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Application News

No. GC-2103

System GC

Analysis and Characterization of ARC's In-jet Methanizer for Permanent Gases, Carbon Dioxide, and Light Hydrocarbons

■ Background

Utilizing a methanizer in a gas chromatograph, carbon monoxide and carbon dioxide can be converted to methane which allows them to be detected by a flame ionization detector (FID) providing higher sensitivity over detection with a thermal conductivity detector (TCD). Traditional methanizers use an activated nickel catalyst that is toxic to the environment and is susceptible to poisoning from analytes such as oxygen and sulfurs, which reduces its effectiveness. Additionally, the response generated from traditional methanizers with FID have a limited range of linearity.

Activated Research Company® (ARC) produces an in-jet methanizer, the Jetanizer™, which uses a proprietary catalyst material that purports to be a more environmentally friendly and more robust methanizer that offers linearity over low ppm to high percentage concentrations of carbon monoxide and carbon dioxide. This analysis will assess the limits of detection and quantification of carbon monoxide, carbon dioxide, methane and C2 hydrocarbons (ethane, ethylene, and acetylene) using the Jetanizer™ on the GC-2030.

■ Instrumentation

The GC-2030 gas chromatograph equipped with an LVO-2030, and 6-port gas loop sampling valve was used for this analysis. The Jetanizer™ is a drop-in replacement for the traditional GC-2030 FID jet which requires no additional hardware or special plumbing. Both capillary and packed columns were used in this analysis to test the capabilities of the Jetanizer™.

To determine the effects of the capillary column phase on the analysis, two different PLOT column phases were used for this analysis, molecular sieve and carbonized molecular sieve. Two different columns of each PLOT phase were used to address if a specific column had any effect on the Jetanizer™ linearity. To confirm the viability of packed column analysis, a custom 1 m carbonized molecular sieve column was used.

For both capillary and packed columns, a ~20 cm piece of 0.53 mm ID MXT tubing was joined with a union to the end of the analytical column and installed in the FID. This capillary tubing acted as a guard column protecting the end of the column from the high operating temperatures of the Jetanizer™ and to serve as a particle trap for any residual particles evolved from the columns used in the analysis. The guard column insertion depth into the FID was 45 mm to ensure the eluting analytes would encounter the catalyst bed in the Jetanizer™

■ Experimentation and Observation

Gas standards containing carbon monoxide, methane, and carbon dioxide at various concentrations were utilized for this analysis. The concentrations tested ranged from 1 ppm up to 99.99%.

Capillary Column Analysis

A total of four capillary columns were used to test the effects of specific columns on the overall response of the Jetanizer™. Two molecular sieve columns were used, and two carbonized molecular sieve columns were used. Linearity and limits of detection and quantitation were determined for each column.

Molecular sieve column

A calibration curve to test the linearity of the Jetanizer™ with molecular sieve columns was produced from a 0.96 ppm to approximately 20% for carbon monoxide and 0.87 ppm to approximately 15% for methane.

A linear regression analysis was performed for each calibration curve. The following method conditions were used:

Table 1: Method Parameters for Molecular sieve PLOT Column

Parameter	Value
Column	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, H2: 32 mL/min, Air: 250 mL/min
FID Column Insertion Depth	45 mm

Table 2: Concentrations used for calibration curve for Molecular Sieve Columns

Concentration of Standards (ppm)						
Analytes	**Low TOGAS Standard 1**	**Low ppm Std Standard 2**	**12% CO2 Standard 3**	**14% CO2 Standard 4**	**8% CO2 Standard 5**	**High TOGAS Standard 6**
Carbon Monoxide	100	0.96	59800	9900	199900	4200
Methane	100	0.87	149900	60100	11900	4200
Carbon Dioxide	400	2.55	120100	140100	78900	20000

