Analysis of low ppb CO and CO_2 using the Low Level CO/CO_2 Analyzer

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Introduction

The Varian 450-GC CO/CO_2 Analyzer is a standard turnkey solution for the analysis of carbon monoxide, methane and carbon dioxide. These components are separated from various gaseous hydrocarbon matrices. The instrument is specially suited for sub ppm levels of CO, CH_4 and CO_2 in hydrocarbon matrices such as ethylene or propylene.

To further enhance the detection limit a second configuration was developed using a 10 mL sample loop and a different column set able to accommodate large sample amounts. With this setup a detection limit of low ppb levels of CO can be achieved.

Instrumentation

The Varian Low Level CO/CO_2 Analyzer is 450-GC based and includes a gas sampling valve, two high performance packed columns, a methanizer to convert CO and CO_2 into methane and a Flame Ionization Detector (FID) (Figure 1).

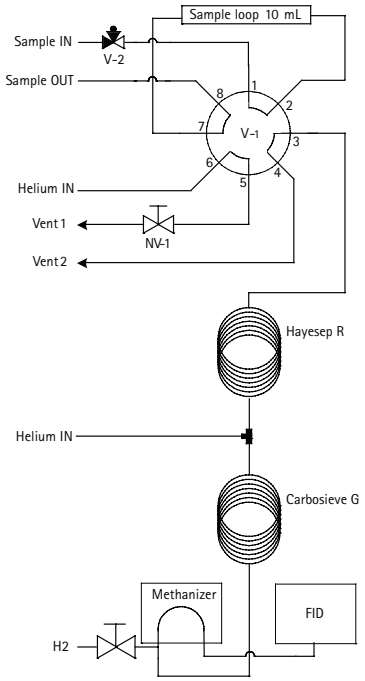

Figure 1. Low level CO/CO_2 analyzer configuration.

The sample is injected onto the system via a gas sampling valve equipped with a sample loop. In the first column the volatile components through carbon dioxide are separated from the higher boiling components. These higher boiling components are back flushed to vent.

Conditions

Carrier Gas:	Helium, settings are factory tuned
Column Oven:	50 °C
Valve Oven:	100 °C
Detector:	Methanizer 400 °C, FID 200 °C

Table 1. Valve and event table.

Time (min)	Inj + Bfl to Vent	Sample
Initial	Fill + Bfl	Off
0.01	Fill + Bfl	On
1.80	Fil + Bfl	Off
2.00	Inject	Off
3.50	Fil + Bfl	Off

Results and Discussion

In order to show the improvement in detection limit 5 ppm CO, CH_4 and CO_2 in ethylene were analyzed with the standard analyzer and with the low level analyzer

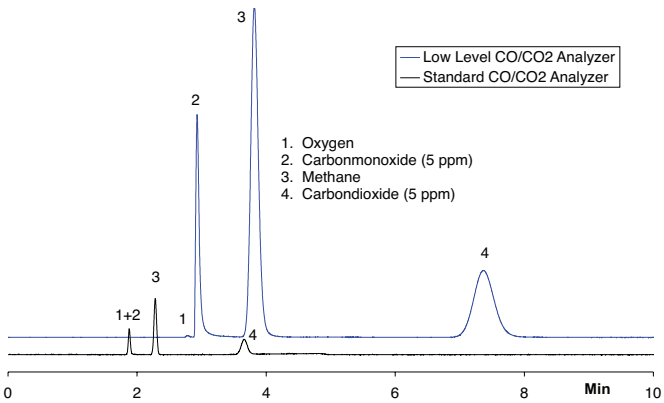

Figure 2. 5 ppm CO and CO_2 in ethylene on two analyzer configurations.

In Table 2 the Limit of Detection (LOD) and Limit of Quantification (LOQ) is calculated. The LOD uses a signal to noise ratio of 3. The LOQ uses a signal to noise ratio of 5.

Table 2. LOD and LOQ calculations.

Standard configuration

Component	*Concentration (ppm)*	*Peak Height*	*Noise*	*S/N*	*S/N=3 LOD (ppb)*	*S/N=5 LOQ (ppb)*
CO	5	1511	14.33	105.4	142	237
CH4	5	3251	14.33	226.9	66	110
CO2	5	893.9	14.30	62.5	240	400

Low level configuration

Component	*Concentration (ppm)*	*Peak Height*	*Noise*	*S/N*	*S/N=3 LOD (ppb)*	*S/N=5 LOQ (ppb)*
CO	5	25767.6	15.16	1699.7	9	15
CH4	5	38366.2	15.16	2530.8	6	10
CO2	5	7720.8	15.16	509.3	29	49

Table 2 clearly shows the improved LOD and LOQ of the low level configuration. For example, the LOD for CO on a standard system is 142 ppb; on the low level configuration the LOD for CO is 9 ppb. This is an improvement by a factor of 15 compared to conventional approaches. Methane and CO_2 show somewhat less improvement as the peaks appear later in the chromatogram and thus have decreased peak heights. Nevertheless, the improvement here is also clear, by a factor of 8 to 11.

Another advantage of the low level configuration is that oxygen is separated from carbon monoxide. When oxygen passes through the methanizer, small amounts of an FID detectable gas are formed. With this low level configuration, separation is complete, making low level detection of carbon monoxide possible.

Figure 3 shows the analysis of CO, CH_4 and CO_2 in a propane sample.

