

Real-Time ppt-Level Analysis of CO, CO₂ and CH₄ in Semiconductor UHP Gas

HALO Max QCL CO · HALO Max QCL CO₂ · HALO KA Max CH₄

GASES & CHEMICALS

CEMS

ENERGY

SEMI & HB LED

ATMOSPHERIC

LAB & LIFE SCIENCE

Optical Analysis Beyond Moisture

Spectroscopic gas analyzers based on Cavity Ring-Down Spectroscopy (CRDS) have dominated trace H₂O analysis in semiconductor and UHP gas applications for many years due to their ppt-level sensitivity, reliable 24/7 operation, and extremely low cost of ownership. In 2013, SEMI F-112 established CRDS as the method of choice for trace moisture analysis, cementing its position in the industry. The success and the significant cost savings attributed to the use of CRDS for moisture analysis has recently prompted semiconductor manufacturers to look into expanding the use of CRDS for other analytes, such as CO, CO₂ and CH₄. Until recently, the necessary sub-ppb-level sensitivity could not be achieved for these trace molecules, requiring the industry to keep relying on gas chromatography (GC), which offers the necessary sensitivity, but has significant downsides in terms of complexity and operational cost. Now, a new generation of CRDS instruments based on the latest mid-infrared Quantum Cascade Laser (QCL) technology offers the opportunity to replace GCs with reliable CRDS analyzers.



Fig. 1 Illustrations of the HALO KA Max CH₄ (top) and the HALO Max QCL CO (bottom) analyzers

Introducing the HALO Max QCL Family

With the new HALO Max QCL family, Tiger Optics offers, for the first time, a CRDS analyzer based on mid-infrared technology. A continuous-wave QCL serves as the instrument's light source. The ability to access the mid-infrared spectral region comes with a massive increase in detection sensitivity for certain molecules, which include CO and CO₂, but also N₂O, HBr and many others. As one can see in Table 1, the QCL-based detection limits for CO and CO₂ are as much as about a thousand times lower than Tiger's near-infrared analyzers for CO and CO₂; the mid-IR detection limits range between 100 and 200 ppt in typical semi bulk gases.

For a complete detection system for all three light carbon compounds, the HALO KA Max CH₄ is the perfect addition to the HALO Max QCL series. The KA Max is based on Tiger's latest near-infrared analyzer platform and offers detection limits in the range of 500 ppt and below.

Figure 1 shows pictures of both analyzer types: The HALO KA Max CH₄ comes in Tiger's typical space-saving half-rack design, allowing side-by-side mounting of two units in one 19" rack slot. The HALO Max QCL is a full 19" rack slot and has integrated mounting holes for straightforward rack installation.

Table 1. HALO Max QCL and KA Max detection limit (LDL, 3σ) summary

Background Gas	HALO Max QCL CO	HALO Max QCL CO ₂	HALO KA Max CH ₄
N ₂	200 ppt	100 ppt	500 ppt
O ₂	170 ppt	90 ppt	500 ppt
CDA	200 ppt	100 ppt	500 ppt
Ar	150 ppt	80 ppt	450 ppt
He	130 ppt	90 ppt	400 ppt
H ₂	200 ppt	200 ppt*	500 ppt

*pending experimental verification

Comparison to Gas Chromatography

Until now, most ultra-trace CO, CO₂ and CH₄ analyses have been performed using gas chromatographs (GCs). To measure analytes in the sub-ppb range, specially configured GCs with plasma emission detection (PED) are the standard in the industry because they offer superior sensitivity compared to GCs with flame ionization detection (FID). The demanding detection limits, however, necessitate the use of He carrier

gas, which is expensive, especially at the purity grade and flow rate required by GC/PED. In addition, GCs require a significant amount of maintenance, as well as regular and frequent calibration. This means that the cost of ownership will exceed the initial cost of the instrument many times within a few years; and the seeming advantage of analyzing multiple species with one analyzer also means that—in case of instrument downtime—all detections become unavailable rather than only a single one. In addition, GC measurements can only be performed in batches and take several minutes per batch, making continuous, real-time monitoring impossible.

