

UOP 603-13: Analysis of Trace CO and CO₂ in bulk H₂ and Light Gaseous Hydrocarbons by GC

- **Fast Analysis in <5 Minutes**
- **Excellent Repeatability & Linearity**
- **Robust Solution using AC proprietary Methanizer**
- **No Matrix Interference**

Keywords:

Carbon Monoxide, Carbon Dioxide, UOP 603-13



INTRODUCTION

Permanent gases such as CO, CO₂, O₂, N₂, and methane are common analytes in refinery gases, natural gas, fuel cell gases, and many other industrial processes. Understanding the concentration of these components can be very important for controlling manufacturing processes, and their negative impact on quality and commercial value of end products. Impurities such as CO and CO₂ in feedstocks can be deleterious to certain catalysts resulting in disruption and increased cost of production.

UOP recently released the updated method 603-13 which is effectively based on the configuration developed by AC Analytical Controls (see Fig 1).

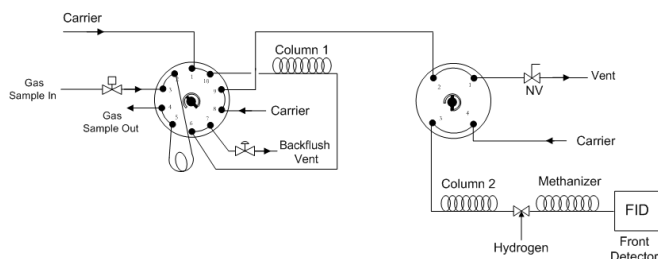


Figure 1. Plumbing diagram for UOP 603-13

INSTRUMENTATION

The analyzer is dedicated to the analysis of CO and CO₂ in ethylene, hydrogen and methane gas flows. The analyzer is configured with 3 valves, 2 columns, 1 inlet and 1 detector. All flows are EPC controlled.

An AC proprietary Methanizer is used for more robust and reliable conversion of CO and CO₂ in Methane, combined with a 4-port valve, acting in conjunction with a deans switch configuration to avoid bulk matrix entering the methanizer.

A repeatable volume of the sample is introduced through the gas sampling / back flush valve into a pre column (Column 1). After the elution of CO₂ into the analysis column (Column 2), the valve is switched to back flush the remaining components to the vent. For samples containing high methane, the 4-port switching valve is used as a heart cut valve to vent the bulk of the methane eluting from the pre column. CO, CO₂ and (remaining) Methane are separated on the analysis column and are converted in the Methanizer into Methane. Detection is done by FID and the external standard method is used for the calibration.

VALIDATION

The system and methodology of the trace CO and CO₂ analyzer are thoroughly tested for separation efficiency, repeatability, response linearity, Methanizer conversion efficiency, and detection levels.

SEPARATION EFFICIENCY

If baseline resolution ($R > 1.5$) is obtained between all three components, the separation efficiency of the chromatographic columns is satisfactory. As depicted in Figure 2, this specification is easily achieved. The resolution between Carbon Monoxide and Methane is > 7).