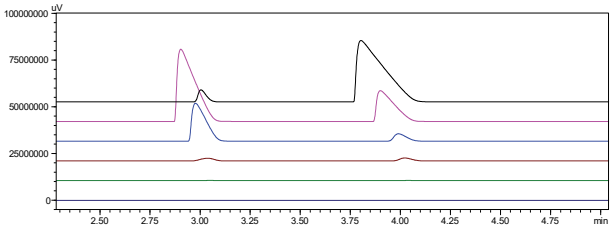

Figure 1A: Representative Stacked Calibration Curve Chromatograms for HP-PLOT MS5A

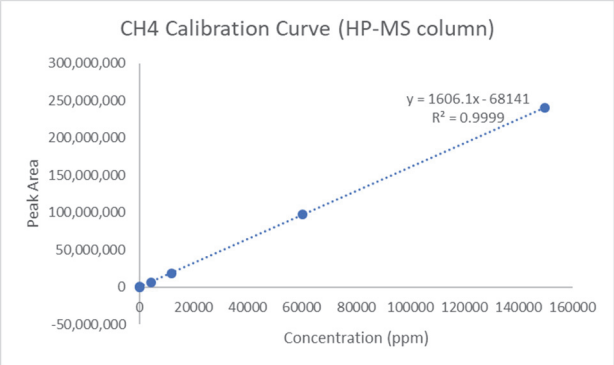

Figure 1B: Calibration curve for methane using the HP-PLOT MS5A

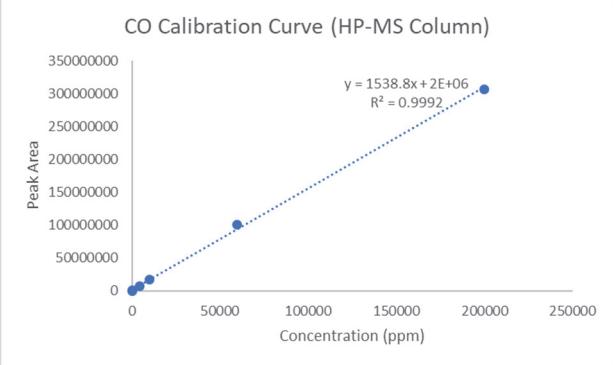

Figure 1C: Calibration curve for carbon monoxide using the HP-PLOT MS5A

It was noted that there was a high degree of linearity within the tested range for methane though some nonlinearity was observed between the 6% and 20% standard for carbon monoxide.

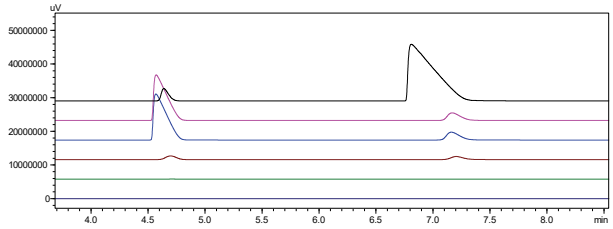

Figure 2A: Representative Stacked Calibration Curve Chromatograms for CP-Molesieve 5A