Both the cost of ownership and the continuous measurement aspects are significant advantages of CRDS-based analyzers, which neither require expensive utility gases nor regular maintenance & calibration. Although one analyzer per analyte is required, the almost complete lack of operational costs makes it possible to recuperate the initial investment within a few years. With an expected service life of the analyzer of at least 10–15 years, the overall cost savings are significant, not to mention the convenience of having analyzers that deliver hassle-free, continuous and reliable measurements around the clock. Table 2 summarizes the main points of comparison between GC/PED and CRDS.

Table 2. Comparison between Gas Chromatograph and CRDS

Specifications	Gas Chromatograph	Tiger Optics CRDS Analyzer
Detection Type	GC with PED (plasma emission detector)	All-optical CRDS
Measurement	Batch analysis, as long as 20 min of analysis time per batch	Continuous online measurement with response in seconds
Analytes	Measures multiple analytes (column-dependent)	Each analyzer optimized for a specific analyte
Carrier Gas	Helium (typical)	None
Cost of Ownership	High due to helium gas, replacement columns, labor cost for frequent calibration	minimal—no replacement parts or labor cost (CO ₂ unit only requires N ₂ purge gas)
Detection Limits	0.5 to 0.8 ppb (with He carrier gas)	0.1 to 0.5 ppb (gas & analyte dependent)
User Skill Level & Labor Intensity	Experienced user needed, frequent calibration required	Simple touchscreen operation requires no special skills, no regular maintenance

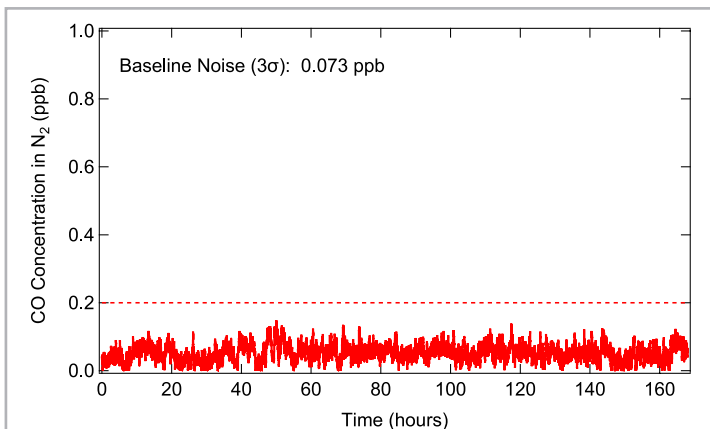


Fig. 2 Baseline performance of the HALO Max QCL CO in N₂ (1 week).

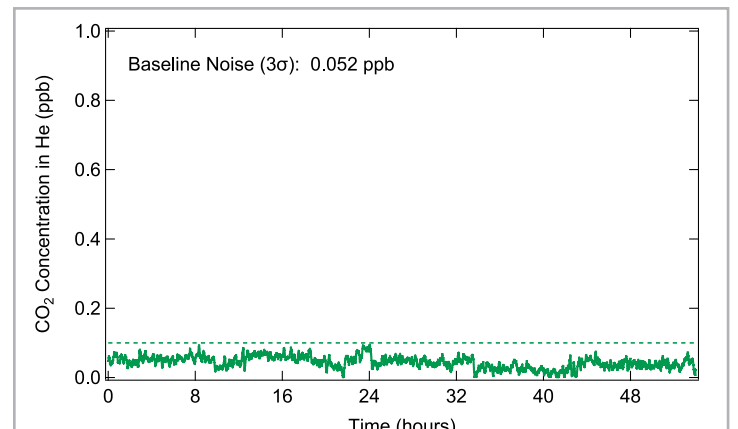


Fig. 4 Baseline performance of the HALO Max QCL CO₂ in He.

