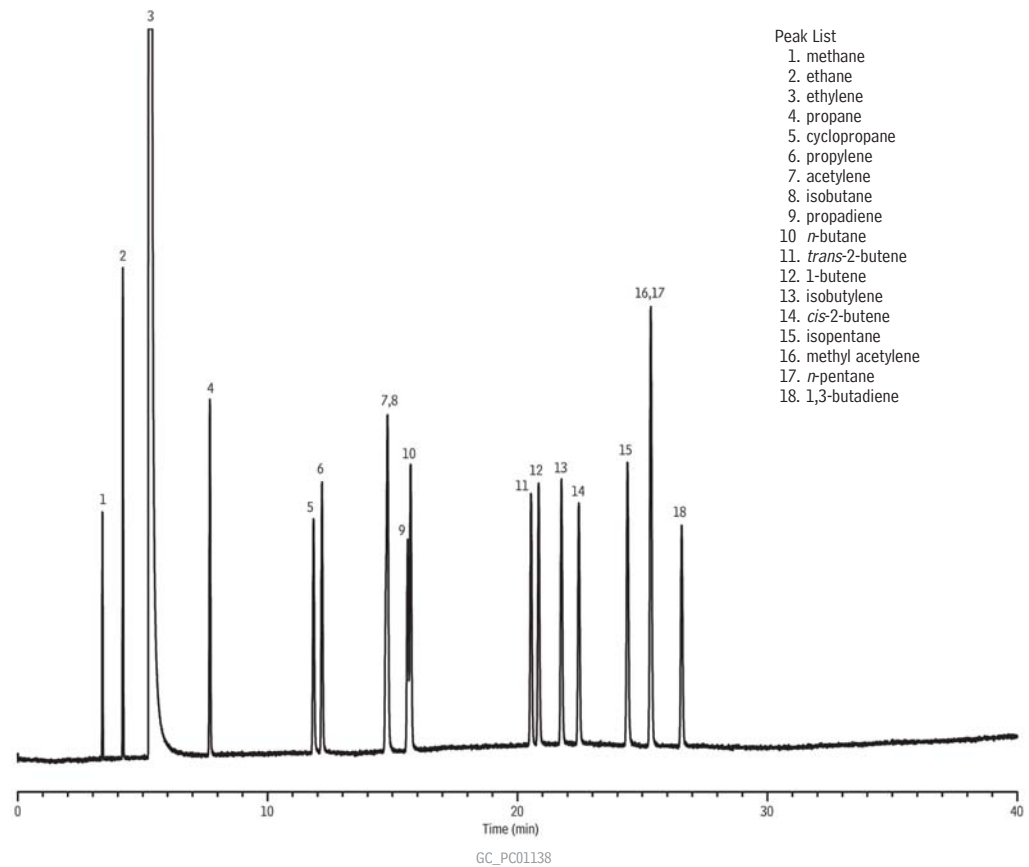
Det.: FID @ 200°C

Instrument: Agilent 5890

Samples of high purity ethylene typically contain only two minor impurities, methane and ethane, which can be detected in low ppmV concentrations (Figure 1). However, steam cracking can also produce higher molecular weight hydrocarbons, especially when propane, butane, or light liquid hydrocarbons are used as starting materials. Although fractionation is used in the final production stages to produce a high purity ethylene product, it is still important to be able to identify and quantify any other hydrocarbons present in an ethylene sample. Achieving sufficient resolution of all of these compounds can be challenging due to their similarities in boiling point and chemical structure. ASTM D6159-97 addresses this issue by combining the separation power of two different types of capillary columns.

The Rt[®]-Alumina BOND/KCl PLOT column has excellent separation capabilities for low molecular weight hydrocarbons ranging from C1 through C12, but complete resolution of all compounds is not always possible, depending on the conditions that are employed. Figure 2 shows the analysis of an ethylene sample that has been spiked with the typical hydrocarbons that may be present after ethylene production. When using the temperature conditions supplied in the method, there are coelutions between three different peak pairs. Acetylene and isobutane (peaks 7 and 8) elute at the same retention time, propadiene and *n*-butane (peaks 9 and 10) are only partially resolved, and there is a complete coelution between methyl acetylene and *n*-pentane (peaks 16 and 17).