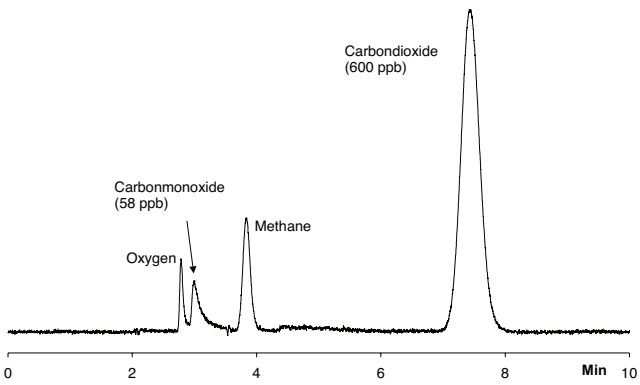

Figure 3. Analysis of gases in a propane sample.

Figure 3 depicts the excellent separation of oxygen and carbon monoxide. Oxygen cannot be quantified as the conversion in the methanizer is not controlled and varies depending on the contamination of the methanizer.
The analysis of another ethylene sample is shown in Figure 4. Again, excellent separation of all components and analysis at low ppm level are evident.

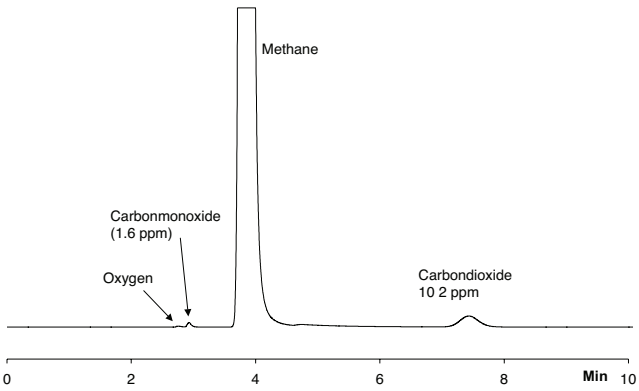

Figure 4. Analysis of gases in an ethylene sample.

The ethylene sample in Figure 4 was analyzed many times. Repeatability data are presented in Table 3 and Figure 5.

Table 3. Repeatability figures for an ethylene sample.

Run #	*Area CO*	*Area CH4*	*Area CO2*
1	37146.9	82992602.7	346293.8
2	36936.7	83168836	349159.6
3	36543.9	83355460.2	343262.5
4	36521.7	83498650.9	348612
5	36379.5	83662589.5	363218.5
6	36164.3	83667561.7	366011.7
7	35816.3	83724241.2	366008.4
8	35750	83647514.4	358569.8
9	35468.7	83446499.2	352556.4
10	35211.6	83428913.7	353663.9
11	35006.6	83162642.7	357820.8
12	34761.6	83021134.6	357907.7
13	34637.7	82922018.9	353037.4
14	34442.6	82751570.7	359377.6
15	34245.6	82549036.6	364962.9
Average	**35668.9**	**83266618.2**	**356030.9**
Std Dev	**932**	**363234**	**7279**
Rsd %	**2.61**	**0.44**	**2.04**

A relative standard deviation of 2.61 for CO, 0.44 for CH_4 and 2.04 for CO_2, clearly shows the suitability of the low level CO/CO_2 analyzer for these types of samples.

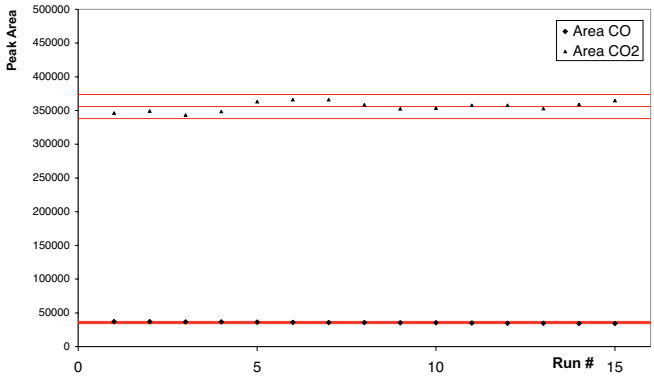

Figure 5. Repeatability data from Table 3 with 5% variation limits.

In Figure 5 the repeatability data of CO and CO_2 peak area is plotted with 5% variation limits. All values are nicely within these limits.

Figure 6 shows the analysis of a propylene sample. Again, separation is good. In this case low ppm range concentrations of CO, CH_4 and CO_2 are revealed.

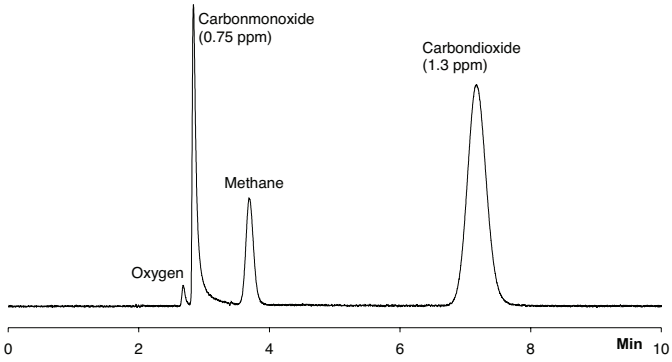

Figure 6. Analysis of gases in a propylene sample.

Conclusion

The development of a specially configured 450-GC based CO/CO_2 analyzer achieves detection limits of low ppb in the analysis of carbon monoxide, methane and carbon dioxide in various gaseous hydrocarbon mixtures.

The improvement with respect to the standard CO/CO_2 analyzer varies by a factor of 8 - 15, depending on the component of interest.

Repeatability of such a system is very good, with a relative standard deviation of approximately 2%.

These data represent typical results.
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