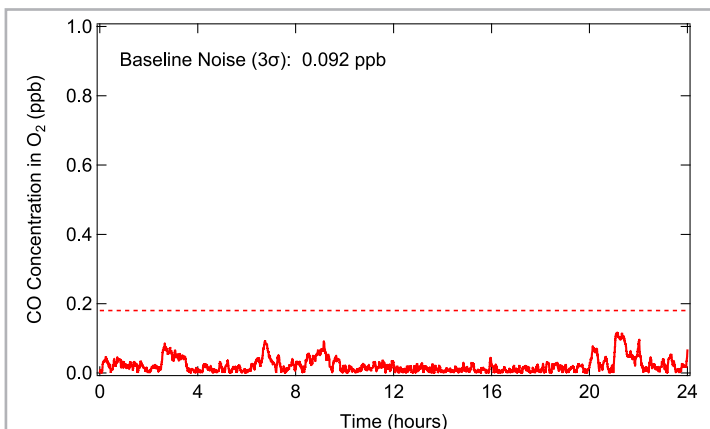


Fig. 3 Baseline performance of the HALO Max QCL CO in O₂.

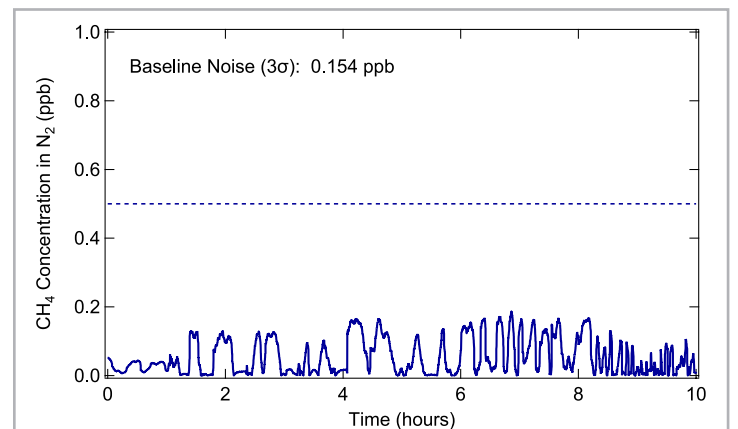


Fig. 5 Baseline performance of the HALO KA Max CH₄ in N₂.

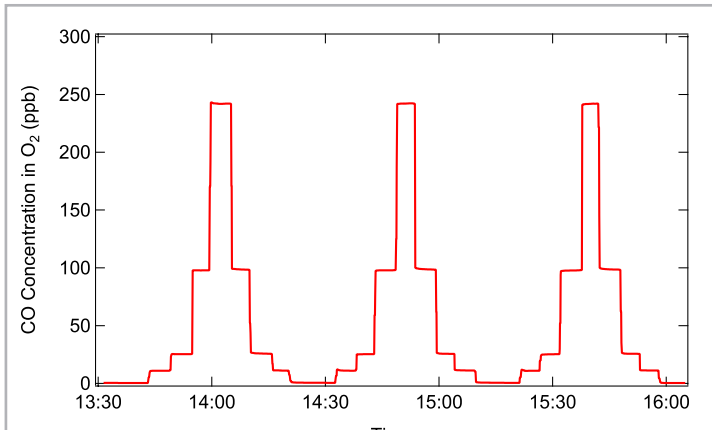


Fig. 6 Three repeated HALO Max QCL CO step intrusions in O₂.

HALO Max QCL and HALO KA Max Performance

Extensive tests were conducted to highlight the performance of the new analyzer models for CO, CO₂ and CH₄ detection at sub-ppb levels. To demonstrate the detection limit capabilities (the most critical performance parameter) of the three analyzers, zero gas data was collected in N₂, O₂, Ar and He for timeframes of several hours up to an entire week. Figures 2 to 5 shows zero gas results for all three analytes with the specified LDL plotted as dashed line in each graph. Furthermore, step intrusion tests were also performed to test for speed of response, measurement repeatability and linearity. In this application note, we focus on a few typical examples for each of these measurement results, but all analyzers have successfully completed the entire set of experiments.

Zero Data and LDL Verification

Figures 2 and 3 show zero performance for the HALO Max QCL CO in nitrogen and oxygen. The data in N₂ highlights the analyzer's excellent baseline stability over an entire week. The 3 σ -noise of 73 ppt is well below the guaranteed specification of 200 ppt. The zero-CO data in O₂ also shows performance well below the LDL specification (180 ppt) with a 3 σ -noise of 92 ppt over 24 hours.

