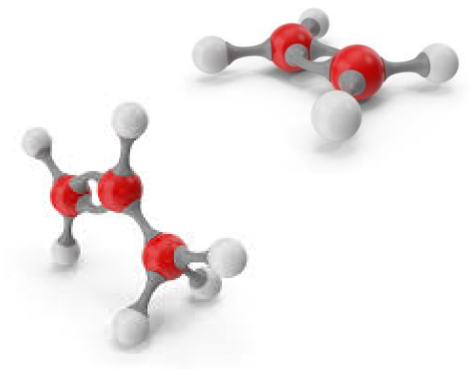
Trace Impurities in polymer grade Ethylene & Propylene

- Trace level analysis of ethylene & propylene analysis
- Two-GC setup with dedicated applications
- Deals with all analytical challenges
- Delivered as factory tested, calibrated, and validated analyzer
- Based on the robust and reliable Agilent 8890 GC platform



Keywords: Ethylene, Propylene, impurities analysis, D5234, D5273

Introduction:

In the plastics industry, polyethylene and polypropylene are produced from their monomer feedstock, ethylene, and propylene. These are produced in the petrochemical and refining industry by steam cracking of naphtha, or as a byproduct from refining processes. High purity of the monomers is of prime importance, as to protect catalysts used in the polymerization process, and guarantee final product quality of the polymers. An extensive range of impurities needs to be analyzed, usually requiring separate injections onto different analyzers.

ASTM D5234 lists the various analytical test methods that can quantify impurities, which test methods are suitable, the units of measurement and concentration levels of possible components present in ethylene. ASTM D5273 is listing the same analytical recommendations for propylene.

Analysis

These “standard guide for analysis” typically group the test methods as follows:

1. Hydrocarbons, includes all the main C1-C5 or heavier hydrocarbons, which may include components like benzene, arsine & phosphine.
2. Inerts or non-condensables: H2, N2, O2, CO & CO2
3. Total sulfur & nitrogen or specific sulfur & nitrogen components such COS, mercaptans, NO & NO2
4. Oxygenated components like methanol and other alcohols

These components (groups) are analyzed using chromatography-based methods.

Moisture is listed as well, but typically analyzed using on-line techniques as it is extremely difficult to obtain a valid sample for lab analysis. For total sulfur and nitrogen other methods are used like UVF and/or chemiluminescence (like for example the PAC Antek ElemeNtS).

System configuration:

PAC – AC Analytical Controls offers a specially designed GC solution dedicated to analyzing almost all component group as listed above. The solution consists of two GC's each configured with two dedicated channels optimized to the specific requirements. That includes heart-cutting, backflush of heavier components, valve purging, inert tubing, and dedicated detectors (such SCD & HID).

The sample loops of the GC's can be linked, and the GC's started simultaneously, allowing the 4 channels to operate parallel.

	GC 1		
Component group	**Hydrocarbons**		**Inerts & non-condensables**
Method compliancy	ASTM D2163 ASTM D2505 ASTM D2712 ASTM D6159		ASTM D2504 ASTM D2505 ASTM D8098
Components	Ethylene* Propylene* Methane Ethane Ethyne (Acetylene) cyclo-Propane methyl-Acetylene	Propadiene Butene's 1,3-Butadiene C5's C6's & heavier Benzene	Hydrogen Oxygen Nitrogen Carbon monoxide Carbon dioxide
Sample introduction	GSV		GSV
Column configuration	Al_2O_3 column with optional backflush		Micropacked columns
Detection	Flame Ionization Detector (FID)		Pulsed Discharge Helium Ionization Detector (HID)
Detection limits	≤ 1 ppm weight		≤ 0.2 ppm mol

* Depending on the matrix

	GC 2	
Component group	**Sulfur components**	**Oxygenates**
Method compliancy	ASTM D5504	ASTM D7423
Components	Hydrogen sulfide Carbonyl sulfide Mercaptans	Methanol Other alcohols
Sample introduction	GSV	GSV
Column configuration	Single column	Heart-cut configuration & Lowox column
Detection	Sulfur Chemiluminescence Detector (SCD)	Flame Ionization Detector (FID)
Detection limits	≤ 0.05 ppm mol*	≤ 0.1 ppm weight

* Detection limit is component & matrix depending

System features:

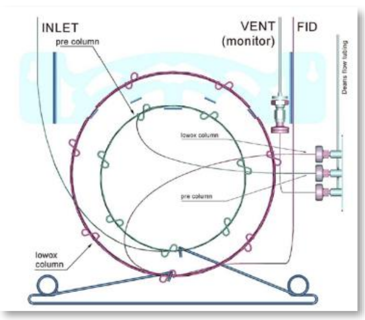
The analysis of these impurities at trace level require special precautions to be taken with respect to the configuration of the analyzer.

