Application News

System GC

No. GC-2108

Impacts of Hydrogen Sulfide and Acetylene on ARC In-jet Methanizer Performance

■ Background

There is increasing interest in the analysis of gaseous streams using gas chromatography with flame ionization detection (GC-FID) with an inline methanizer. A methanizer enables sensitive detection of carbon monoxide and carbon dioxide on an FID by conversion to methane. Hydrogen sulfide and acetylene are two common components found in refinery gases and as byproducts of various biological reactors, both of which are known to cause adverse effects to the catalysts of traditional methanizers. Activated Research Company's® (ARC) proprietary catalyst material used in their in-jet methanizer, the Jetanizer™, boasts increased stability toward catalyst poisoning from sulfurs over the traditional nickel catalysts used in conventional methanizers. Acetylene, however, is believed to stick to the catalyst and cause decreased signal over time. This application aims to evaluate the effects of high sulfur and high acetylene samples on the performance of ARC's Jetanizer.

■ Instrumentation

A GC-2030 equipped with an LVO-2030, FID-2030 and 6-port gas loop sampling valve was used for this analysis. No specialized detectors or injectors were required for this analysis.

■ Experimentation and Observation

Standards evaluated included a natural gas standard as a control standard to monitor signal loss and two challenge standards: a refinery gas standard containing 1% hydrogen sulfide and pure (>99%) acetylene. To test the effects of hydrogen sulfide and acetylene independently, the injection scheme outlined in Table 2 was used. The reduction in signal of carbon dioxide relative to other hydrocarbon species was used to determine the effects of catalyst poisoning in these analyses.

Table 1: Standards and analyte concentrations

Analyte	Natural Gas	Refinery Gas	Acetylene
Hydrogen	N/D	25.97%	N/D
Hydrogen Sulfide	N/D	1.07%	N/D
Argon	N/D	1.01%	N/D
Nitrogen	2.50%	1.52%	N/D
Carbon Dioxide (CO_2)	3.00%	N/D	N/D
Methane (CH_4)	89.47%	20.12%	N/D
Ethane (C2)	3.50%	14.04%	N/D
Ethylene	N/D	12.04%	N/D
Acetylene	N/D	0.49%	>99%
Propane (C3)	1.00%	9.98%	N/D
Propylene	N/D	8.02%	N/D
i-Butane (i-C4)	0.40%	2.00%	N/D
n-Butane (n-C4)	0.40%	1.00%	N/D
Isobutylene	N/D	0.50%	N/D
cis-2-Butene	N/D	0.50%	N/D
trans-2-Butene	N/D	0.50%	N/D
neo-Pentane (neo-C5)	0.10%	N/D	N/D
i-Pentane (i-C5)	0.15%	0.50%	N/D
n-Pentane (n-C5)	0.15%	0.50%	N/D
n-Hexane (n-C6)	0.05%	0.25%	N/D
n-Heptane (n-C7)	0.02%	N/D	N/D

Table 2: Injection scheme used for analysis

Standard	Number of Injections
Natural Gas	3
Refinery Gas	1
Natural Gas	3
Refinery Gas	3
Natural Gas	3
Acetylene	1
Natural Gas	3
Acetylene	3
Natural Gas	3

Method conditions

Method conditions were selected to provide separation of methane and carbon dioxide and for full speciation of the C2 through C7 hydrocarbon components as demonstrated in Figure 1.