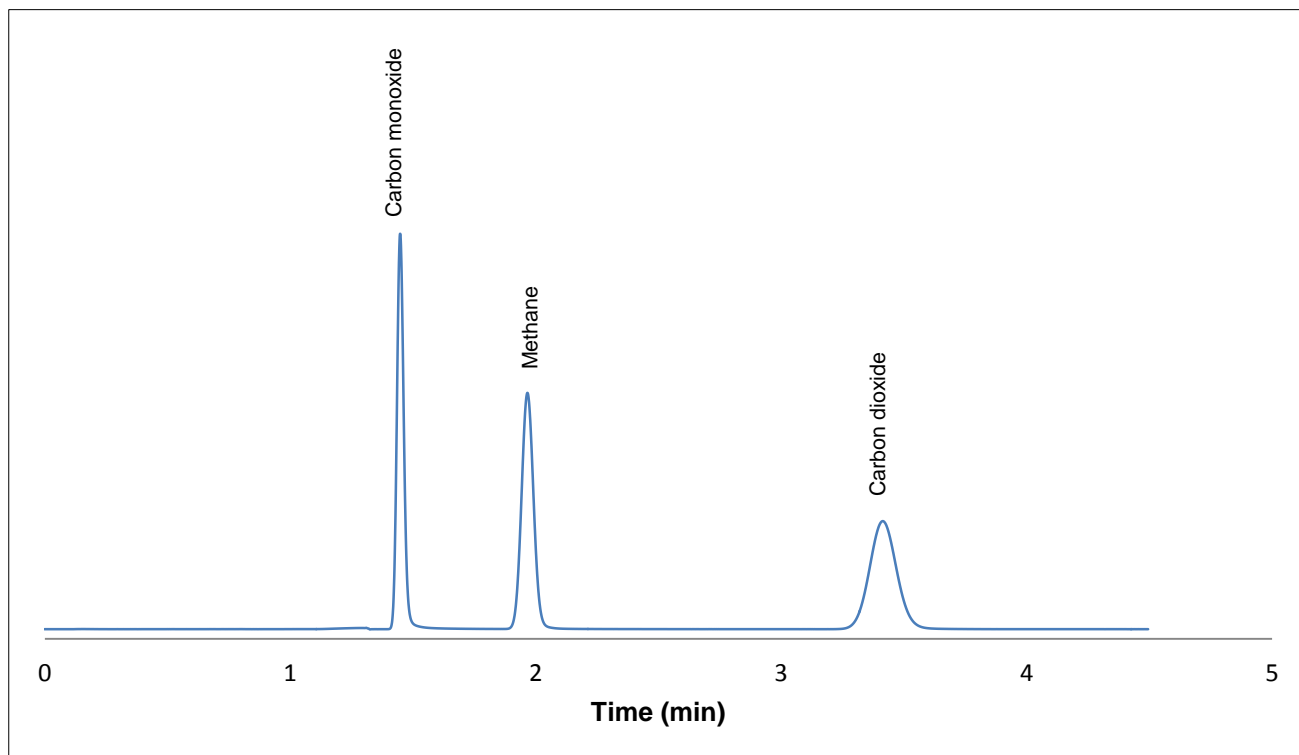


Figure 2. Separation efficiency of 200 ppm standard blend

REPEATABILITY

Area and retention time are the two primary measurements in gas chromatography. The precision in which they are measured ultimately determines the validity of the generated quantitative data. Retention time and area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exacting tolerances. Furthermore, the inertness of the flow path can dramatically affect area precision, especially for active components at low levels.

Area and retention time repeatability for the AC CO and CO₂ analyzer according UOP 603-13 are measured for 10 consecutive runs (table 1) for a standard blend containing approximately 200 ppm per component. Very good repeatability values are obtained.

Compound:	Carbon monoxide			Methane			Carbon dioxide			
	Run	RetTime [min]	Area [pA*s]	Amount [ng/ul]	RetTime [min]	Area [pA*s]	Amount [ng/ul]	RetTime [min]	Area [pA*s]	Amount [ng/ul]
	1	1.448	1040.83	208.73	1.966	1084.84	210.03	3.414	1111.18	208.63
	2	1.448	1041.23	208.81	1.966	1084.73	210.01	3.414	1111.28	208.64
	3	1.447	1040.98	208.76	1.966	1085.12	210.08	3.414	1110.78	208.55
	4	1.448	1041.93	208.95	1.966	1084.18	209.90	3.414	1111.32	208.65
	5	1.447	1040.95	208.76	1.965	1084.60	209.98	3.413	1110.67	208.53
	6	1.449	1041.73	208.91	1.968	1084.77	210.02	3.415	1110.90	208.57
	7	1.447	1042.00	208.97	1.966	1084.69	210.00	3.414	1110.78	208.55
	8	1.449	1041.35	208.84	1.967	1084.26	209.92	3.415	1110.25	208.45
	9	1.447	1040.35	208.64	1.966	1084.74	210.01	3.413	1110.11	208.42
	10	1.447	1041.00	208.77	1.966	1084.92	210.05	3.414	1110.79	208.55
Mean		1.448	1041.23	208.81	1.966	1084.69	210.00	3.414	1110.80	208.55
S.D.		0.00082	0.52345	0.10539	0.00071	0.28330	0.05507	0.00068	0.40170	0.07592
RSD %		0.049	0.050	0.050	0.036	0.026	0.026	0.020	0.036	0.036

