Analyze trace non-condensable gases in ethylene & propylene

- Trace level analysis of non-condensable gases
- Listed as ethylene & propylene test method
- Meets requirements of ASTM D2504
- Pre-configured analyzer with Helium Ionization Detector
- Special precautions for sample introduction

Keywords: non-condensable gases, HID, ethylene, propylene, trace level analysis

Introduction:

Ethylene and propylene are some of the most important petrochemical intermediates and are feedstocks for many different products. Products made from ethylene and propylene are for example polyethylene, polypropylene, ethylene dichloride, ethylene oxide, propyl benzene, ethyl benzene, and vinyl acetate. These products are used as food packaging, foil, toys, food containers, bottles, pipes, antifreeze, carpets, insulation, household items, etc.

It is therefore very important that the raw materials are of the best quality with as few impurities as possible, as the presence of trace amounts of various components such as hydrogen, oxygen and carbon monoxide can have an adverse effect on the processes and the end product.

When using the feedstocks or when trading the products, it is good to mutually agree on how to quantify impurities and which test methods are suitable. ASTM D5234 lists the various analytical methods used, the units of measurement and concentration levels of possible components present in ethylene. Same with ASTM D5273 for propylene.

Both ASTM D5234 and D5273 list the same method for measuring some of these impurities:

> ***ASTM D2504: Standard Test Method for Non-condensable Gases in C2 and Lighter Hydrocarbon Products by Gas Chromatography***
>
> *This test method covers the determination of hydrogen, nitrogen, oxygen, and carbon monoxide in the parts per million volume (ppmv) range in C2 and lighter hydrocarbon products. This test method should be applicable to light hydrocarbons other than ethylene, but the test program did not include them*

Analyzing permanent gases at trace level in the different matrices is a very common but challenging analysis and not that easy to perform. There are a number of key factors that make this analysis a success: sample introduction, the minimization of the introduction of air during the different steps of the analysis, avoiding oxygen absorption on the columns, a detector that detects all analytes on highly sensitive levels and separation of the components to be analyzed, such as argon and oxygen..

PAC offers a dedicated analyzer for trace-level analysis of hydrogen, oxygen, nitrogen, methane and carbon monoxide in ethylene and propylene that addresses all these challenges and provides reliable data.

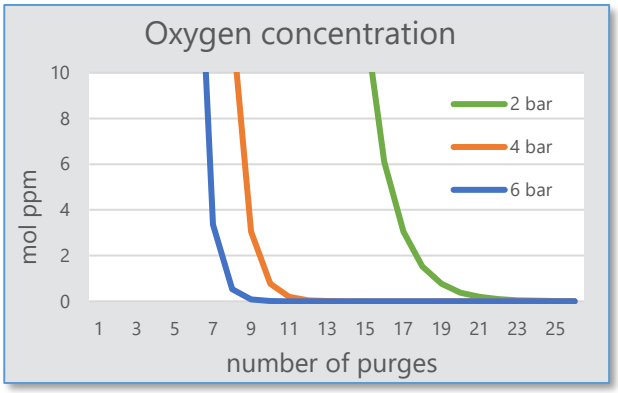
SAMPLE INTRODUCTION

The sample introduction is probably one of the most critical parts of the analysis as it is very easy to lose analytes through absorption or to introduce oxygen and nitrogen (via air). All materials used for samples and calibration gases must be clean, made of stainless steel or other inert material, and must be connected through the proper connection material. Using inferior material for transport and connection will result in higher oxygen and nitrogen reporting since the surrounding air consists of mostly oxygen and nitrogen.

There are two ways to correctly insert the sample, by flushing the regulator or by applying a constant flow over a period of time:

Purging:

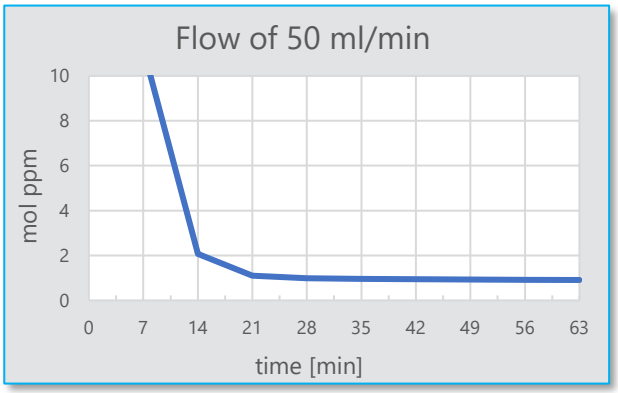
As shown in the graph, if a pressure regulator has been disconnected, it must be flushed at least 18 times to remove the oxygen (and nitrogen) introduced from the environment. This is also the case when a new sample or calibration gas is connected to the sampling part of the system.