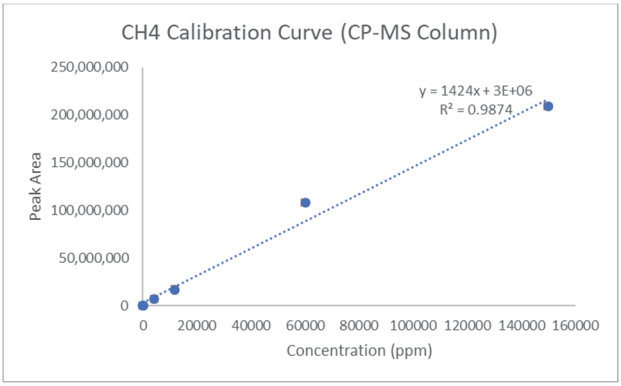

Figure 2B: Calibration curve for methane using the CP-Molesieve 5A

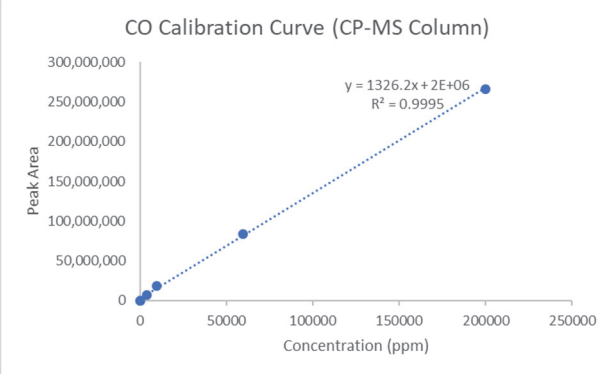

Figure 2C: Calibration curve for carbon monoxide using the CP-Molesieve 5A

Within the tested range of both methane and carbon monoxide, both are observed to be nonlinear between 1 percent and 6 percent. This may indicate a column dependency on linear range given the differences observed between the two molecular sieve columns used in this analysis.

Carbonized Molecular Sieve Column Linearity

A calibration curve to test the linearity of the Jetanizer™ with carbonized molecular sieve columns was produced from a 0.96 ppm to approximately 20% for carbon monoxide, 0.87 ppm to approximately 15% for methane and between 2.55 ppm and 99.99% carbon dioxide.

A linear regression analysis was performed for each calibration curve. The following method conditions were used:

Table 3: Method Parameters for Carbonized Molecular sieve PLOT Column

Parameter	Value
Column	GS-Carbon Plot 30 m X 0.53 mm X 3 µm (115-3133), CarboBond 25 m X 0.53 mm 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

Table 4: Concentrations used for calibration curve for Carbonized Molecular Sieve Columns

Concentration of Standards (ppm)						
Analytes	**Low TOGAS Standard 1**	**Low ppm Std Standard 2**	**12% CO_2 Standard 3**	**14% CO_2 Standard 4**	**8% CO_2 Standard 5**	**CO_2 Balance Standard 7**
Carbon Monoxide	100	0.96	59800	9900	199900	0
Methane	100	0.87	149900	60100	11900	53.5
Carbon Dioxide	400	2.55	120100	140100	78900	999935

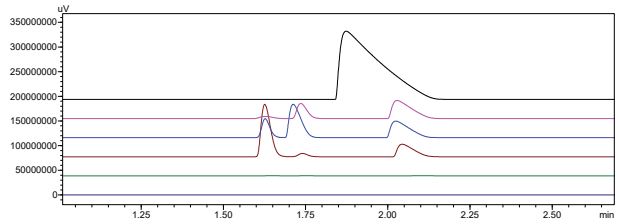

Figure 3A: Representative Stacked Calibration Curve Chromatograms for GS-CarbonPLOT