Table 3: Method parameters

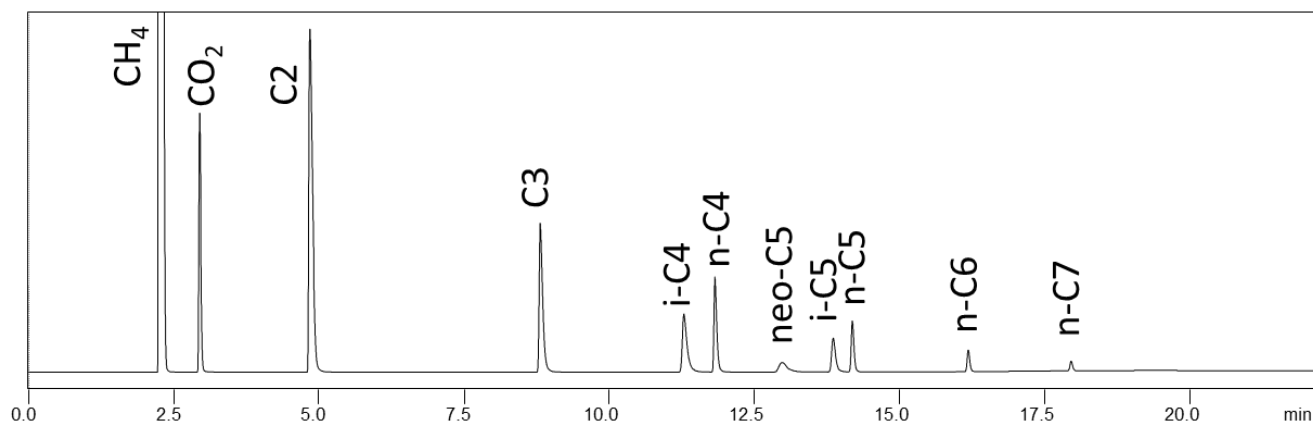| Parameter	Value
Column Used	SH-Rt-Q-BOND PLOT 30x0.53x20 (P/N 221-75765-30)
Valve Box Temperature	125° C
Injection Volume	1 mL gas sampling loop
Injector Temperature	250° C
Linear Velocity	36.6 cm/sec He
Split Ratio	20:1
Oven Ramp	35° C hold 3.0 min, Ramp to 250° C at 15° C/min, hold for 5 minutes
FID Temperature	400° C
FID Gas Flows	Makeup (He): 24 mL/min, H2: 32 mLl/min, Air: 250 mL/min

Figure 1: Representative chromatogram of natural gas standard

Refinery gas/H_2S injections

Three samples of natural gas were injected to evaluate the initial signal intensity. A single injection of the refinery gas standard containing 1% hydrogen sulfide was then injected, followed by an additional triplicate injection of natural gas to observe the effects of a single exposure to a high sulfur sample. Next, three additional injections of the refinery gas standard were completed followed by three additional injections of natural gas to assess signal loss with repeated exposure to high sulfur samples.

Representative chromatograms of the carbon dioxide in the natural gas standard were overlayed to provide more details on the chromatography between the initial separation, the chromatography after a single refinery gas injection, and the chromatography after an additional three refinery gas injections.