Figure 4 shows the baseline performance of the HALO Max QCL CO₂ in helium over more than two days, with a 3 σ noise of 52 ppt, well below the guaranteed LDL specification of 100 ppt. Note that for O₂ and N₂ (not shown here), measurements reveal similar performance, and the LDL specification is also 100 ppt.

Finally, zero baseline performance of the HALO KA Max CH₄ in N₂ is shown in Figure 5. Over these 10 hours of data, the 3 σ -baseline noise is 154 ppt, which considerably exceeds the 500 ppt guaranteed LDL.

In summary, the baseline tests performed with various background gases in all three systems confirm that CO, CO₂ and CH₄ can be detected in typical semi bulk gases, such as N₂, O₂, Ar or He with a sensitivity that far exceeds typical GC capabilities while delivering data in real-time at a much lower cost of ownership. Figures 2 to 5 demonstrate, in particular, the

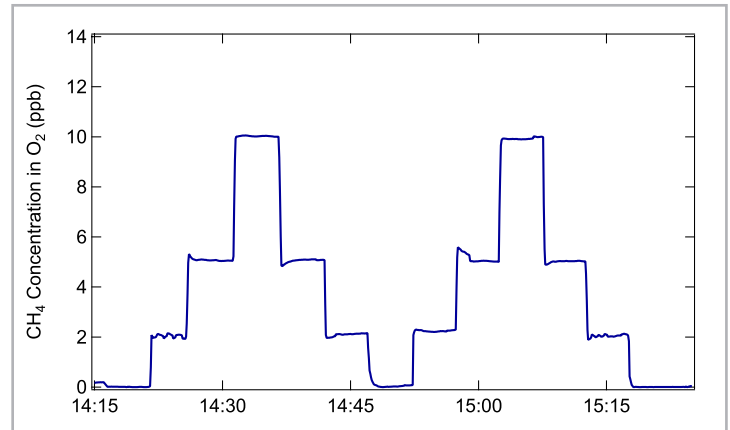


Fig. 7 Back-to-back HALO KA Max CH₄ low-level step intrusions in O₂.

excellent drift-free baseline stability of Tiger's CRDS systems over any timeframe, be it hours, days or weeks.

Step Intrusion Data

Extensive step intrusion testing was performed for all systems in different background gases. Here, we show two examples in O₂, including a linearity analysis for CO detection.

Figure 6 shows step intrusion data for CO in O₂ using the HALO Max QCL CO. The nominal intrusion levels used are 10 ppb, 25 ppb, 100 ppb, and 250 ppb. Each step is 5 min and the entire step pattern is repeated three times. The graph illustrates the analyzer's flawless performance with a response time for each concentration change below 1 min, as well as excellent repeatability from one step pattern to the next. As an example, the six 100-ppb steps measure an average concentration of (98.2 \pm 0.5) ppb, not only agreeing well with the expected concentration of 98.6 ppb[†], but also showing an outstanding repeatability of 0.5%, even though the steps include both directions, which is typically more challenging than a

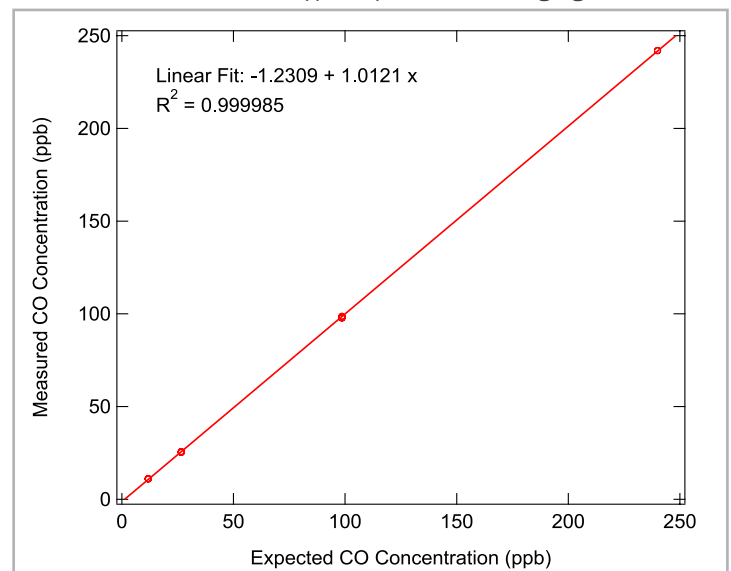


Fig. 8 Typical example of a CRDS linearity plot taken from CO step intrusions shown in Figure 6.