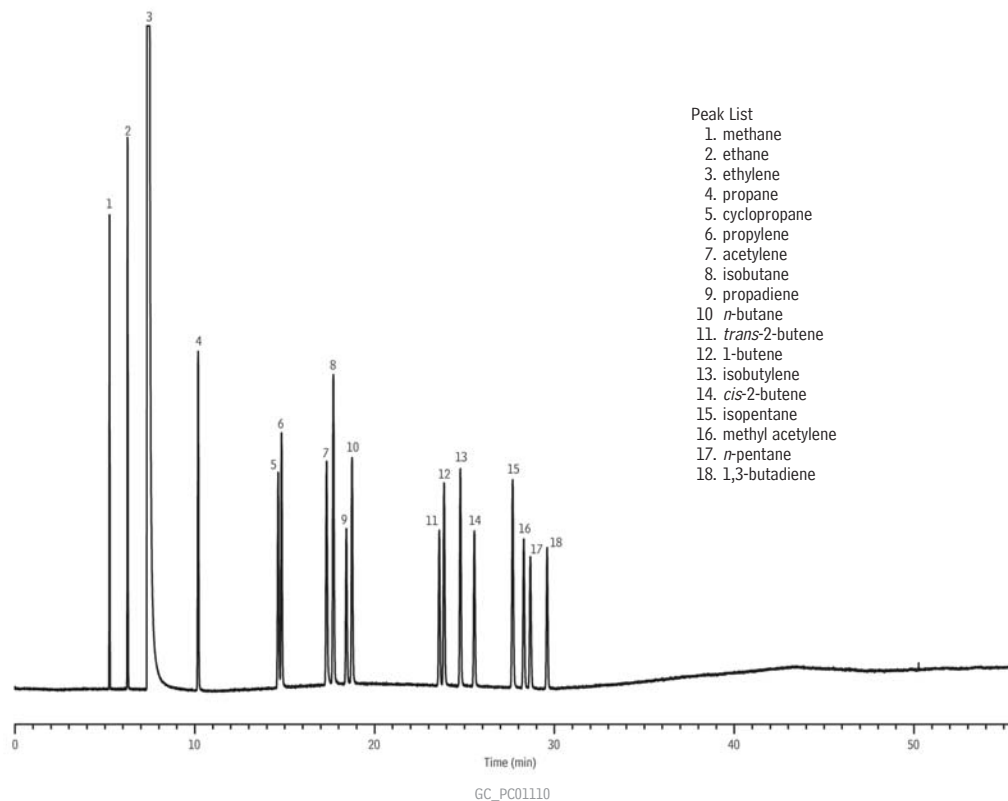
Figure 2 Analyzing ethylene on an alumina column alone results in coelutions that prevent quantification of several impurities.



Column: Rt[®]-Alumina BOND/KCl, 50m, 0.53mm ID, 10.0 μ m (cat.# 19760)
 Sample: ethylene and C1-C5 hydrocarbons
 Inj.: 1 μ L split, 60mL/min. split vent flow rate
 2mm splitless liner (cat.# 20712)
 Inj. temp.: 200°C
 Carrier gas: helium, constant pressure (5.0psi, 34.5kPa)
 Linear velocity: 25.0cm/sec. @ 35°C
 Oven temp.: 35°C (hold 2 min.) to 190°C @ 4°C/min. (hold 15 min.)
 (conditions as per ASTM D6159-97)
 Det.: FID @ 200°C
 Instrument: Agilent 5890

By combining an Rt[®]-Alumina BOND/KCl column with an Rtx[®]-1 column, complete resolution for all of the compounds of interest can be achieved. The Rtx[®]-1 column supplements the separation achieved on the Rt[®]-Alumina BOND/KCl column by contributing additional selective retention of less polar compounds like isobutane, *n*-butane, and *n*-pentane. The extra retention of these compounds allows for the complete separation of the slightly more polar compounds like acetylene, propadiene, and methyl acetylene. Figure 3 shows the analysis of the same ethylene sample spiked with hydrocarbons. All of the compounds that are identified in the method can now be resolved for accurate identification and quantitation.

Figure 3 All impurities are fully resolved and easily quantifiable when using an Rt[®]-Alumina BOND/KCl column coupled to an Rtx[®]-1 column.



Column: Rt[®]-Alumina BOND/KCl, 50m, 0.53mm ID, 10.0 μ m (cat.# 19760) in series with Rtx[®]-1, 30m, 0.53mm ID, 5.0 μ m (cat.# 10179), connected using a Universal Press-Tight[®] Connector (cat.# 20401)
 Sample: ethylene and C1-C5 hydrocarbons
 Inj.: 1 μ L split, 60mL/min. split vent flow rate
 2mm splitless liner (cat.# 20712)
 Inj. temp.: 200 $^{\circ}$ C
 Carrier gas: helium, constant pressure (8.0psi, 55.2kPa)
 Linear velocity: 25.4cm/sec. @ 35 $^{\circ}$ C
 Oven temp.: 35 $^{\circ}$ C (hold 2 min.) to 190 $^{\circ}$ C @ 4 $^{\circ}$ C/min. (hold 15 min.)
 (conditions as per ASTM D6159-97)
 Det.: FID @ 200 $^{\circ}$ C
 Instrument: Agilent 5890

When testing for impurities in ethylene using ASTM D6159-97, the combination of an Rt[®]-Alumina BOND/KCl column coupled to an Rtx[®]-1 column provides the best resolution of the most common hydrocarbon contaminants. Restek PLOT columns are manufactured using a new technology that significantly reduces particle release, extending column lifetime and giving highly reproducible retention times. Restek columns provide reliable results that can be used to protect expensive catalysts, make faster process adjustments, and improve product yield.



