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Application News

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System GC

Characterization of Capillary Molecular Sieve and Carbonized Molecular Sieve Columns for the Separation of Permanent Gases using an FID with ARC in-jet Methanizer

■ Background

The molecular sieve is a predominant column material for the separation of permanent gases but will trap heavier analytes such as carbon dioxide and hydrocarbons. Carbonized molecular sieve is a chemically-modified variant of the molecular sieve material which allows for the separation of carbon dioxide and light hydrocarbons while maintaining some resolving power of permanent gases. In this application, we compare the retention characteristics of different molecular sieve columns and carbonized molecular sieve columns for permanent gas and light hydrocarbon analyses. These separations are often required in time-sensitive analyses where an isothermal temperature program is ideal.

■ Instrumentation

The GC-2030 gas chromatograph equipped with an LVO-2030 and a 6-port gas loop sampling valve was used for this analysis. The traditional FID jet was replaced with a Jetanizer™, an in-jet methanizer. This drop-in replacement jet provides traditional methanizer capabilities and requires no additional hardware or special plumbing. A total of four capillary columns were used in this analysis: two molecular sieve columns (HP-PLOT MS5A and CP-Molsieve 5A) and two carbonized molecular sieve columns (CarboBOND and GS-CarbonPLOT).

■ Experimentation and Observation

A single gas standard was used in this analysis to directly compare both the molecular sieve columns and carbonized molecular sieve columns. For each column, the gas standard was injected in triplicate. The following concentrations were used:

Table 1: Concentrations of Low TOGAS Standard

Analyte	Concentration (ppm)
Methane	100
Carbon Monoxide	100
Carbon Dioxide	400
Acetylene	100
Ethylene	100
Ethane	100

Assessment of Column Performance

Molecular Sieve Columns

Method conditions

To directly compare the molecular sieve columns, the same analytical conditions were used. Below are the methods conditions used for each run.

Table 2: Method Parameters for Molecular sieve PLOT Column

Parameter	Value
Column Used	HP-Plot MS-5A 30 m X 0.53 mm X 50 µm (19095P-MS0), CP-Molsieve 5A 25 m X 0.53 mm X 50 µm (CP7538)
Valve Box Temperature	80° C
Injection Volume	1 mL gas sampling loop
Injector Temperature	200° C
Linear Velocity	36.6 cm/sec He
Split Ratio	7:1
Oven Ramp	Isothermal 100° C
FID Temperature	400° C
FID Gas Flows	Makeup (He): 24 mL/min, H_2: 32 mL/min, Air: 250 mL/min
FID Column Insertion Depth	45 mm (places column into the catalyst bed region)

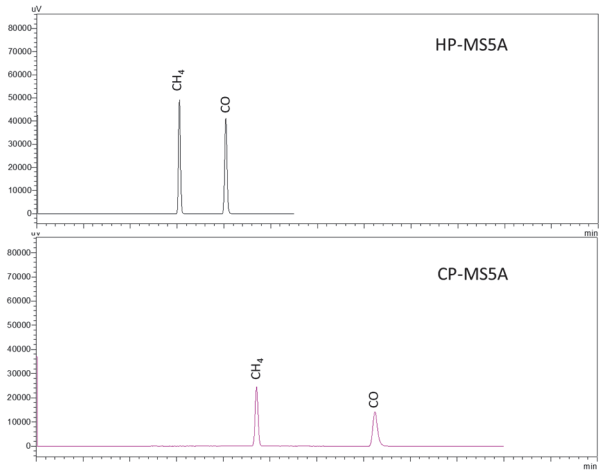

Figure 1: Representative chromatogram for MS5A columns

A notable difference in retention time was observed between the two columns. The HP-PLOT MS5A column eluted methane and carbon monoxide at 3.05 min and 4.04 min, respectively, with approximately 0.99 min between the two peaks.

The CP-Molsieve 5A column was more retentive with an elution time for methane and carbon monoxide at 4.71 min and 7.24 min, respectively, with approximately 2.53 min between the two peaks.

As a result of the differences in retention, the peaks appear broader on the CP-Molsieve 5A compared to the HP-Plot MS5A. It was found that the CP-Molsieve 5A column displayed wider peaks as indicated by the peak width at half height for methane and carbon monoxide when compared to the HP-Plot MS5A column. The tailing factor value shows a higher degree of symmetry for the HP-PLOT MS5A column for carbon monoxide compared to the CP-Molsieve 5A column. There also appears to be an inverse relationship between the number of theoretical plates/plate heights for carbon monoxide and methane when comparing the two columns.

