Application Note

Energy and Chemicals

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Analysis of Trace Permanent Gas Impurities in Ethylene or Propylene by GC

Achieve low detection limits using an Agilent 8890 GC fitted with a pulsed discharge helium ionization detector (PDHID)

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Abstract

An Agilent 8890 GC-PDHID method was developed to detect ppb to low-ppm concentration permanent gas impurities in ethylene or propylene, including carbon monoxide, carbon dioxide, hydrogen, argon/oxygen, nitrogen, and methane. The GC method provided low detection limits, good repeatability, and excellent linearity, meeting the requirements specified in ASTM D8098-17[1] and T/CIESC 0021-2022.[2]

Introduction

Trace amounts of permanent gas impurities can have deleterious effects in certain processes using ethylene or propylene hydrocarbon products as feed stock. It is therefore important to be able to measure sub-ppm levels of those impurities during or before polymer production. The pulsed discharge helium ionization detector (PDHID) is a highly sensitive detector with minimal detectable levels (MDLs) of fixed gases in the low-ppb range.

The valve configuration example used in ASTM D8098-17[1] has an isolation valve. The activation and deactivation of the isolation valve can cause baseline fluctuations which, in practice, affects the analysis of ppb-level impurities. On the other hand, the configuration T/CIESC 0021-2022[2] uses two sample loops for consecutive injections in one run: one injection for CO_2 only and the other for other permanent gases. This application note proposes a new configuration that allows analysis using one injection with no isolation valve. An ethylene standard is used as an example to demonstrate the system's performance in separation, repeatability, linearity, and detection limit.

Experimental

Samples

Details of the ethylene calibration standard (bought from Air Liquide) are shown in Table 1. The standard contained ppm levels (varying between 5.0 and ~7.4 ppm) of CO_2, CO, CH_4, Ar, O_2, N_2 and H_2. To test the dynamic range and detection limits of the method, an Agilent dynamic dilution system was used to dilute the calibration standard. Typically, pure ethylene would be used as the diluent. However, it is almost inevitable that there will be a little air background in the purchased ethylene, sometimes making it difficult to test the detection limit. Since ethylene elutes after those permanent impurities, demonstrating minimal to no matrix effect, ultrahigh purity helium (99.999% grade, Air Liquide) was used as the diluent instead. To eliminate as many impurities as possible, the diluent helium can be further purified using a helium purifier. Table 1 lists the concentrations of each analyte in different dilution levels.

Instrumentation

An Agilent 8980 GC was configured with one PDHID detector and three diaphragm valves, as shown in Figure 1. The 10-port valve is used for sample injection and backflushing. After CO_2 elutes out of column 1, the valve is deactivated to backflush all components heavier than CO_2. The elution order in column 1 is H_2, air/CO, CH_4 and CO_2. Valve 2 and valve 3 are 6-port valves, and are used for switching between CO_2 and other permanent gases. Components other than CO_2 are sent to column 2 for further separation, and CO_2 is sent to the column 3, a fused silica tube that has the same restrictions as column 2. Detailed instrument configurations and operating conditions are given in Table 2 and Table 3. To eliminate atmospheric air contamination, a helium purge chamber is designed to protect the valve body and all connections to the valves. It allows the PDHID baseline to be reduced to less than 1,000 pA, which is helpful for achieving ppb-level detection limits.

Table 1. Concentration of calibration standards in different dilution levels.

Component	Concentration (ppb)					
	Level 1 (dilute × 120.68)	Level 2 (dilute × 60.18)	Level 3 (dilute × 30.62)	Level 4 (dilute × 11.61)	Level 5 (dilute × 5.95)	Level 6 (undiluted)
CO_2	46	91	180	474	924	5,500
H_2	51	101	199	525	1,025	6,100
Ar +O_2	103	206	405	1,068	2,083	12,400
N_2	61	123	242	637	1,243	7,400
CH_4	51	101	199	525	1,025	6,100
CO	56	113	222	586	1,143	6,800