Injections of the refinery gas standard resulted in a signal loss for carbon dioxide of 1.55% from a single injection of the refinery gas and an additional 1.63% loss after three additional injections of the refinery gas. The peak repeatability remained below 0.5% RSD for each triplicate natural gas injection. A shift in retention time was observed during the injections.
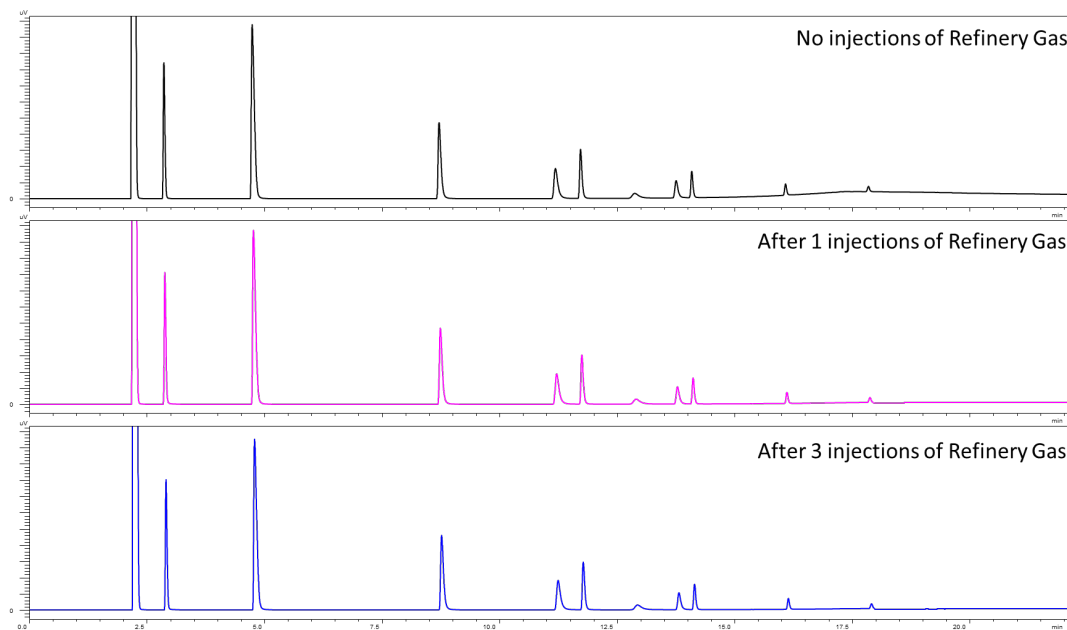
Figure 2: Chromatograms of natural gas injections. Black = Initial injection, Pink = After 1 injection of refinery gas, Blue = After 3 injections of refinery gas.
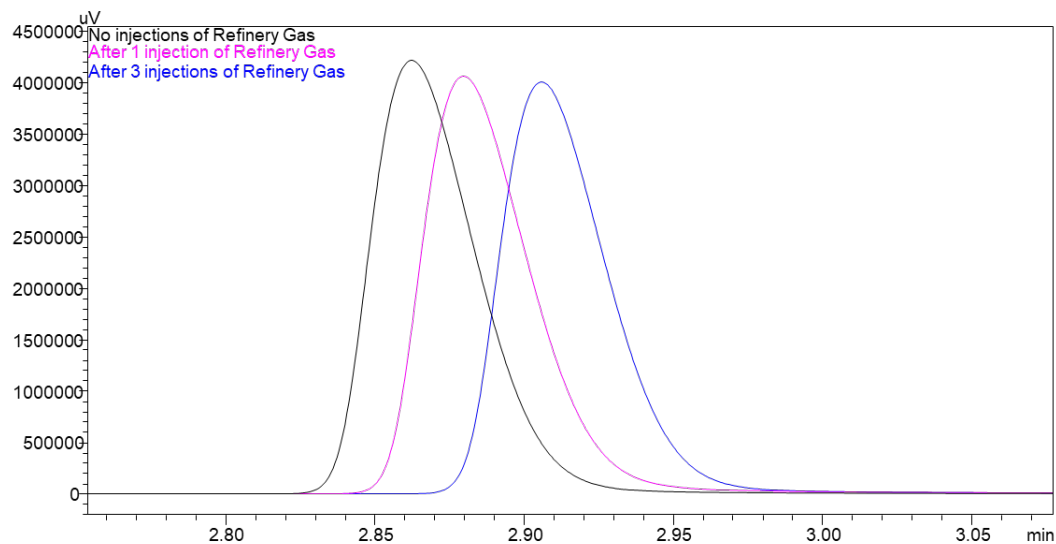

Figure 3: An overlay of chromatograms showing carbon dioxide peaks in natural gas. Black = Initial injection, Pink = after 1 Injection of Refinery Gas, and Blue = after 3 additional injections of refinery gas

Table 4: Average peak area and relative standard deviation for carbon dioxide in natural gas

Injection Condition	Average Peak Area	RSD
Initial Injections	10,360,217	0.437%
After 1 injection of refinery gas	10,199,575	0.021%
After 3 injection of refinery gas	10,032,930	0.312%

Acetlyene injections

The final injections of natural gas for the sulfur analysis were used as the initial evaluation point in the acetylene analysis. A single sample of acetylene was injected followed by an additional triplicate injection of natural gas to observe the effects of a single exposure to an acetylene sample. Three additional injections of acetylene followed by a three additional injections of natural gas were performed to evaluate signal loss with repeated exposure to high acetylene samples.