Table 1. Repeatability for 200 ppm standard blend (n=10)

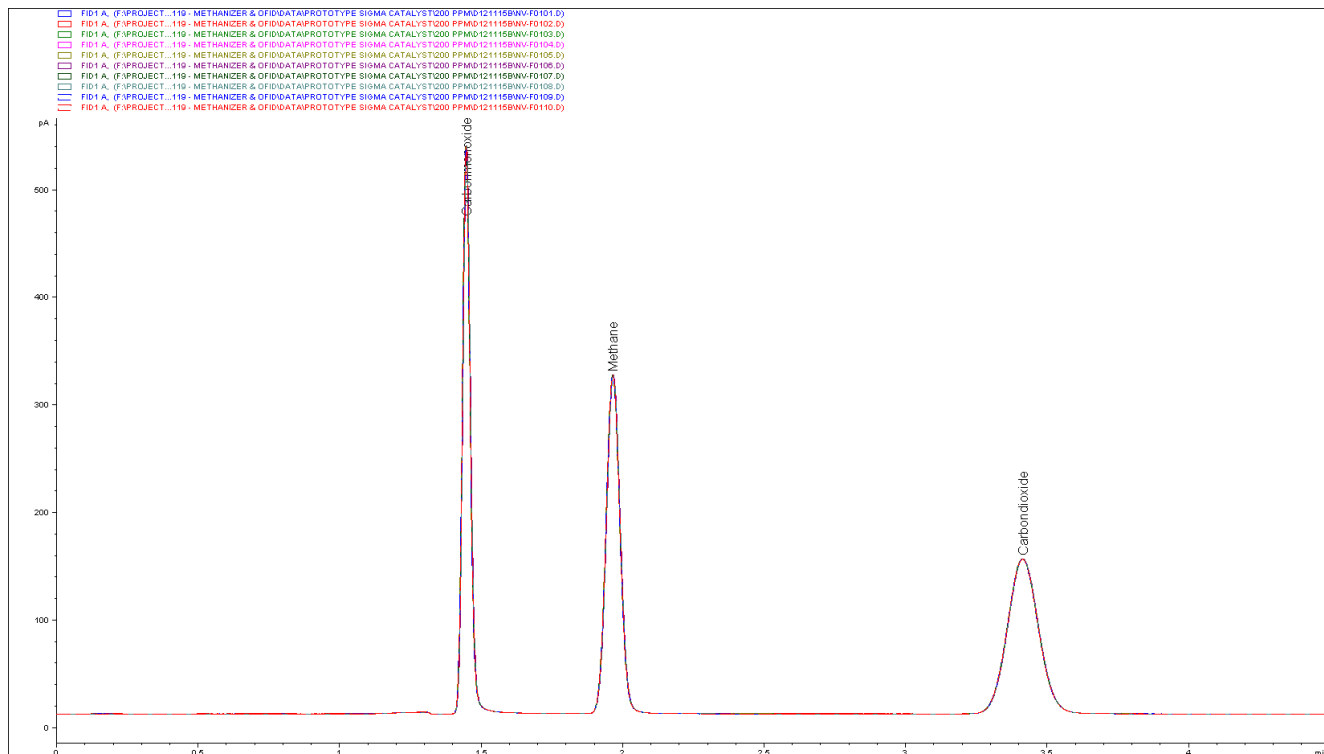


Figure 3. 200 ppm calibration blend: overlay of 10 runs

LINEARITY

The linearity of response for the analyzer is verified by analyzing 5 different certified calibration gases over a range of concentration covering the scope of UOP 603-13, as in Table 2. For each component the linearity plots are created (see figures below). All calibration lines have a linearity correlation > 0.9999. Note: Gas 5 contains approximately 1000 ppm of each component which is outside the range specified in UOP 603-13 (0,2 – 500 mole-ppm).

