Application Note

Energy & Chemicals, Polymers

Trace analysis of permanent gases in ethylene and propylene hydrocarbon products

Capillary gas chromatography and pulse discharge helium ionization detection, by ASTM D8098[1]

Authors

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Abstract

A gas chromatography method has been developed for the measurement of trace permanent gases in ethylene and propylene hydrocarbons by capillary gas chromatography and pulse discharge helium ionization detector (PDHID). The analysis is intended to determine the concentrations of hydrogen, nitrogen, oxygen, carbon monoxide, and carbon dioxide in the parts per million (ppm) to parts per billion (ppb) range.

Introduction

The measurement of trace impurities in polymer grade ethylene and propylene is important in the production of polymers. Using a PDHID allows for sub-ppm detection limits. This Application Note discusses a gas chromatograph configuration to analyze permanent gas impurities at low-ppm levels in ethylene and propylene.

Experimental

The instrument consists of an Agilent 7890B gas chromatograph configured with a PDHID, a 10-port gas sample valve with backflush to vent, and a 6-port column bypass switching valve. The valves include internally purged rotors, with helium purge gas, for added protection against atmospheric air contamination. Figure 1 shows the system diagram. The Agilent OpenLab Chromatography Data System was used for instrument control and data analysis.

The analysis procedure begins with flushing the 0.5-mL sample loop with standard or sample. After the sample introduction purge, the 10-port valve (Valve 1) is activated to inject sample. Valve 1 remains activated, allowing carbon dioxide to elute from Column 1 onto Column 2; Valve 1 is then deactivated, and the matrix ethylene or propylene is backflushed to prevent overloading of the detector. Hydrogen, nitrogen, oxygen, methane, and carbon monoxide elute from Column 2, and progress onto Column 3. Before carbon dioxide elutes from Column 2, the bypass valve (Valve 2) is activated, effectively trapping hydrogen, nitrogen, oxygen, methane, and carbon monoxide on Column 3. Carbon dioxide is carried through the restrictor, bypassing Column 3, and is delivered to the detector. Valve 2 is then deactivated, and all other gasses elute from Column 3. Figure 2 shows an example chromatogram.

Instrumentation

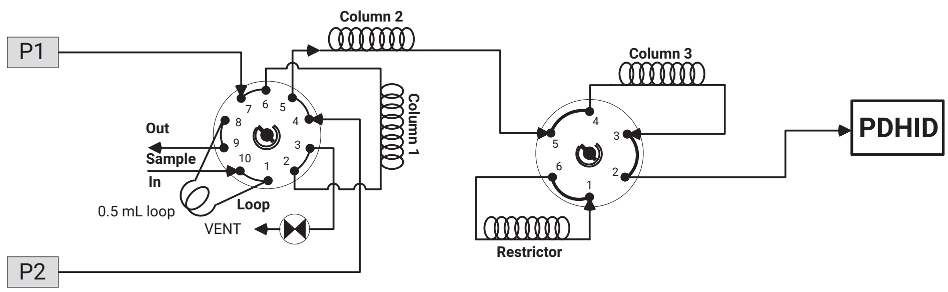

Figure 1. System diagram.

Chromatographic conditions

Temperatures	
Valve/Valve box	100 °C
Column oven	50 °C (hold 5 minutes), ramp 20 °C/min to 85 °C (hold 1 minute)
PDHID	200 °C
Flows	
Column 1	15 mL/min Helium GS-Q, 115-3432, 50 m × 0.530 mm, 6 µm
Column 2	15 mL/min Helium GS-Q, 115-3432, 50 m × 0.530 mm, 6 µm
Column 3	15 mL/min Helium HP Molesieve 5A, 19095P-MS6E, 30 m × 0.530 mm, 25 µm
Valve timing	
Valve 1 (10-port)	On at 0.01 minutes, Off at 2.00 minutes
Valve 2 (6-port)	On at 3.20 minutes, Off at 3.80 minutes