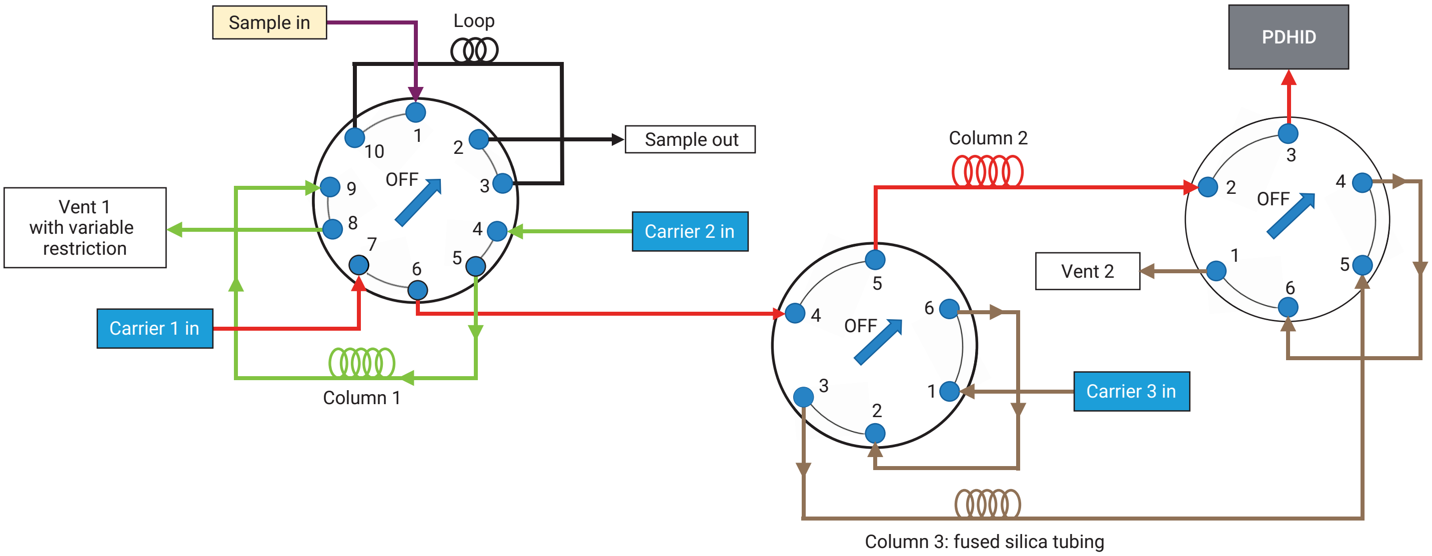

Figure 1. System diagram.

Table 2. Agilent 8890 GC-PDHID system configuration.

Agilent 8890 GC-PDHID System Configuration	
Valve System	– Valve 1 is a 10-port valve, valves 2 and 3 are 6-port valves – Loop volume 0.25 mL – Purge chamber uses helium to protect the four valves from atmospheric air contamination
Analytical Column	– **Column 1:** Agilent HP-PLOT-Q, 30 m × 0.53 mm × 40 µm, with 2 PT (p/n 19095P-QO4PT) – **Column 2:** Agilent HP-MOLESIEVE, 30 m × 0.53 mm × 50 µm (p/n 19095P-MS0), adding 2.5 m × 0.53 mm particle traps at both ends (p/n 5181-3352) – **Column 3:** Fused silica, 0.8 m × 0.18 mm (p/n 160-2610-10)
Detector	Pulsed discharge helium ionization detector (PDHID)
Dynamic Dilution System	Pneumatic control module (PCM) channel 1 is used for diluent control

Table 3. Agilent 8890 GC-PDHID operating conditions.

Agilent 8890 GC-PDHID Operating Conditions		
Valves	Helium purge flow rate, 2 mL/min Ambient temperature	
Time Events	Events Valve 1 ON, Valve 4 ON Valve 2 ON Valve 1 OFF Valve 4 OFF Valve 2 OFF	Time (min) 0.01 2.2 2.4 3 8.5
Column Flow	Column 1: Constant pressure, 30 psi (~9.5 mL/min) Column 2: Constant pressure, 12.3 psi (~9.5 mL/min) Column 3: Constant pressure, 12.3 psi (~9.5 mL/min)	
Column Temperature	Constant temperature at 60 °C Duration: 8.5 min	
PDHID	150 °C Helium flow rate: 31 mL/min	
Data Collection Rate	5 Hz	