[†]The expected concentration is calculated from the certified cylinder concentration and the actual ratio of the dilution system and may not match the nominal level exactly.

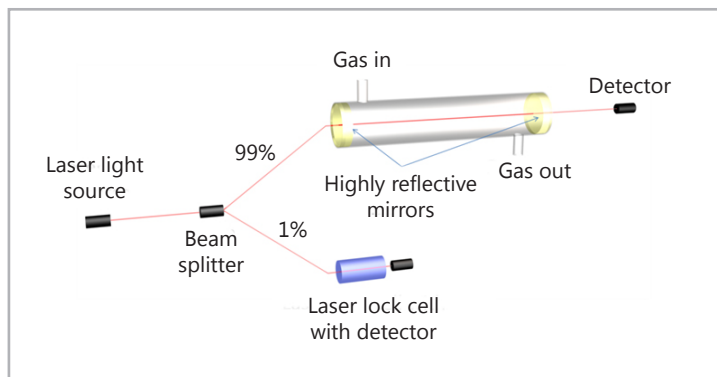


Fig. 9 Principle of CRDS

unidirectional step intrusion due to the fact that the sampling system can contribute to a hysteresis effect.

The step intrusion data for the HALO KA Max CH₄ (see Figure 7) focuses on a narrower range of concentrations in the low-ppb range. In back-to-back up-and-down step patterns, the concentration levels are 2 ppb, 5 ppb, and 10 ppb. Again, the analyzer is able to reproduce the intrusion steps extremely well and shows near-instant response to a change in concentration. Taking the 5-ppb data as an example, the average concentration measured is (5.060 ± 0.022) ppb, which is an excellent repeatability of 0.43% at a level that is only a factor of ten above the analyzer's LDL.

In conclusion, the step intrusion tests show that all-optical CRDS offers near instant response with outstanding repeatability. Furthermore, the step intrusion data can be used to infer the analyzer linearity. As an example, we take all the measurements from the step intrusion of CO in O₂ (shown in Figure 6) and plot measured versus expected concentration results in the graph depicted in Figure 8. The linear fit has an R² value of 0.999985, which denotes almost perfect linearity and is actually very typical for any CRDS measurement.

Cavity Ring-Down Spectroscopy

All Tiger Optics instruments are based on CRDS. The key components of the CRDS system are shown in Figure 9.

CRDS works by tuning laser light to a unique molecular fingerprint of the sample species. By measuring the time it takes the light to decay or "ring-down", you receive an accurate molecular count in milliseconds. The time of light decay, in essence, provides an exact, non-invasive, and rapid means to detect contaminants.

Tiger Optics Overview

Founded in 2001, Tiger Optics has been the preferred provider for high-performance, laser-based gas analyzers to advance industrial standards and enable cutting-edge research. By leveraging the expertise of scientists, engineers and industry specialists, we offer advanced total solutions, field support, analyzer training, and advice to help customers improve yields and reduce costs. By creating out-of-the-box solutions that deliver fast, reliable and stable measurements, Tiger Optics supports continuous innovation for gas & chemical production, semiconductor fabrication, and many other markets.

First ISO-Certified CRDS Company

Tiger Optics is the first CRDS company certified to the ISO 9001:2008 and the current ISO 9001:2015 standard of process consistency and continuous quality improvement.



©Tiger Optics, LLC · Ver. 10/2021

Tiger Optics, LLC

275 Gibraltar Road, Horsham, PA 19044
 Phone: +1 (215) 656 4000 · Fax: +1 (215) 343 7168
 sales@tigeroptics.com · www.tigeroptics.com