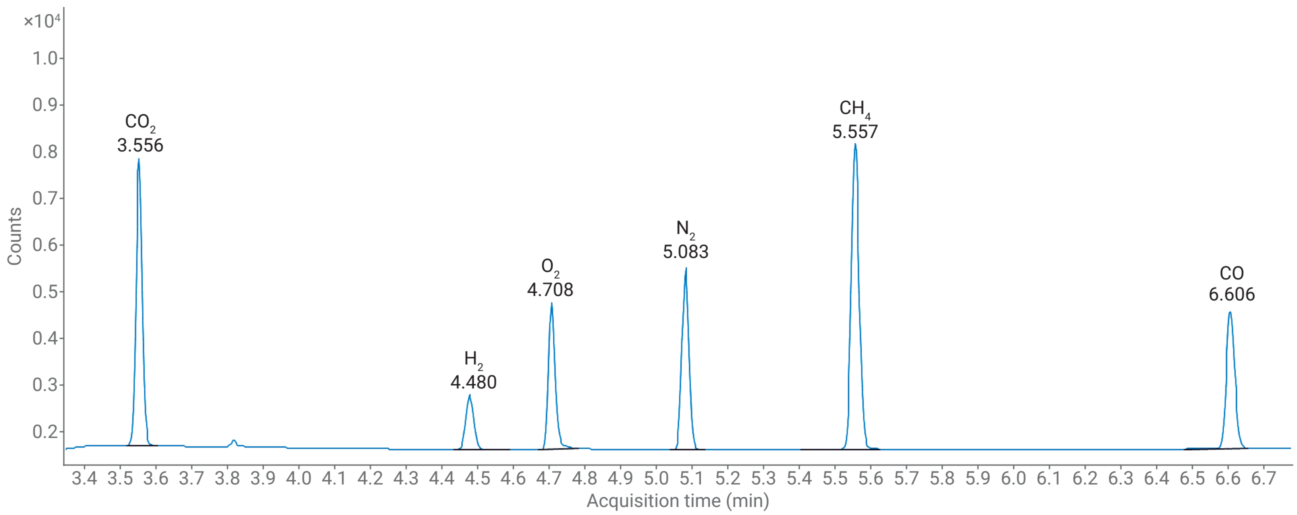

Figure 2. Example chromatogram.

Results and Discussion

Precision

Precision was investigated by analyzing 16 consecutive standards, at four different concentration levels. Eight standards were used, four in an ethylene matrix, and four in a propylene matrix. Tables 1 and 2 detail the concentrations for the different standards. Tables 3 and 4 respectively show the precision results for ethylene and propylene. Note that performance may be improved by incorporating an automated sampling system, minimizing air contamination of the samples. These data were generated using manual sample inlet purging.

Table 1. Standards in ethylene[2].

Component	Standard 1 (ppm, mol)	Standard 2 (ppm, mol)	Standard 3 (ppm, mol)	Standard 4 (ppm, mol)
Hydrogen	1.2	10.8	26.2	44
Oxygen	6	14.6	29.1	53.7
Nitrogen	17.8	25.4	44.6	68.7
Carbon monoxide	1	10.5	25.7	43.2
Methane	1	11.1	26.5	44.4
Carbon dioxide	1	11.4	26.5	44
Ethane	330	330	330	330
Propane	2	2	2	2
Ethylene	Balance	Balance	Balance	Balance

Table 2. Standard in propylene[2].

Component	Standard 1 (ppm, mol)	Standard 2 (ppm, mol)	Standard 3 (ppm, mol)	Standard 4 (ppm, mol)
Hydrogen	1.2	15	39.1	76.9
Oxygen	10	59.2	87.1	58.3
Nitrogen	35.9	207.9	277	92.4
Carbon monoxide	1	9.9	25.9	51
Methane	1.2	10.5	27.5	54.1
Carbon dioxide	1.3	10.6	27.2	53.3
Propane	2,054	2,052	2,052	2,052
Propylene	Balance	Balance	Balance	Balance

Table 3. Ethylene precision[2].

Compound	Certified concentration (ppm, mol)	Average $\overline{X}$	Variance V	Repeatability standard deviation S_r	Repeatability limit r	RSD %	Average recovery %	Number of outliers rejected per D7915[3]
CO_2	1	0.774	0.0007	0.0273	0.0764	3.52	77.4	0
	11.4	12.959	0.0029	0.0521	0.1458	0.40	113.7	0
	26.5	25.990	0.0011	0.0331	0.0926	0.13	98.1	0
	44	45.185	0.0319	0.1785	0.4998	0.40	102.7	0
H_2	1.1	0.860	0.0004	0.0194	0.0544	2.26	78.2	0
	10.8	8.702	0.0056	0.0740	0.2071	0.85	80.6	0
	26.2	20.467	0.0092	0.0961	0.2690	0.47	78.1	0
	44	46.694	0.6109	0.7816	2.1885	1.67	106.1	0
O_2	6	3.642	0.0058	0.0760	0.2127	2.09	60.7	0
	14.6	12.999	0.0188	0.1325	0.3709	1.02	89.0	0
	29.1	28.974	0.0306	0.1748	0.4894	0.60	99.6	0
	53.7	54.833	0.3519	0.5932	1.6609	1.08	102.1	0
N_2	17.8	28.376	0.1482	0.3849	1.0778	1.36	159.4	0
	25.4	31.097	0.6072	0.7585	2.1237	2.44	122.4	0
	44.6	50.296	0.2781	0.5273	1.4765	1.05	112.8	0
	68.7	79.767	1.5678	1.2521	3.5059	1.57	116.1	0
CH_4	1	0.982	0.0004	0.0192	0.0536	1.95	98.2	0
	11.1	10.575	0.0026	0.0503	0.1410	0.48	95.3	0
	26.5	24.136	0.0018	0.0429	0.1202	0.18	91.1	0
	44.4	42.704	0.0015	0.0384	0.1075	0.09	96.2	2
CO	1	0.857	0.0003	0.0164	0.0459	1.91	85.7	0
	10.5	8.811	0.0018	0.0418	0.1172	0.47	83.9	0
	25.7	22.307	0.0025	0.0502	0.1405	0.22	86.8	0
	43.2	43.627	0.0046	0.0675	0.1889	0.15	101.0	0