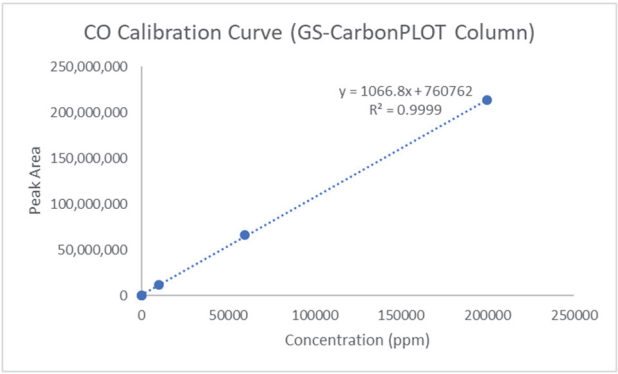

Figure 3B: Calibration curve for carbon monoxide using the GS-CarbonPLOT

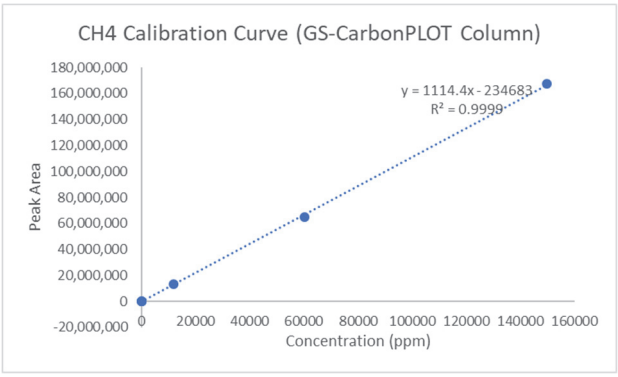

Figure 3C: Calibration curve for methane using the GS-CarbonPLOT

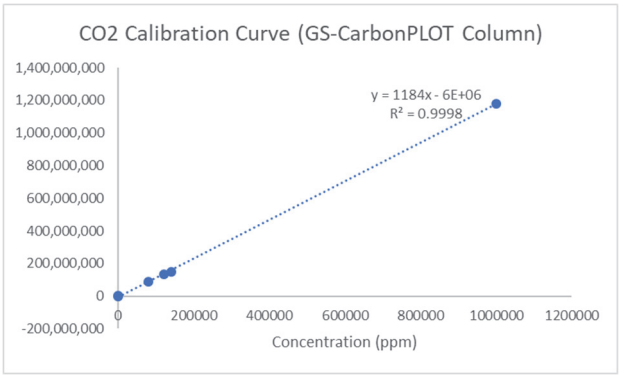

Figure 3D: Calibration curve for carbon dioxide using the GS-CarbonPLOT

There was a high degree of linearity for all analytes within the calibration curve ranges. Some nonlinearity was observed on the 99.99% carbon dioxide standard and 2.55 ppm carbon dioxide standard. This effect is likely due to overloading the column in which the method conditions could be adjusted for higher concentrations.

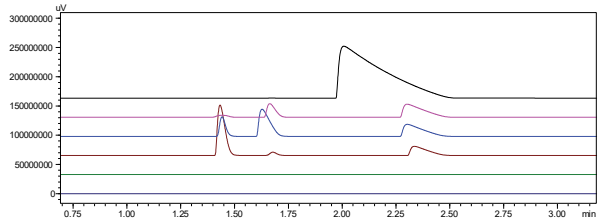

Figure 4A: Representative Stacked Calibration Curve Chromatograms for CP-Carbobond