Injections of the acetylene resulted in a modest signal increase of 0.3 % for carbon dioxide from a single injection and an additional 2 % loss after three additional injections of acetylene. The peak repeatability remained below 0.5% for each triplicate natural gas injection.
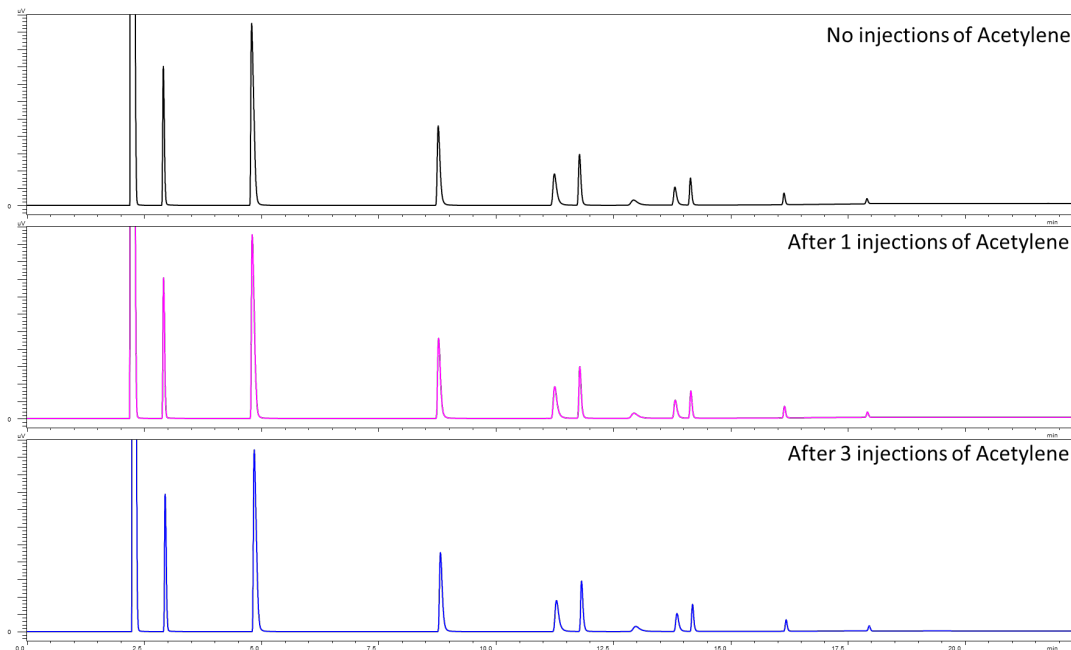

Figure 4: Natural Gas Chromatograms Initially, After 1 Injection of Acetylene, and After 3 Additional Injections of Acetylene
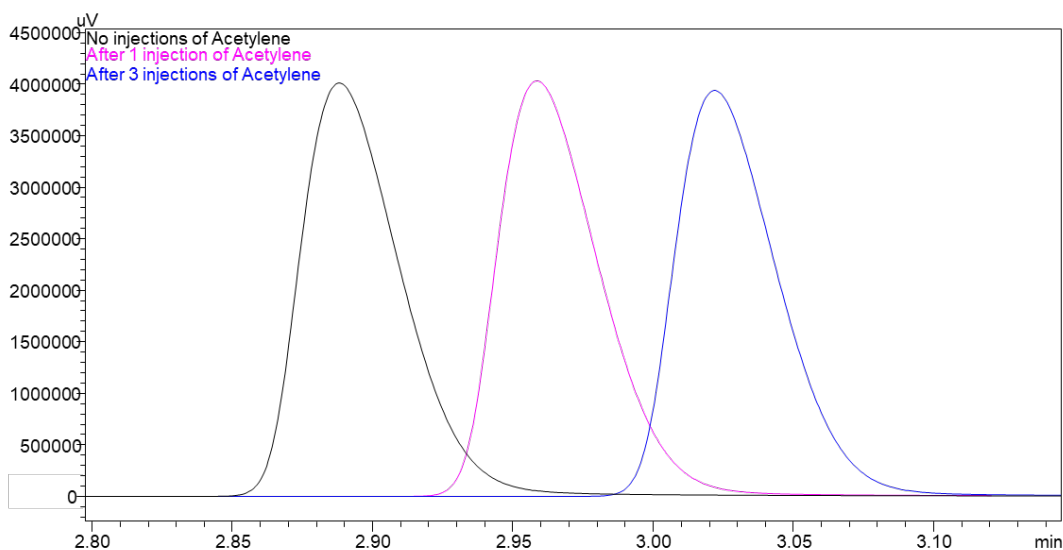

Figure 5: An overlay of chromatograms showing carbon dioxide peaks in natural gas. Black = initial injection, Pink = after 1 injection of acetylene, and Blue = after 3 additional injections of acetylene

Table 5: Average peak area and relative standard deviation for carbon dioxide in natural gas

Injection Condition	Average Peak Area	RSD
No injections of Acetylene	10,032,930	0.312%
After 1 injection of Acetylene	10,062,915	0.454%
After 3 injection of Acetylene	9,863,104	0.354%

Summary of results
Results were calculated by the following equation:

$$\%\Delta Peak\ Area = 100 * \frac{(Control\ Peak\ Area\ after\ Challenge\ Standard - Control\ Peak\ Area\ after\ Challenge\ Standard)}{Control\ Peak\ Area\ before\ Challenge\ Standard}$$

The natural gas injections were used as a baseline control for the response of the system. The refinery gas and acetylene standards were the challenge standards that would potentially impact the performance of the Jetanizer. The percent peak area loss for the control standard was determined for each component in the control standard.