Results and discussion

Chromatogram of ethylene

Two typical chromatograms of the permanent impurities in ethylene, obtained using the 8890 GC-PDHID, are shown in Figure 2. The detailed concentration data for each component can be found in Table 1 (dilution levels 1 and 5). The figure shows good separation of H_2, CO_2, CO, CH_4, Ar/O_2, and N_2 in ethylene. Argon coelutes with oxygen in this method, meaning extra analysis (for example, using an oxygen detector for oxygen determination) needs to be done to quantify both components. The chemisorption effect of oxygen on porous polymers was observed for the low-ppb level calibration standard. This may result in an inaccurate determination of the argon concentration. Another Agilent Molsieve column can be used (part number CP7539PT) that can separate argon from oxygen instead the one listed in Table 2. This column will provide a more accurate quantitation of argon.

Minimal detection limits (MDL)

The level 1 calibration standard (diluted to around 50 ppb) data are used to calculate the MDL based on "signal-to-noise ratio (S/N) = 3" criteria. The results are listed in Table 4. Due to the chemisorption effects of oxygen, argon and oxygen MDL data may be lower than expected. The helium diluent also contains a low-ppb level of nitrogen background, meaning the accuracy of the nitrogen MDL data is lower. As a result of this, the air peak data provided in Table 4 are only for reference. The MDLs of the remaining impurities were all lower than 10 ppb, meeting the requirements specified in ASTM D8098-17[1] and T/CIESC 0021-2022.[2]