Flowing:

Another approach is to connect the sample cylinder and let a constant flow flush the sample path. At a flow of 50 ml/min for 30 minutes (with a gas which contains 1 ppm of oxygen), the oxygen response is stable.

Purging at flow rates lower than 25 ml/min will not work due to diffusion from the sample out line. Pulsed pressure purging accelerates the process of flushing the sample line and removing any unwanted oxygen and nitrogen.



In addition, the system is configured with the AC Sample shut-off valve, to ensure a constant method of introducing the sample and eliminating user errors. Thereby improving the overall system repeatability.

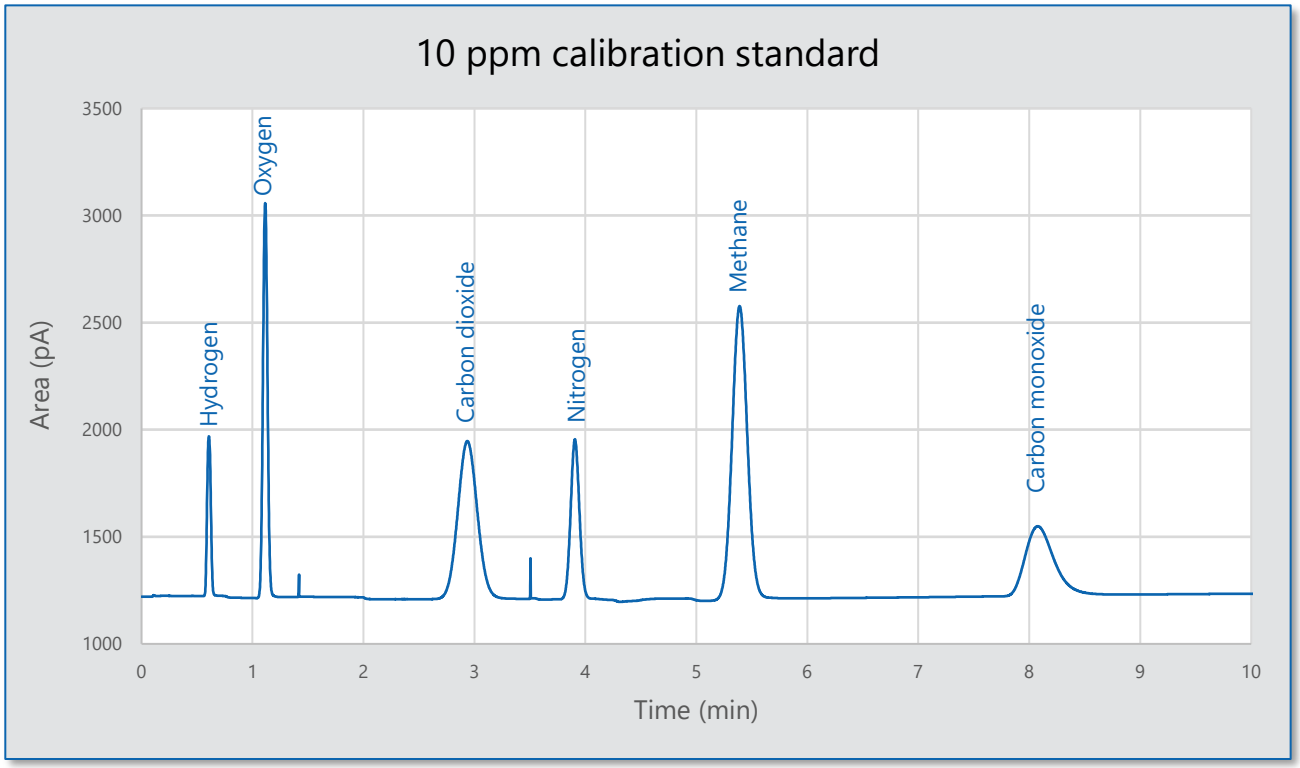
ANALYSIS

One of the challenges in the actual analysis is the possible introduction of air through valve switching. When switching a rotary valve, a very small amount of air may be directed into the columns or one of the other valve connections. This introduced air can elute from the columns together with other components. PAC has developed a valve housing in which the switching parts of the valve are covered with a helium blanket, minimizing the air introduction through the valves.