The reduction in signal of carbon dioxide relative to other hydrocarbon species was used to determine the effects of catalyst poisoning in these analyses. The signal loss was evaluated for each analyte after a single injection of a refinery gas standard and from the injection of the refinery gas standard in triplicate. The total signal loss from the sum of four refinery gas standard injections is also reported in Table 6.

The total signal loss was 4.80% for carbon dioxide and 3-4% for the majority of the other analytes. The column, differences in carrier, and fuel gas purity due to the use of generator gases, as well as degradation of the signal due to coking of the jet, may all be contributing factors in the signal loss. Changes in the C6 and C7 species are suspected to be directly related to the baseline changes at the higher temperatures required for the method.

The signal loss was evaluated for each analyte after a single injection of acetylene and from the injection of the acetylene in triplicate. The total signal loss from the sum of four acetylene injections is also reported in Table 7.

Table 6: Summary of signal loss from hydrogen sulfide injections

Analyte	Percent Area Change After 1 Injection Refinery Gas	Percent Area Change After 3 Injections Refinery Gas	Total Percent Area Change
Methane	-0.06%	-2.08%	-2.14%
Carbon Dioxide	-1.55%	-1.63%	-3.16%
Ethane	-0.30%	-2.00%	-2.30%
Propane	-0.17%	-2.02%	-2.19%
iso-Butane	0.01%	-2.11%	-2.10%
n-Butane	-0.10%	-2.01%	-2.11%
neo-Pentane	0.07%	-1.91%	-1.84%
iso-Pentane	0.63%	-1.95%	-1.33%
n-Pentane	-0.16%	-1.90%	-2.06%
n-Hexane	-2.06%	-1.99%	-4.00%
n-Heptane	-6.52%	-2.18%	-8.55%

Table 7: Summary of signal loss from acetylene injections

Analyte	Acetylene		
	Percent Area Change After 1 Injection Acetylene	Percent Area Change After 3 Injections Acetylene	Total Percent Area Change
Methane	0.22%	-2.06%	-1.84%
Carbon Dioxide	0.30%	-1.99%	-1.69%
Ethane	0.35%	-2.01%	-1.67%
Propane	0.26%	-1.99%	-1.74%
iso-Butane	0.55%	-2.23%	-1.69%
n-Butane	0.23%	-2.01%	-1.78%
neo-Pentane	0.43%	-1.83%	-1.41%
iso-Pentane	0.15%	-1.96%	-1.82%
n-Pentane	0.16%	-1.98%	-1.82%
n-Hexane	0.15%	-2.04%	-1.89%
n-Heptane	-0.12%	-1.93%	-2.05%

Normalization with Propane

To eliminate system variance as a contributing factor to signal loss, each peak area was normalized to a hydrocarbon peak by dividing the peak area of the analyte with the propane peak area. Calculations for percent differences were calculated using the same approach as the unnormalized values. Propane was selected since this peak has a retention time approximately in the middle of the run and is well resolved from all other analytes.

The signal loss when normalized to propane shows a significant decrease in signal loss compared to the non-normalized results.

After the injections of hydrogen sulfide, the normalized results show less than a 1% decrease in peak area for most analytes.

Carbon dioxide displayed a loss of 1.38% from a single injection of hydrogen sulfide but displayed a modest recovery of 0.40% after three additional injections. This indicates an initial shock of the catalyst material with the hydrogen sulfide followed by some recovery with additional runs.

After the injections of acetylene, the normalized results show less than a 0.5% decrease in peak area for all analytes. Carbon dioxide displayed a modest increase in signal of 0.04% after a single injection of acetylene and a modest increase in signal of 0.01% after three additional injections. This indicates no significant change in signal as a result of the acetylene injections.

