

Using a Methanizer for CO and CO₂ Analysis at Low Levels

By Mark Badger

Accurate carbon monoxide (CO) and carbon dioxide (CO₂) analysis is critical in many industries, ranging from food and beverage applications to a multitude of petrochemical methods. In most cases these gases are in the percent range and can easily be analyzed using techniques such as GC-TCD. However, if sample concentrations are below 100 ppm, they may be below the detection limits of a TCD. In this case, less common, more expensive detectors—such as BID, HID, or PDD—can be used instead. But, using a methanizer with an FID is a better alternative because FIDs are ubiquitous in labs around the world, and this combination allows for the analysis of CO and CO2 at ppb levels.

Methanizers are a simple, well-established way to catalytically convert CO and CO2 to methane (CH4), which can then be detected at very low levels using an FID. Here's how it works: First, a gas sample is introduced into the GC and separated on the analytical column. Then, when the sample elutes from the column, it is passed over a hot nickel-based catalyst in the presence of hydrogen, where the main reactions are the reduction of CO and CO2 to CH4. Conversion is most efficient at 380 °C, so the catalyst tube is located within a heated, insulated chamber that maintains a constant temperature.

CO + nH2
$$\frac{catalyst}{}$$
 CH4 + non-carbon byproducts $\frac{}{}$ Reaction 1 CO₂ + nH2 $\frac{}{}$ CH4 + non-carbon byproducts $\frac{}{}$ Reaction 2

Using a methanizer for CO and CO2 analysis is quite simple, and they require very little effort to maintain. However, as with any piece of equipment, there are some limitations: for methanizers, care must be taken to prevent poisoning the catalyst. Analysts should be aware that the following elements and compounds can deactivate the catalyst and take appropriate precautions:

- Hydrogen Sulfide (H2S), Sulfur Hexafluoride (SF6), and Other Sulfur-Containing Gases Very small amounts of H2S, SF6—and probably other sulfur-containing gases—cause immediate, complete deactivation of the catalyst. It is not possible to regenerate a poisoned catalyst that has been deactivated by sulfur using either oxygen or hydrogen treatment. If sulfur-containing gases are present in the sample, a switching valve should be used to bypass the catalyst or to backflush the column to vent after the elution of CO₂.
- Air and Oxygen (O2) Instances of oxygen poisoning a catalyst are reported from time to time, but in my experience, small amounts of air will not kill a catalyst; however, exposure to 5 cc/min or more will cause immediate, continual catalyst degradation. I have observed this firsthand on multiple systems during my 30 years of experience with a catalytic FID designed for analyzing U.S. EPA Method 25 and 25C samples.
- *Unsaturated Hydrocarbons*

Samples of pure ethylene will cause immediate, but partial, degradation of the catalyst, as evidenced by slight tailing of CO and CO2 peaks. The effect of a few samples might be tolerable, but since the effect is cumulative, such gases should be backflushed or bypassed. Samples of pure acetylene affect the catalyst even more severely than ethylene does. It is likely that with high concentrations of unsaturates some carbonization occurs, resulting in soot being deposited on the catalyst surface. (Aromatics would probably have the same effect.) Note that low concentrations of ethylene and acetylene have no effect.



Other Compounds

Water has no effect on the methanizer catalyst, as is also the case with various Freon compounds and ammonia (NH₃). Here again, with NH₃, there is conflicting evidence: some users have observed degradation after several injections, but other researchers could not confirm it. As with sulfur-containing gases, NH₃ can be backflushed to vent or bypassed if desired.

For laboratories interested in using a methanizer for CO and CO₂ analysis, several options are available. Some GC systems are equipped with built-in methanizers; however, if you only need to use a methanizer occasionally or if you want to retrofit one into an existing GC, then a separate aftermarket methanizer may be a better solution. Restek has developed modern, user-friendly methanizers for most Agilent GC-FIDs and Thermo Trace 1300/1310 GC-FIDs that can be coupled with any analytical column (capillary, micropacked, or packed), making them suitable for a wide range of applications. Visit www.restek.com/CH4izer for more details.



Specifications

Input Power Rating: 100-240 VAC, 50/60 Hz, 2.0 A
Operating Temperature Range for Control Box:
32–120 °F (0–48 °C)

Operating Temperature Range for Catalyst and Heater Chamber Assembly: 350–450 °C (factory preset at 380 °C) Controller Temperature Accuracy: ±1 °C

Warranty: 1 year Certifications: CE Compliance: WEEE, RoHS Indoor Use Only

Methanizer (CH4izer)

- Allows ppb-level GC-FID determination of CO and CO2 without expensive equipment.
- Precise temperature control ensures complete conversion of CO and CO₂ to CH₄.
- Simple, reliable operation—factory-set temperature (380 °C) can be adjusted with just the touch of a button.
- Convenient installation kit (sold separately) includes all parts needed for quick installation.
- Fast, easy catalyst tube replacement keeps maintenance time to a minimum.
- Includes methanizer control box, country-specific power cable, heater chamber, catalyst tube, hydrogen supply line, transition tubing, adaptor for capillary FID, adaptor for packed FID, ¹/₈" Swagelok nut and ferrules, and right angle wrench.

Low-level detection of carbon monoxide (CO) and carbon dioxide (CO₂) is critical for many applications. Restek's methanizer (CH4izer) allows ppb-level determination of CO and CO₂ using a cost-effective GC-FID instead of more expensive instrumentation. The methanizer is factory set to 380 °C to ensure efficient and complete conversion of CO and CO₂ to CH₄, but the operator can easily adjust the temperature as desired with the touch of a button. This unit controls temperatures precisely and reliably to within \pm 1 °C of the defined set point, and the actual temperature is displayed in real time on an easy-to-read monitor. The Restek methanizer is less cumbersome than other models and is designed for easy installation and fast catalyst tube replacement so you spend more time analyzing samples and less time on maintenance.

Description	Instrument	qty.	cat.#
Methanizer, power cable for U.S./Japan	for Agilent GC-FIDs	kit	22650-US
Methanizer, power cable for Europe	for Agilent GC-FIDs	kit	22650-EU
Methanizer, power cable for Australia	for Agilent GC-FIDs	kit	22650-AU
Methanizer, power cable for United Kingdom	for Agilent GC-FIDs	kit	22650-UK
Methanizer, power cable for China	for Agilent GC-FIDs	kit	22650-CN
Methanizer, power cable for U.S./Japan	for Thermo TRACE 1300/1310 GCs	kit	22651-US
Methanizer, power cable for Europe	for Thermo TRACE 1300/1310 GCs	kit	22651-EU
Methanizer, power cable for Australia	for Thermo TRACE 1300/1310 GCs	kit	22651-AU
Methanizer, power cable for United Kingdom	for Thermo TRACE 1300/1310 GCs	kit	22651-UK
Methanizer, power cable for China	for Thermo TRACE 1300/1310 GCs	kit	22651-CN



Accessories for Methanizers

Description	qty.	cat.#
Installation Kit for Methanizer (includes: $^{1}/8$ " Stainless-steel metering gas valve, 10 ' x $^{1}/8$ " 304 stainless-steel gas supply line (rinsed and cleaned), $^{1}/8$ " Swagelok tee union, $^{1}/8$ " tube end reducer, $^{1}/8$ " stainless-steel Swagelok ball shutoff valve, MINICYL regulator with $^{1}/8$ " fittings)	kit	27213
Hydrogen Supply Line	ea.	27208
Catalyst Tube	ea.	27209
Heater Chamber	ea.	27210
Adaptor for Capillary FID	ea.	27211
Adaptor for Packed FID	ea.	27212



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