The actual system contains two columns, a pre-column separating the matrix from the analytes, and an analytical column that separates the components of interest: hydrogen, oxygen, nitrogen, methane and carbon monoxide.

After introducing the sample, hydrogen and oxygen will quickly elute from the analytical column. After the elution of oxygen this column is put into a stop flow position allowing, although not indicated by the method, carbon dioxide to elute directly from the pre-column to the detector. After the elution of carbon dioxide, the pre-column is switched to vent, while the analysis column is switched back into flow for the elution of the remaining components, nitrogen, methane and carbon monoxide.

Commonly used micro packed columns such as "Haysep or Porapak Q" types are known to absorb oxygen up to a level of a few ppm. PAC uses a micro packed pre-column that does not absorb oxygen. This pre-column also benefits from the excellent separation between methane/carbon monoxide and carbon dioxide/ethylene, resulting in optimal chromatographic performance and easy to tune application.

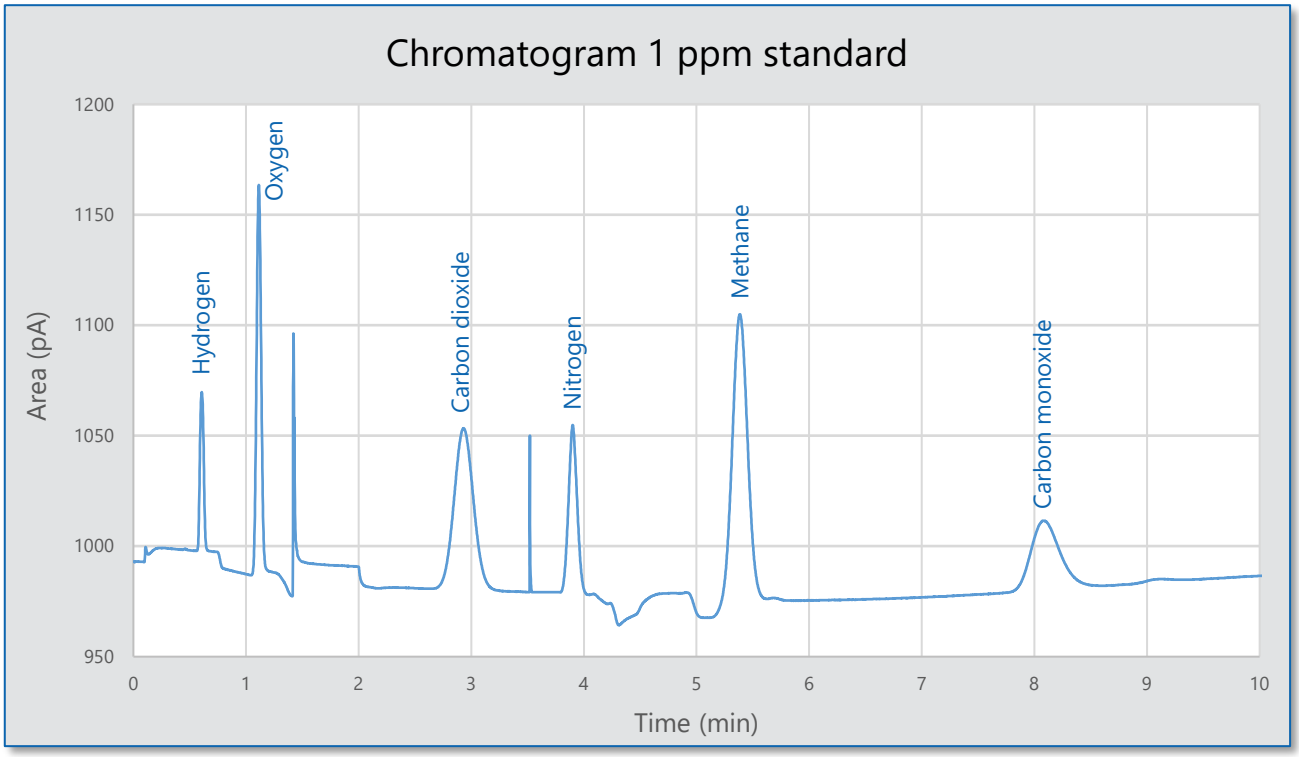


The pulsed discharge detector (PDD) or Helium Ionization Detector (HID) creates a stable, pulsed DC discharge in helium, as ionization source. Components eluting from the column, flowing counter to the flow of helium from the discharge zone, are ionized by photons from the helium discharge. Resulting electrons are focused toward the collector electrode by two bias electrodes, generating a signal recorded by the GC. The HID is a universal, non-destructive, high sensitivity detector.