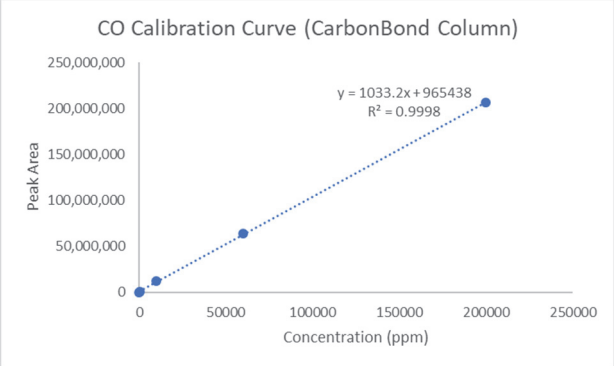

Figure 4B: Calibration curve for carbon monoxide using the CarbonBond

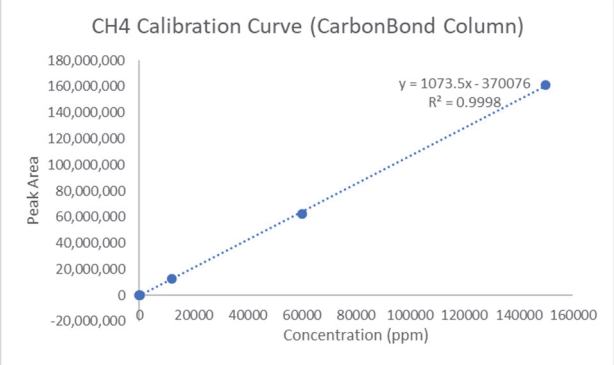

Figure 4C: Calibration curve for methane using the CarbonBond

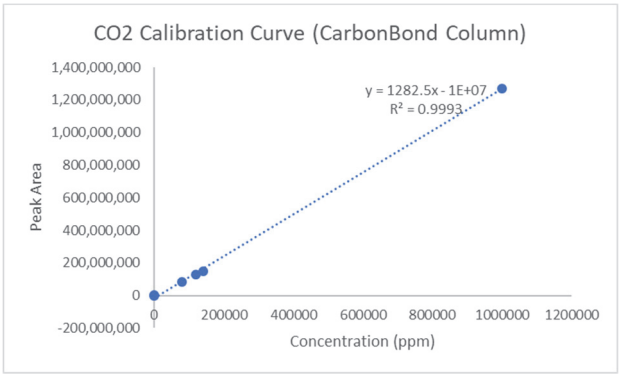

Figure 4D: Calibration curve for carbon dioxide using the CarbonBond

There was a high degree of linearity for all analytes within the calibration curve ranges. Some nonlinearity was observed on the 99.99% carbon dioxide standard and 2.55 ppm carbon dioxide standard in a similar behavior to the other column tested in this analysis.

Capillary Column Analysis of Limits of Detection and Quantitation

For limit of detection and quantitation determinations, the following standard was selected due to the presence of light hydrocarbons:

Table 5: Concentrations of Low TOGAS Standard (Standard 1)

Analyte	Concentration (ppm)
Methane	100
Carbon monoxide	100
Carbon dioxide	400
Acetylene	100
Ethylene	100
Ethane	100

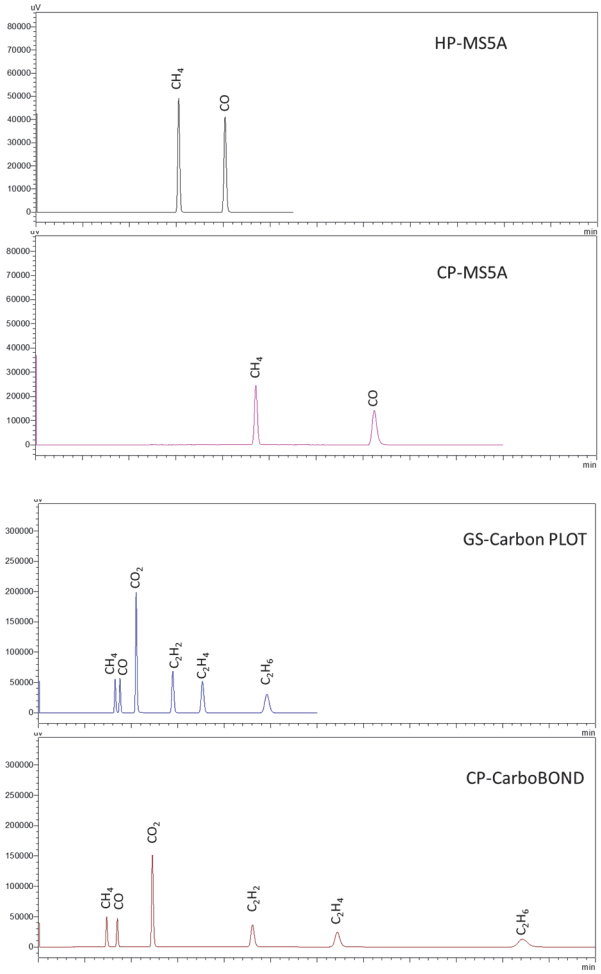

Figure 5: Representative Chromatogram for each capillary column with Standard 1

Table 6. Determined Limits of Quantitation from Standard 1 Results

LOQ	Concentration (ppm)			
Analyte	**HP-MS**	**CP-MS**	**CarboB**	**GS-Carb**
Methane	0.6	1.4	0.7	0.7
Carbon Monoxide	0.7	2.4	0.7	0.7
Carbon Dioxide	N/D	N/D	0.9	0.8
Acetylene	N/D	N/D	0.9	0.6
Ethylene	N/D	N/D	1.4	0.7
Ethane	N/D	N/D	2.5	1.3