Cal Gas	CO ppm	CH ₄ ppm	CO ₂ ppm
Gas 1	1.19	1.19	1.19
Gas 2	5.0	26	5.1
Gas 3	59	59	59
Gas 4	210	210	210
Gas 5	1000	990	990

Table 2. Calibration gas compositions used for linearity study

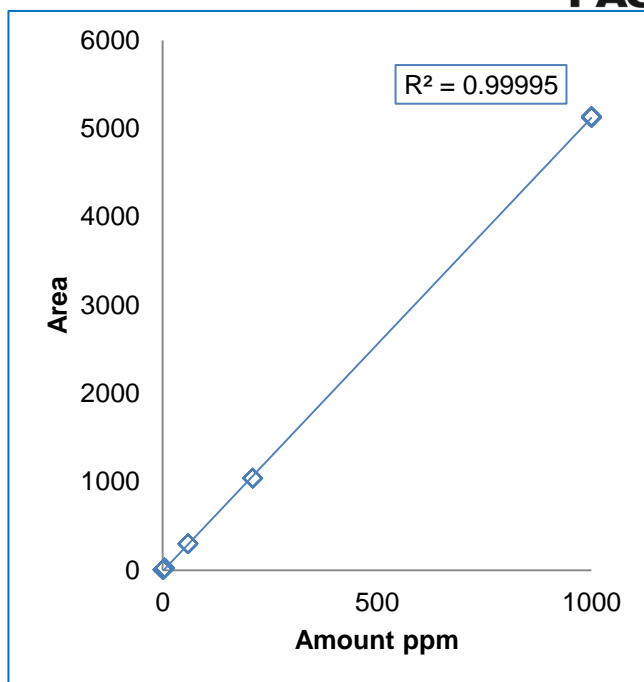


Figure 4. Linearity plot Carbon Monoxide