Table 3: Analytical figures of merit for tested MS5A columns

	Column	Ret. Time (min.)	Area	Height	Noise	S/N	Tailing Factor	Tailing Factor (10%)	NTP (USP)	HETP (USP)	Theoretical Plates/meter (USP)	Peak Width Half Height
Carbon Monoxide	HP-Plot MS-5A	3.05	144332	49125	20	1657	1.08	1.07	24581	6.1	163874	0.05
	CP-Molsieve 5A	4.71	105428	24396	35	724	1.04	1.03	27017	5.55	180113	0.07
Methane	HP-Plot MS-5A	4.04	143133	40947	20	1381	1.08	1.06	30538	4.91	203583	0.05
	CP-Molsieve 5A	7.24	102776	14240	35	423	1.27	1.2	24773	6.06	165149	0.11

Carbonized Molecular Sieve Columns

Method conditions

To directly compare the molecular sieve columns, the same analytical conditions were used for the carbonized molecular sieve columns. Below are the methods conditions used for each run.

Table 4: Method Parameters for Carbonized Molecular sieve PLOT Column

Parameter	Value
Column Used	GS-Carbon Plot 30 m X 0.53 mm X 3 µm (115-3133), CarboBond 25 m X 0.53mm X 10 µm (CP7374)
Valve Box Temperature	80° C
Injection Volume	1 mL gas sampling loop
Injector Temperature	200° C
Linear Velocity	36.6 cm/sec He
Split Ratio	7:1
Oven Ramp	Isothermal 60° C
FID Temperature	400° C
FID Gas Flows	Makeup (He): 24 mL/min, H_2: 32 mL/min, Air: 250 mL/min
FID Column Insertion Depth	45 mm (places column into the catalyst bed region)

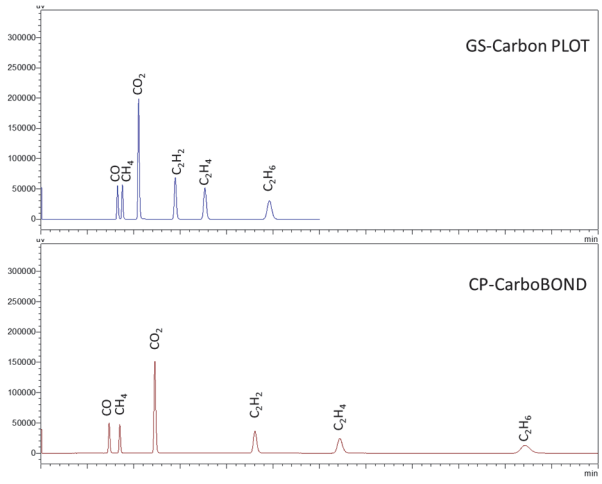

Figure 2: Representative chromatogram for carbonized molecular sieve columns

A notable difference in retention time was observed between the two columns. The CP-CarboBOND provided a higher retention for all analytes with the exception of carbon monoxide which was slightly less retained.

As a result of the differences in retention, the peaks appear broader on the CarboBOND compared to the GS-CarbonPLOT. It was found that the later eluting peaks on the CarboBOND, ethylene and ethane, had almost double the peak width of GS-CarbonPLOT when comparing the peak width at half height values in Table 5.

The tailing factor is provided to assess the peak shape. Since carbon monoxide and carbon dioxide notoriously have tailing associated with their separation, the peak shape for these two analytes is an important assessment on the efficiency of the column. A higher tailing factor indicates a more pronounced tail on a peak and thus a less Gaussian peak shape.

It was shown from the tailing factor for each analyte that there was more asymmetry to the earlier eluting peaks on the GS-CarbonPLOT but more asymmetry on the later eluting peaks on the CarboBOND column. It was also observed that the number of theoretical plates was determined to be higher with a smaller plate height on the GS-CarbonPLOT compared to the CarboBOND, which indicates a higher separation efficiency on the GS Carbon PLOT.

An important aspect to note is the potential for higher resolution of permanent gases using the CarboBOND. Testing for these components is outside of the scope of this application note. Method conditions presented here were roughly optimized to suit both columns tested and provide sufficient separation of permanent gas and hydrocarbon components in an isothermal oven program. Optimal conditions may vary between the two columns, which may provide similar chromatography between the two columns.

Table 5: Analytical figures of merit for tested carbonized molecular sieve columns