The limit of detection (LOD) is calculated using the formula: $LOD = \left(\frac{3 * c * N}{A}\right) * W * 60$

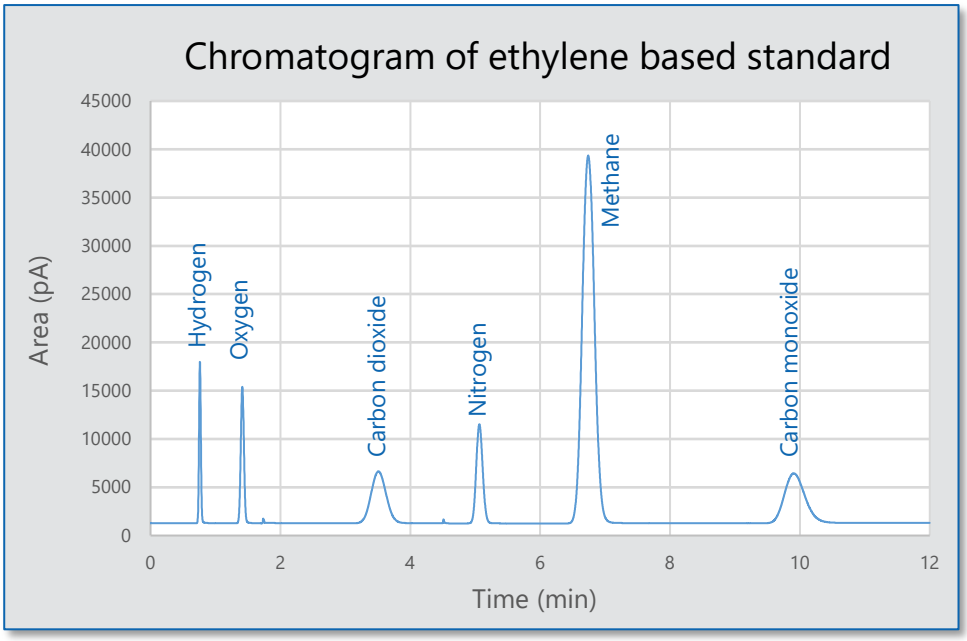
Where: LOD = Limit of Detection
C = Concentration of the component of interest (ppm)
N = Noise (peak to peak in µV)
A = Area of peak of interest (µV * s)
W = Width of peak at half height (minutes)

The below chromatogram and table show an analysis of a 1 ppm standard and the LOD's calculated based on this analysis.



Component	Noise (pA)	Area (pA*s)	Conc. (ppm)	Width (min)	LDL (ppm)
Hydrogen	0.15	169	0.97	0.039	< 0.1
Carbon dioxide	0.15	501	0.94	0.045	< 0.1
Oxygen	0.15	873	0.96	0.176	< 0.1
Nitrogen	0.15	401	0.97	0.081	< 0.1
Methane	0.15	1282	0.99	0.151	< 0.1
Carbon monoxide	0.15	532	0.94	0.214	< 0.1

Below chromatogram shows an analysis of a calibration standard of the components of interest in an ethylene matrix. It is clearly visible that there is no interference from ethylene.



Component	Concentration (ppm)
Hydrogen	200
Carbon dioxide	100
Oxygen	100
Nitrogen	200
Methane	500
Carbon monoxide	200
Ethylene	Balance

Conclusion

With the guaranteed turnkey analyzer, PAC offers a system for the analysis of trace non-condensable gases and carbon dioxide in ethylene and propylene that meets and exceeds the requirements as listed in ASTM D2504. It overcomes all the challenges that may occur, has a linear dynamic range of 0.1 – 100 ppm, an LOD of <0.1 ppm and a repeatability of less than 1%. All within an analysis time of about 10 minutes.

This application can easily be combined in one or two analyzers with the other PAC applications for analyzing impurities in ethylene or propylene:

- hydrocarbons according to ASTM D2712
- sulfur components according ASTM D5504
- oxygenated components according ASTM D7423

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