Table 8: Summary of signal loss from refinery gas injections normalized to propane

Analyte	Percent Area Change After 1 Injection Refinery Gas	Percent Area Change After 3 Injections Refinery Gas	Total Percent Area Change
Methane	0.11%	-0.06%	0.05%
Carbon Dioxide	-1.38%	0.40%	-0.99%
Ethane	-0.13%	0.02%	-0.10%
Propane	N/A	N/A	N/A
iso-Butane	0.19%	-0.09%	0.10%
n-Butane	0.08%	0.01%	0.09%
neo-Pentane	0.24%	0.12%	0.36%
iso-Pentane	0.81%	0.07%	0.88%
n-Pentane	0.01%	0.12%	0.13%
n-Hexane	-1.89%	0.04%	-1.85%
n-Heptane	-6.35%	-0.16%	-6.50%

Table 8: Summary of signal loss from acetylene injections normalized to propane

Analyte	Percent Area Change After 1 Injection Acetylene	Percent Area Change After 3 Injections Acetylene	Total Percent Area Change
Methane	-0.04%	-0.07%	-0.10%
Carbon Dioxide	0.04%	0.01%	0.05%
Ethane	0.09%	-0.02%	0.07%
Propane	N/A	N/A	N/A
iso-Butane	0.29%	-0.24%	0.05%
n-Butane	-0.03%	-0.02%	-0.04%
neo-Pentane	0.17%	0.17%	0.34%
iso-Pentane	-0.11%	0.03%	-0.08%
n-Pentane	-0.10%	0.01%	-0.08%
n-Hexane	-0.11%	-0.05%	-0.16%
n-Heptane	-0.38%	0.06%	-0.31%

Recovery after signal loss

Previous investigations of the Jetanizer have shown that exposure to air/oxygen help to decoke the jet and recover some of the signal loss caused by acetylene coking. The feasibility of decoking the system was tested by injecting 2.5 mL of zero grade air over a series of twenty injections to see if any signal could be recovered. A natural gas standard was injected in triplicate before and after the air injections.

After the air injections, a further decrease in signal loss was observed instead of an expected regeneration of signal. From these results, it appears the effects of the signal loss caused by acetylene and hydrogen sulfide are non-reversible using air injections. It was noted there was an increase in baseline after the injection at higher temperatures, which may indicate the column is a contributing factor in this signal loss. Further investigation of the proper regeneration procedure for the GC-2030 Jetanizer may be required.
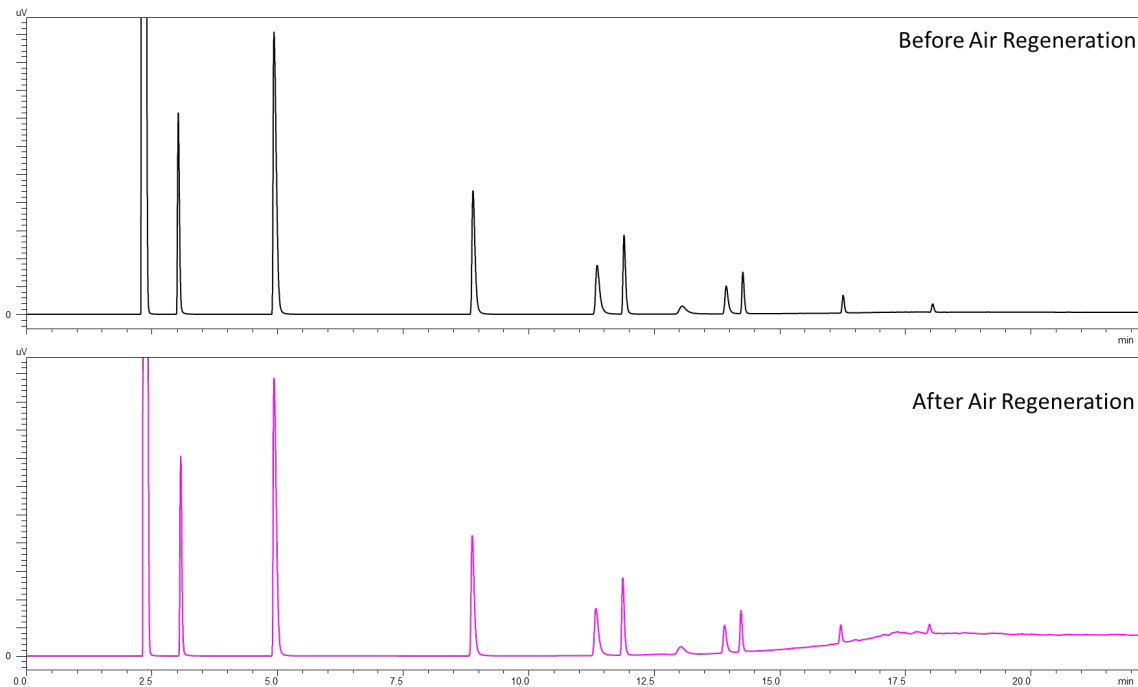
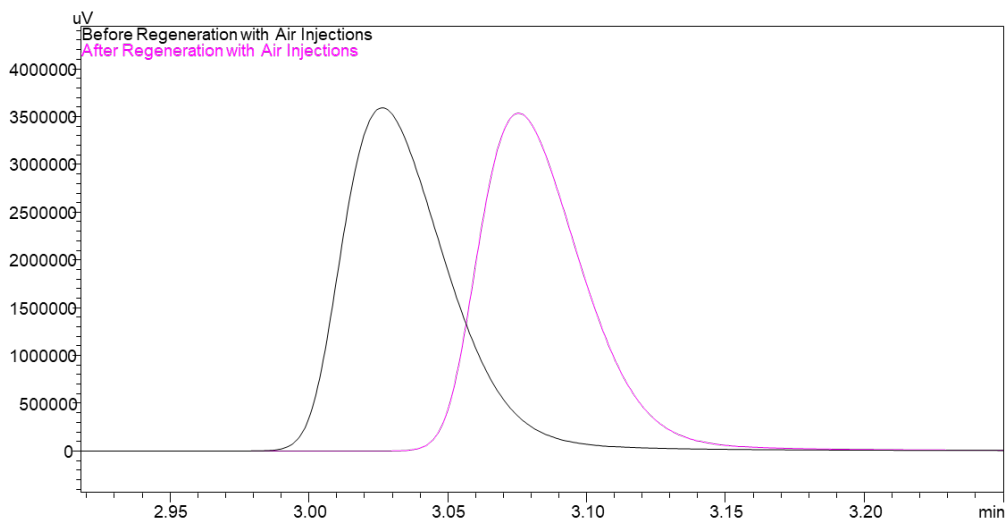**Figure 5**: Stacked chromatograms of natural gas before and after air regeneration