- The properties of the sulfur and oxygenated components are such that they are susceptible to absorption on metal surfaces, which can cause loss of components or carry-over between sample runs. Therefore, the instruments are configured fully inert, with Hastelloy-C valves and Sulfinert tubing.

- For the low-level detection of the inerts & non-condensables the GC with this application is configured with a pulsed discharge detector (PDD), configured as a Helium Ionization Detector (HID). This is a universal, non-destructive, highly sensitive detector having a linear range over five orders of magnitude and a positive response to fixed gases.

- The analysis of trace levels of oxygen and nitrogen is particularly challenging, due to obviously large abundance of these components in atmospheric air. This can cause false positive results for these components due to introduction of air during the sampling process. But, due to the sensitivity of the Helium Ionization Detector, diffusion of these components into the analytical system can cause high baseline levels, resulting in increased detection limits for all components detected on this channel. AC designed dedicated valve enclosures to overcome this problem. By purging the enclosure with helium carrier gas, diffusion of atmospheric air into the valves is prevented, resulting in improved detection limits for non-condensable gasses.

- For the analysis of sulfur compounds, either Pulsed Flame Photometric Detector (PFPD) or Sulfur Chemiluminescence Detector (SCD) can be used. SCD has an advantage over PFPD in terms of linearity and more importantly selectivity. Quenching effects seen on PFPD, caused by co-elution of hydrocarbon components with the sulfur components of interest, are not seen on SCD due to its superior selectivity. This is a significant advantage, especially when analyzing both ethylene and propylene on the same configuration, where optimization of column phase to avoid co-elution is more difficult. Traditionally, the PFPD is preferred over the SCD due to its stability, however recent developments in SCD detector design by AC Analytical Controls have greatly improved SCD stability, allowing it to be easily employed in this application.



- For the oxygenates channel the system can be configured with a so-called Deans switch. A pre-separation is made on the methyl-silicone pre-column. The oxygenated components are cut from the matrix by applying a pressure switch, directing the effluent from the pre-column either to the monitor column (vent) or to the analysis column. This concept ensures that there is no co-elution of the matrix with any of the oxygenates to be analyzed.

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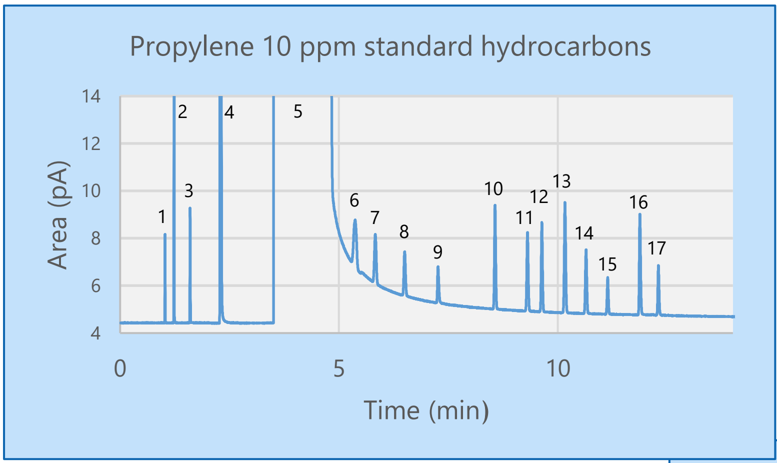
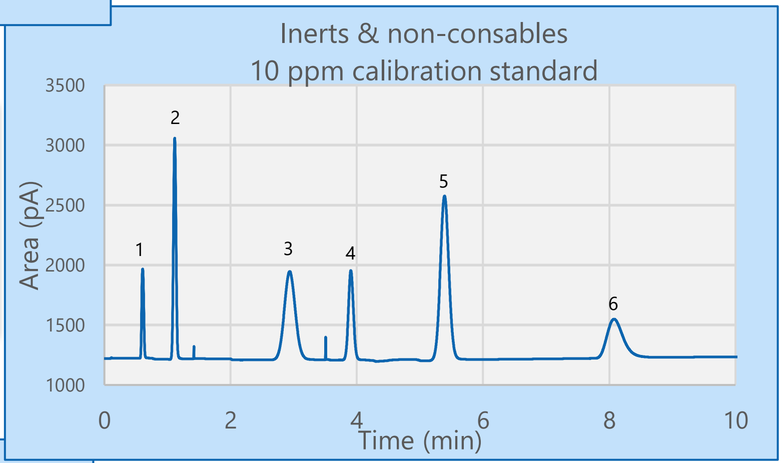