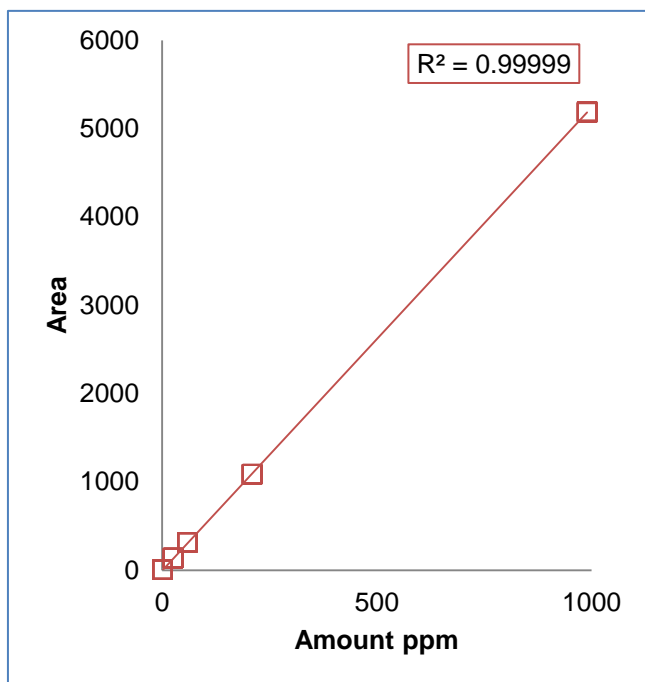


Figure 5. Linearity plot Methane

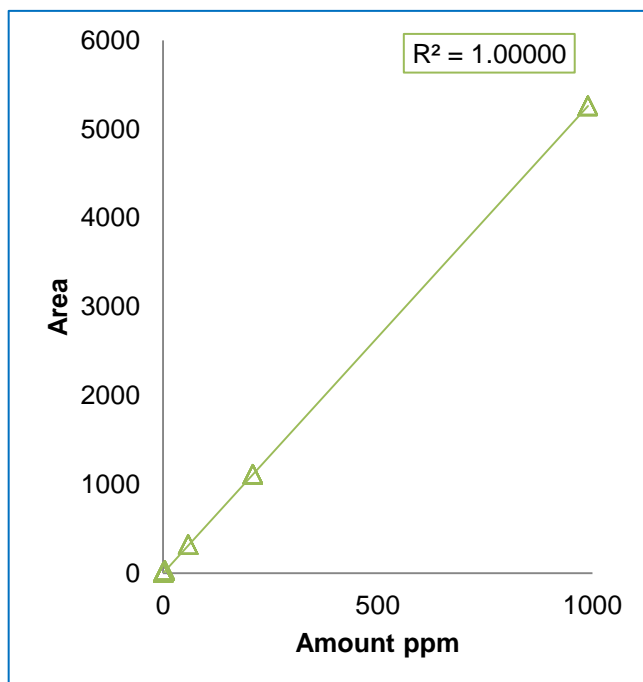


Figure 6. Linearity plot Carbon Dioxide

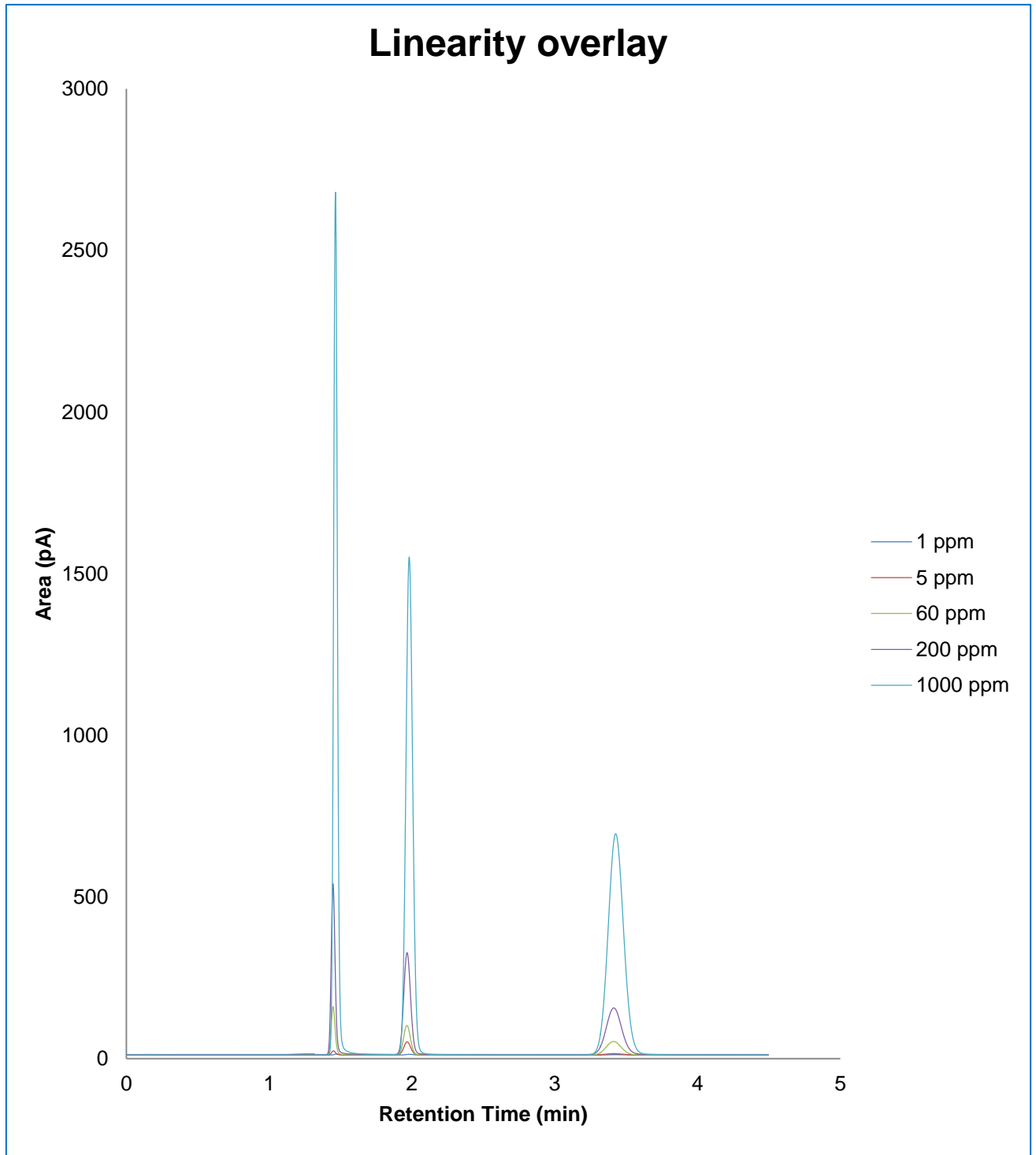


Figure 7. Chromatogram overlay of 5 different calibration blends in range 1-1000 ppm