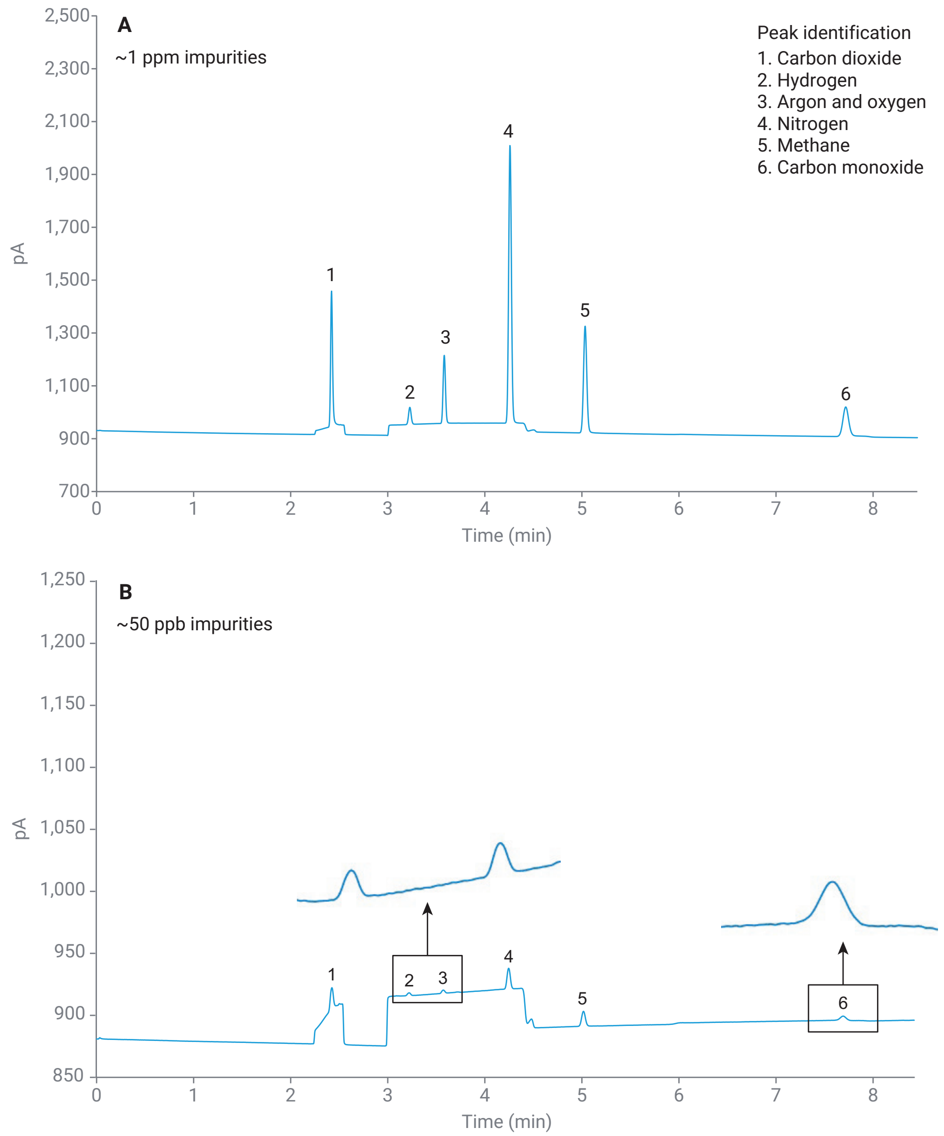

Figure 2. Typical chromatogram obtained from the analysis of impurities in ethylene (dilution levels 5 and 1, respectively).

Table 4. Agilent 8890 GC-PDHID minimal detection limits (MDL) of impurities in ethylene.

Component	Dilute × 120.7 times to ~50 ppb sample						
	RT (min)	RT RSD	Peak Height (pA)	Peak Height RSD	S/N	Concentration (ppb)	MDL(S/N = 3) (ppb)
CO_2	2.4379	0.013%	25.71	0.74%	417	45.6	0.3
H_2	3.2470	0.056%	3.23	0.92%	52	50.5	2.9
Ar + O_2*	3.5981	0.026%	11.77	1.01%	191	102.7	1.6
N_2*	4.2765	0.015%	19.98	4.82%	324	61.3	0.6
CH_4	5.0522	0.016%	15.87	0.56%	257	50.5	0.6
CO	7.7471	0.018%	5.23	2.03%	85	56.3	2.0

* Ar + O_2 and N_2 MDL may be affected due to the O_2 chemisorption effect and atmospheric air interference; the data listed are only for reference.

Linearity and repeatability

Linearity of permanent gas impurities is evaluated by dynamically diluting the calibration standard to five different lower concentration levels. Repeatability for each concentration level is calculated from six replicate runs. The results are summarized in Table 5. Excellent linearities of CO_2, H_2, CH_4, and CO are obtained across the 50 ppb to 5 ppm concentration range, with R^2 larger than 0.995. Air peak (Ar/O_2, N_2) linearity is affected by the chemisorption effects of O_2 and air leaking through the sample line.The linearity and repeatability performance may also be affected by air contamination of the sample line. Other than Ar/Ov and N_2, other analytes demonstrated good area repeatability.

Table 5. Agilent 8890 GC-PDHID area repeatability at each concentration level and linearity.

Component	Area RSD						R^2
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	
CO_2	0.66%	0.24%	0.41%	0.19%	0.12%	0.15%	0.9986
H_2	1.08%	1.51%	0.52%	0.34%	0.28%	0.20%	0.9995
Ar +O_2	1.45%	1.09%	0.63%	0.53%	1.25%	1.22%	0.9895
N_2	4.87%	2.21%	1.29%	1.13%	2.12%	2.06%	0.9821
CH_4	1.20%	0.57%	0.61%	0.27%	0.14%	0.44%	0.9993
CO	3.02%	1.85%	1.59%	0.45%	0.18%	0.18%	0.9995

Conclusion

The Agilent 8890 GC equipped with a PDHID detector was used for analyzing trace permanent gas impurities in ethylene. A helium purge chamber prevented air from leaking into the GC system through the valve connection points, generating a low PDHID baseline condition critical for the analysis of real samples containing impurities in the low-ppb level. Qualitative and quantitative detection of CO_2, CO, CH_4, Ar/O_2, N_2 and H_2 were achieved in the same run from one injection. The detection limit of each impurity was less than 20 ppb, meeting the requirements of ASTM D8098-17[1] and T/CIESC 0021-2022[2] standards. The system also demonstrated good repeatability and linearity, both of which are required for polymer grade ethylene or propylene samples.

References

1. ASTM D8098-17. Standard Test Method for Permanent Gases in C2 and C3 hydrocarbon Products by Gas Chromatography and Pulse Discharge Helium Ionization Detector.
2. T/CIESC 0021-2022. Standard Test Method for Permanent Gases in Polymer Grade Ethylene and Propylene by Gas Chromatography and Helium Ionization Detector.

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