Table 4. Propylene precision[2].

Compound	Certified concentration (ppm, mol)	Average $\overline{X}$	Variance V	Repeatability standard deviation S_r	Repeatability limit r	RSD %	Average recovery %	Number of outliers rejected per D7915[3]
CO_2	1.3	1.499	0.0001	0.0273	0.0764	0.49	115.3	1
	10.6	12.615	0.0117	0.0521	0.1458	0.86	119.0	0
	27.2	29.344	0.6933	0.0331	0.0926	2.84	107.9	0
	53.3	51.091	0.5488	0.1785	0.4998	1.45	95.9	0
H_2	1.2	1.149	0.0013	0.0361	0.1011	3.14	95.8	0
	15	15.064	0.0126	0.1121	0.3139	0.74	100.4	0
	39.1	38.772	0.0023	0.0476	0.1333	0.12	99.2	0
	76.9	76.676	0.0206	0.1436	0.4021	0.19	99.7	0
O_2	10	9.817	0.7229	0.9192	2.5738	9.36	98.2	0
	58.3	57.956	0.1331	0.3649	1.0216	0.63	99.4	0
	59.2	64.318	5.1303	2.2650	6.3420	3.52	108.6	0
	87.1	84.289	2.9170	1.7079	4.7822	2.03	96.8	0
N_2	35.9	60.514	18.7320	4.6770	13.0956	7.73	168.6	0
	92.4	110.578	3.9894	1.9973	5.5926	1.81	119.7	0
	207.9	224.308	111.3517	10.5523	29.5465	4.70	107.9	0
	277	251.665	45.1103	6.7164	18.8060	2.67	90.9	0
CH_4	1.2	1.061	0.0008	0.0288	0.0807	2.72	88.4	0
	10.5	11.653	0.1880	0.4336	1.2142	3.72	111.0	0
	27.5	29.808	0.0025	0.0498	0.1394	0.17	108.4	3
	54.1	48.883	0.0172	0.1312	0.3675	0.27	90.4	3
CO	1	0.978	0.0003	0.0193	0.0540	1.97	97.8	0
	9.9	11.533	0.0191	0.1383	0.3871	1.20	116.5	1
	25.9	28.405	0.0017	0.0418	0.1171	0.15	109.7	3
	51	50.908	0.0086	0.0929	0.2600	0.18	99.8	3

Linearity

Linearity was established by analyzing the 16 replicate samples, described in the Precision section, at four different concentrations for each matrix (ethylene and propylene). Table 5 shows the results.

Conclusion

Using a 7890B gas chromatograph in conjunction with a PDHID and internally purged valves provides an effective way to analyze trace permanent gases in ethylene and propylene hydrocarbons to parts per billion concentrations, and meets the precision statement described in D8098[1]. The approach provides the sensitivity, reproducibility, and linearity required for olefin producers and the polymer industry.

Table 5. Linearity.

Ethylene		Propylene	
Compound	Linearity R^2	Compound	Linearity R^2
CO_2	0.9972	CO_2	0.9906
H_2	0.9572	H_2	0.999
O_2	0.9927	O_2	0.9863
N_2	0.9698	N_2	0.9438
CH_4	0.9986	CH_4	0.9856
CO	0.9878	CO	0.9958

References

1. ASTM Standard, D8098, 2017, Standard Test Method for Permanent Gases in C2 and C3 Hydrocarbon Products by Gas Chromatography and Pulse Discharge Helium Ionization Detector, *ASTM International*, West Conshohocken, PA, **2017**, www.astm.org
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3. ASTM Standard, D7915, 2014, Standard Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set, *ASTM International*, West Conshohocken, PA, **2017**, www.astm.org

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Printed in the USA, April 6, 2018
5991-9231EN