CONVERSION EFFICIENCY

The 200 ppm calibration blend is analyzed according to the settings mentioned in the method. The peak areas of methane and the converted CO and CO₂ are determined. The response factor relating to the mole ppm/unit of peak area for each component are calculated using next equation:

$$K = \frac{P}{A}$$

Where:

A = peak area for converted CO, CO₂ or methane

K = response factor for converted CO, CO₂ or methane

P = mole ppm of CO, CO₂ or methane

If the response factors for CO and CO₂ are within 5% of the methane factor, the hydrogenation reactor (methanizer) efficiency is satisfactory.

	Response factor Carbon Monoxide	Response factor Methane	Response factor Carbon Dioxide
Conc. (ppm)	210	210	210
Area (pA)	1041	1085	1111
Resp. Factor	0.202	0.194	0.189

Table 3. Response factor components

Both response factors of CO and CO₂ are within 5% of the methane factor (4.1% and 2.4 % respectively), demonstrating proper conversion.

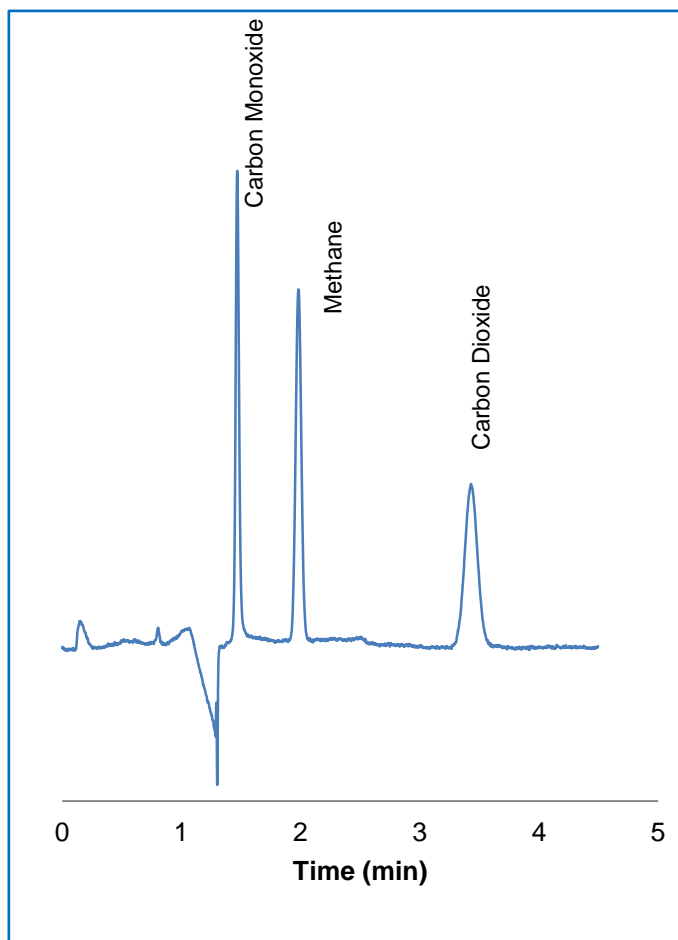


Figure 8. Chromatogram of 1 ppm blend for LOD determination

DETECTION AND QUANTIFICATION LIMIT

Detection and quantification limit of CO and CO₂ is calculated using the lowest level calibration blend (~ 1 ppm). LOD is defined as 3 * standard deviation of the noise, LOQ is defined as 10 * standard deviation of the noise.

$$LOD = \frac{3 * N * C * W}{A}$$

Where:

N = Noise of signal (pA)

C = Concentration of component (ppm)

W = Peak width (s)

A = Area (pA*s)

	CO	Methane	CO ₂
LOD (ppm)	0.03	0.04	0.10
LOQ (ppm)	0.11	0.14	0.32

Table 4. Detection and quantification limits (n=10)

HIGH METHANE CONCENTRATION

Samples with high methane concentrations can cause carbon build-up on the catalyst of the methanizer. For samples containing high methane concentrations, carbon monoxide and carbon dioxide can be resolved from interfering methane using the additional valve.