	Column	Ret. Time (min.)	Area	Height	Noise	S/N	Tailing Factor	Tailing Factor (10%)	NTP (USP)	HETP (USP)	Theoretical Plates/meter (USP)	Peak Width Half Height
Carbon Monoxide	CarboBond	1.47	111242	50182	33	1524	1.14	1.12	10747	13.96	71646	0.03
	GS CarbonPLOT	1.65	109082	54457	39	1420	1.21	1.17	16037	9.35	106914	0.03
Methane	CarboBond	1.7	101472	47030	33	1427	1.13	1.11	14514	10.34	96756	0.03
	GS CarbonPLOT	1.75	108611	56323	39	1469	1.14	1.11	19310	7.77	128732	0.03
Carbon Dioxide	CarboBond	2.45	407178	151877	33	4613	1.13	1.1	19568	7.67	130454	0.04
	GS CarbonPLOT	2.1	429869	197738	39	5157	1.17	1.13	22191	6.76	147937	0.03
Acetylene	CarboBond	4.61	192266	36744	33	1114	1.13	1.09	18499	8.11	123323	0.08
	GS CarbonPLOT	2.89	213124	68771	39	1794	1.08	1.07	20131	7.45	134209	0.05
Ethylene	CarboBond	6.44	189644	24418	33	741	1.15	1.11	16531	9.07	110209	0.12
	GS CarbonPLOT	3.53	211261	51756	39	1350	1.06	1.05	17197	8.72	114649	0.06
Ethane	CarboBond	10.42	193598	13203	33	401	1.23	1.17	12296	12.2	81971	0.22
	GS CarbonPLOT	4.92	214549	30873	39	805	1.07	1.05	11519	13.02	76792	0.11

Zero Free Noise Values

The baseline noise from each column was determined by observing the zero free detector value to provide insight into the potential background noise resulting from the column.

Since both methods were isothermal, a direct comparison between the two column and column types could be elicited. The table below shows the average resulting zero free values across three injections for each column:

Table 6: Average zero-free noise levels for each column

Column	Zero Free Noise Level (uV)
HP-PLOT MS5A @ 100 C	42416 (+/- 106)
CP-Molsieve 5A @ 100 C	37034 (+/- 41)
CarboBOND @ 60 C	39488 (+/- 152)
GS-CarbonPLOT@ 60 C	51840 (+/- 137)

It was noted that the CP-Molsieve 5A showed the lowest zero free value with the lowest variation in signal. The highest zero free value was observed on the GS-CarbonPLOT indicating a high degree of column bleed.

Repeatability

Each column and analyte were assessed for repeatability by comparing the percent relative standard deviation for retention time, peak area and peak height for each set of triplicate injections.

It was noted that all columns had excellent repeatability for almost all analytes. Carbon monoxide and carbon dioxide on the Carbobond column displayed the highest variability in peak area and peak height. Given the repeatability of the analytes on this column, there is an indication that the phase may be a contributing factor to the observed variance.

Table 7: Percent relative standard deviation for retention time, peak area and peak height for each column

	Column	RSD% Retention time	RSD% Peak Area	RSD% Peak Height
Carbon Monoxide	HP-PLOT MS5A	0.000%	0.14%	0.14%
	CP-Molsieve 5A	0.008%	0.15%	0.23%
	CarboBOND	0.039%	2.85%	1.53%
	GS-CarbonPLOT	0.000%	0.39%	0.34%
Methane	HP-PLOT MS5A	0.000%	0.11%	0.03%
	CP-Molsieve 5A	0.012%	0.24%	0.09%
	CarboBOND	0.034%	0.35%	0.26%
	GS-CarbonPLOT	0.033%	0.29%	0.14%
Carbon Dioxide	HP-PLOT MS5A	N.D.	N.D.	N.D.
	CP-Molsieve 5A	N.D.	N.D.	N.D.
	CarboBOND	0.024%	1.39%	1.52%
	GS-CarbonPLOT	0.000%	0.27%	0.22%
Acetylene	HP-PLOT MS5A	N.D.	N.D.	N.D.
	CP-Molsieve 5A	N.D.	N.D.	N.D.
	CarboBOND	0.022%	0.31%	0.67%
	GS-CarbonPLOT	0.020%	0.35%	0.33%
Ethylene	HP-PLOT MS5A	N.D.	N.D.	N.D.
	CP-Molsieve 5A	N.D.	N.D.	N.D.
	CarboBOND	0.016%	0.32%	0.17%
	GS-CarbonPLOT	0.016%	0.28%	0.25%
Ethane	HP-PLOT MS5A	N.D.	N.D.	N.D.
	CP-Molsieve 5A	N.D.	N.D.	N.D.
	CarboBOND	0.006%	0.45%	0.20%
	GS-CarbonPLOT	0.012%	0.12%	0.15%

■ Conclusion

All four columns performed well in the separation and repeatability. The two columns that performed best for heavier analytes were the HP-PLOT MS5A and CarboBOND columns when comparing theoretical plates and tailing factors due to the less retentive nature of the columns.

It was noted that the CarboBOND column may not be as inert for carbon monoxide and carbon dioxide compared to the other columns tested, which is an important consideration for column selection. The two more retentive columns, the CP-Molsieve 5A and HP-CarbonPLOT, could be used for more retention of the lighter analytes and will likely provide better separation for mixes of heavier and lighter analytes.

More extensive testing with a universal detector such as a BID or TCD would elicit more information about the separation power for permanent gases. Additionally, further method optimization may improve the resolving power and repeatability of the columns.

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