*N/D = not determined

Table 7. Determined Limits of Detection from Standard 1 Results

LOD	Concentration (ppm)			
Analyte	**HP-MS**	**CP-MS**	**CarboB**	**GS-Carb**
Methane	0.2	0.5	0.2	0.2
Carbon Monoxide	0.2	0.8	0.2	0.2
Carbon Dioxide	N/D	N/D	0.3	0.3
Acetylene	N/D	N/D	0.3	0.2
Ethylene	N/D	N/D	0.4	0.2
Ethane	N/D	N/D	0.8	0.4

*N/D = not determined

Packed Column Limit of Detection and Quantitation

The packed column used for this analysis was a custom packed carbonized molecular sieve column which was selected to provide sufficient separation between a composite permanent gas peak, carbon monoxide, methane, carbon dioxide and C2 hydrocarbons while minimizing run times required. The method conditions below were used for this analysis:

Table 8: Parameters for Packed Carboxen Column

Parameter	Value
Column	Custom Carboxen 1006 60/80, 1 m x 1/8"
Valve Box Temperature	80° C
Injection Volume	1 mL gas sampling loop
Injector Temperature	250° C
Linear Velocity	124.5 cm/sec He
Split Ratio	0.7:1
Oven Ramp	40° C hold for 2.0 min, ramp 30° C/min to 170° C hold for 6 min
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

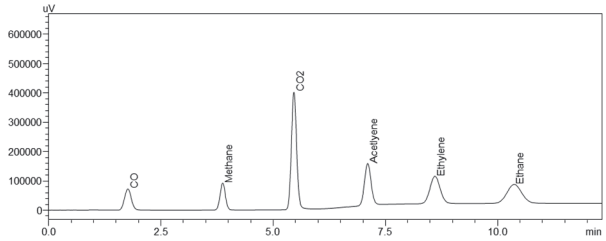

Figure 6: Representative Chromatogram for Packed Carboxen Analysis

Limits of detection were determined based on triplicate injections of the Low TOGAS standard.

Table 9: LOD and LOQ values for Packed Column Analysis

Analyte	LOD	LOQ
Carbon monoxide	0.15	0.45
Methane	0.12	0.36
Carbon dioxide	0.11	0.33
Acetylene	0.07	0.23
Ethylene	0.12	0.35
Ethane	0.17	0.51

The overall response between the methane and carbon dioxide was fairly consistent with the expected concentrations. Carbon monoxide displayed a marginally higher LOD and LOQ which is suspected to related to inadequate separation of carbon monoxide from the composite permanent gas peak.

■ Conclusion

The Jetanizer™ is a simple and effective way to add a methanizer to an existing GC-2030 for both packed and capillary columns with only a replacement of the FID jet and no additional hardware required. The increased ruggedness toward oxygen allows for more simplified flowpaths compared to traditional systems. The difference in column phase materials may play an impact on the linearity of the detector. The more retentive MS-5A capillary experienced more issues with nonlinearity which may be due to adhesion of the lower concentration analytes or other column specific factors. Adjustments to the method such as increasing the split ratio for higher concentrations may aid in overcoming issues of overloading the column and provide superior peak shape over the displayed chromatograms. Despite column overloading, the response was mostly linear over the concentration ranges analyzed in this study. Further testing at a more evenly distributed standard concentrations may be required for a more accurate assessment of linearity.

The limits of detection for each column and analyte were shown to be sub-ppm levels for both the packed and capillary columns. The lower limits of detection and quantitation observed on the packed columns are likely due to more standard being injected on column. Further optimization for lower concentration analytes could be performed but the method conditions used were intended to meet the broad concentration range required for linearity testing. Adverse effects from the repeated injections of oxygen onto the Jetanizer™ were not observed during this study, indicating a higher tolerance of oxygen than traditional methanizers.

Jetanizer is a trademark of Activated Research Company

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