The 4-port switching valve is used as a heart cut valve to vent the bulk of methane eluting from the first column. CO, CO₂ and methane are separated on the second column.

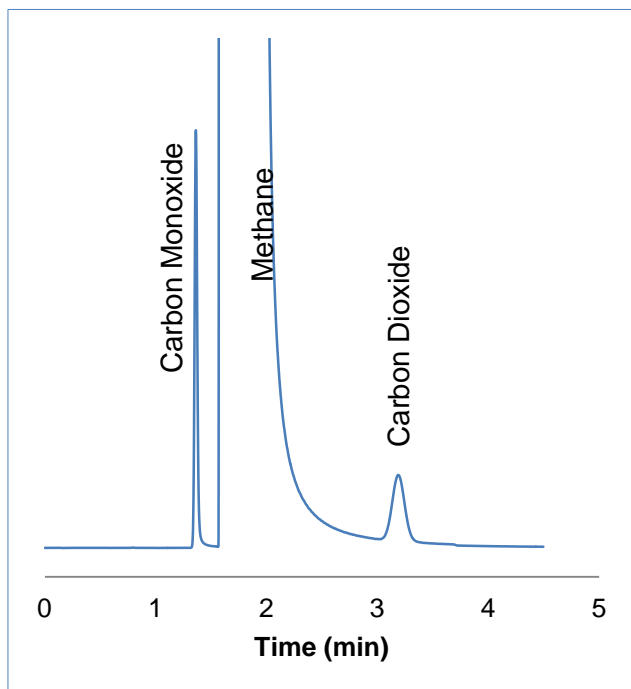


Figure 9. High concentration Methane sample, analyzed without heart cutting (the classical method). A large Methane peak is visible in the chromatogram, complicating trace detection for CO and CO₂

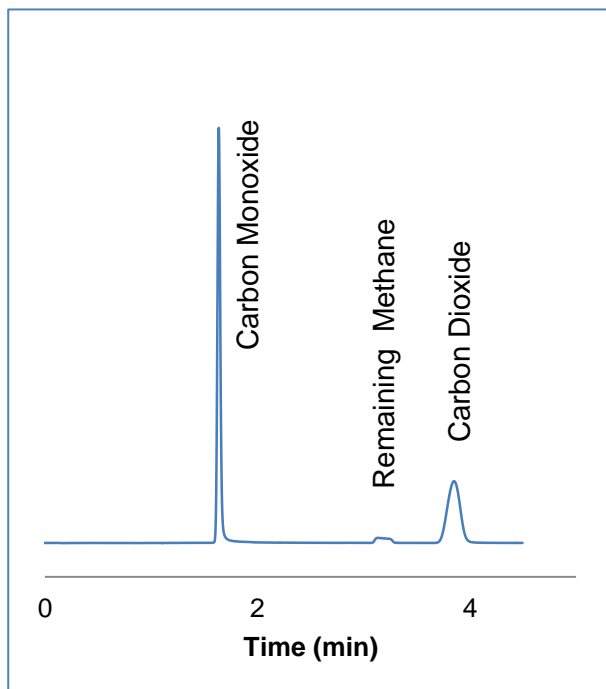


Figure 10. High concentration Methane sample, analyzed with heart cutting. Almost all methane is flushed to vent, ensuring longer lifetime and robust Methanizer performance

CONCLUSION

The AC UOP 603-13 analyzer is a specialized solution for determination of trace CO and CO₂ in hydrogen and light gaseous hydrocarbons analysis. Its performance exceeds UOP 603-13, thus allows accurate value determination.

The fact that the FID detector, well known for its stability and ruggedness, is used in combination with the AC Methanizer makes it very user friendly. Because only CO, CO₂ and (a part of) methane are directed to the analysis column, the analysis column is free of interfering components, providing unambiguous identification and quantitation. High boiling hydrocarbons are back-flushed and directed to vent for a fast analyses in under 5 minutes.

AC Analytical Controls[®] has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer[®], DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.