Figure 6: Overlaid chromatogram for carbon dioxide in natural gas before and after regeneration

Table 8: Summary of regeneration with air results

Injection Condition	Average Peak Area	RSD	Percent Change in Peak Area
Before Regeneration with Air	9,625,111	0.826%	-3.378%
After Regeneration with Air	9,299,951	0.230%	

■ Conclusion

ARC's Jetanizer has been shown to be incredibly robust even to high sulfur concentrations and acetylene which would harm traditional methanizers. With a total of four injections of a refinery gas standard containing 1% hydrogen sulfide and four injections of acetylene, less than a 5% decrease in peak area was observed for carbon dioxide in raw peak areas. Normalizing the peak areas to propane resulted in a decrease of less than 1% for carbon dioxide.

With four injections of 1 % hydrogen sulfide, the carbon dioxide area loss was 3.16%. For all analytes, the normalized results brought the loss in peak area below 1%, with the exception of hexane and heptane. The high variation on the hexane and heptane is thought to be attributed to the baseline rise of the column at higher temperatures. It is suspected that the column suffered damage during this testing which resulted in the increasingly poor baseline and shifting retention times throughout this experiment.

With four injections of acetylene, the carbon dioxide area loss was 1.69%. When the responses were normalized to propane, the signal loss from the acetylene injections dropped to below 0.05%, which further validates limited loss in performance of the Jetanizer when exposed to acetylene. The normalized results brought the loss in peak area for all analytes below 0.5% which is a strong indication of minimal loss in sensitivity as a result of the Jetanizer's exposure to acetylene. Traditional nickel catalyst methanizers would show significant loss in signal when exposed to these quantities of acetylene and hydrogen sulfide. With below a 1% loss in signal, the robustness of the Jetanizer is significantly improved over traditional methanizers.

Using strategies such as normalization and bracketing, the effects of instrumental or column drift are greatly decreased. The performance of the Jetanizer helps confirm its utility in carbon dioxide conversion reactors as well as various other environmental and energy applications. Additional investigation may be required to develop a regeneration procedure to further expand the lifespan of the Jetanizer.