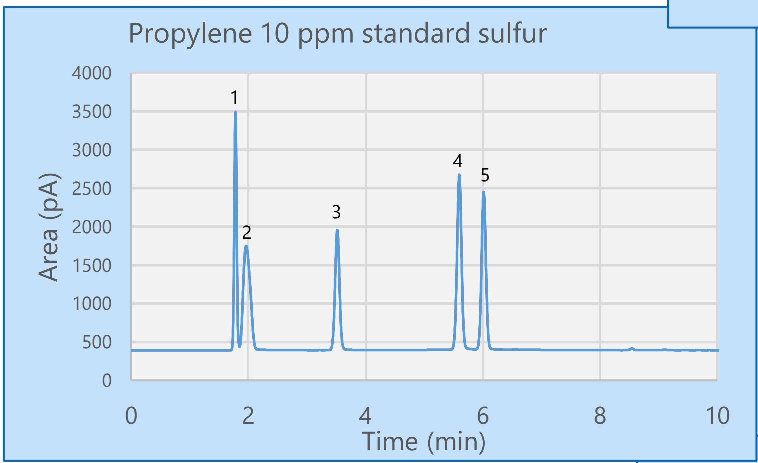
Hydrocarbons

1 Methane
2 Ethane
3 Ethylene
4 Propane
5 Propylene
6 i-Butane
7 n-Butane
8 Propadiene
9 Acetylene
10 t-2-Butene
11 neo-Pentane
12 c-2-Butene
13 i-Pentane
14 n-Pentane
15 1,2-Butadiene
16 1,3-Butadiene
17 Methyle acetylene



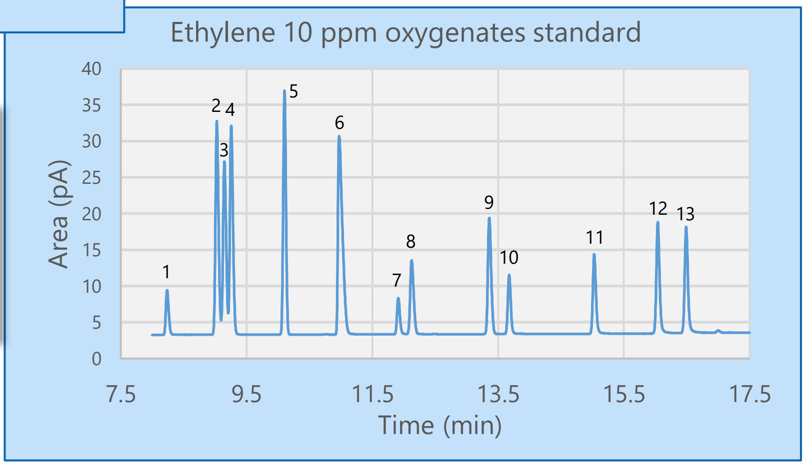
Inerts & non-condensable gases

1 Hydrogen
2 Oxygen
3 Nitrogen
4 Carbon dioxide
5 Methane
6 Carbon monoxide



Sulfur

1 Hydrogen sulfide
2 Carbonyl sulfide
3 Methyl mercaptan
4 Ethyl mercaptan
5 Dimethyl sulfide



Oxygenates

1 Acetaldehyde
2 ETBE
3 MTBE
4 DIPE
5 TAME
6 Acetonitrile
7 Methanol
8 Acetone
9 MEK
10 Ethanol
11 iso- & n-Propanol
12 TBA, IBA & 2-Butanol
13 n-Butanol

Conclusion

AC's "Ethylene & Propylene" impurity analyzer combines 4 channels in 2 GC's, which can operate in parallel to analyze low levels of hydrocarbons, oxygenates, sulfur components, trace gases in just one run.

It includes specifically designed features to solve measurement challenges like:

- Absorbance of active components, by having a fully inert sample path
- Interferences from air with specially designed valve enclosures purged with Helium carrier gas to prevent air diffusion and improve detection limits
- Low concentration measurement with high sensitivity detectors like HID & SCD
- Issues due to co-elution's of HC components with sulphur components are overcome by using an SCD over PFPD, where the SCD has a better linearity, higher selectivity and an improved stability over previous generations of SCD's
- Excellent separation of oxygenates with high selectivity achieved through AC DEANS switch
- The AC Ethylene & Propylene impurity analyzer complies with the test methods as listed in the "*Standard guides for the analysis of ethylene or propylene*".

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