Rt®-Alumina BOND/KCI Columns

(fused silica PLOT)

(KCI deactivation)

ID	df (µm)	temp. limits	length	cat. #
0.32mm	5	to 200°C	30-Meter	19761
0.32mm	5	to 200°C	50-Meter	19762
0.53mm	10	to 200°C	30-Meter	19759
0.53mm	10	to 200°C	50-Meter	19760

Rtx®-1 Columns (fused silica)

(Crossbond® 100% dimethyl polysiloxane)

ID	df (µm)	temp. limits	length	cat. #
0.53mm	5.00	-60 to 270/290°C	30-Meter	10179

Splitless Liners for Agilent GCs



ID* x OD & Length	qty.	cat.#
2mm Splitless		
2.0mm x 6.5mm x 78.5mm	ea.	20712
2.0mm x 6.5mm x 78.5mm	5-pk.	20713
2.0mm x 6.5mm x 78.5mm	25-pk.	20714
Siltek 2mm Splitless		
2.0mm x 6.5mm x 78.5mm	ea.	20712-214.1
2.0mm x 6.5mm x 78.5mm	5-pk.	20713-214.5
2.0mm x 6.5mm x 78.5mm	25-pk.	20714-214.25

*Nominal ID at syringe needle expulsion point.

Restek Super-Clean Gas Filter Kits and Replacements

- High-purity output ensures 99.9999% pure gas (at max. flow of 7L/min.).
- “Quick connect” fittings for easy, leak-tight cartridge changes.
- Glass inside to prevent diffusion; polycarbonate housing outside for safety.
- All traps measure 10³/₈" x 1³/₄" (27 x 4.4 cm).
- Each base plate unit measures 4" x 4" x 1⁷/₈" (10.2 x 10.2 x 4.8 cm).



22020

22022



base plate

Description	qty.	cat.#
Carrier Gas Cleaning Kit (includes mounting base plate, 1/8" inlet/outlet fittings, and oxygen/moisture/hydrocarbon Triple Gas Filter)	kit	22019
Fuel Gas Purification Kit (includes mounting base plate, 1/8" inlet/outlet fittings, and hydrocarbon/moisture Fuel Gas Filter)	kit	22021
Replacement Triple Gas Filter (removes oxygen, moisture and hydrocarbons)	ea.	22020
Replacement Fuel Gas Filter (removes moisture and hydrocarbons)	ea.	22022
Gas Filter Bundle Kit (includes one Triple Gas Filter, cat.# 22020 and two Fuel Gas Filters, cat.# 22022)	kit	22031

Restek Electronic Leak Detector

Why have a small leak turn into a costly repair? Protect your data and analytical column by using a Restek Leak Detector.

Features & Benefits include:

- Optimized sample flow path.
- New ergonomic, hand-held design.
- Rugged side grips for added durability.
- Handy probe storage for cleanliness and convenience.
- Longer lasting battery, up to 6 hours of continuous use.
- Automatic shut-off.
- A convenient carrying and storage case.
- Easy to clean probe assembly.
- A universal charger set (US, European, UK, and Australian plugs included).



Backed by a 1-year warranty, the new Restek Leak Detector sets an industry standard for performance and affordability in hand-held leak detectors.

Description	qty.	cat.#
Leak Detector with Hard-Sided Carrying Case and Universal Charger Set (US, UK, European, Australian)	ea.	22839
Soft-Side Storage Case	ea.	22657
Small Probe Adaptor	ea.	22658

Avoid using liquid leak detectors on a GC! Liquids can be drawn into the system.

Caution: The Restek Electronic Leak Detector is designed to detect trace amounts of hydrogen in a noncombustible environment. It is NOT designed for determining leaks in a combustible environment. A combustible gas detector should be used for determining combustible gas leaks under any condition. The Restek Electronic Leak Detector may be used for determining trace amounts of hydrogen in a GC environment only.

PATENTS & TRADEMARKS

Restek patents and trademarks are the property of Restek Corporation. Other trademarks appearing in Restek literature or on its website are the property of their respective owners.



Lit. Cat.# PCAN1174

© 2009 Restek Corporation.

Restek U.S. • 110 Benner Circle • Bellefonte, PA 16823 • 814-353-1300 • 800-356-1688 • fax: 814-353-1309 • www.restek.com

Restek France • phone: +33 (0)1 60 78 32 10 • fax: +33 (0)1 60 78 70 90 • e-mail: restek@restekfrance.fr

Restek GmbH • phone: +49 (0)6172 2797 0 • fax: +49 (0)6172 2797 77 • e-mail: info@restekgmbh.de

Restek Ireland • phone: +44 (0)2890 814576 • fax: +44 (0)2890 814576 • e-mail: restekurope@aol.com

Restek Japan • phone: +81 (3)6459 0025 • fax: +81 (3)6459 0025 • e-mail: ryosei.kanaguchi@restek.com

Thames Restek U.K. LTD • phone: +44 (0)1494 563377 • fax: +44 (0)1494 564990 • e-mail: sales@thamesrestek.co.uk

