Carbon Monoxide Gas Sensing Technologies in Combustion Process

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Abstract: Three major carbon monoxide gas sensing technologies for combustion environment are reviewed with many theoretical and practical aspects, test results as well as basic operation details. A comprehensive CO gas sensing technologies review is supported with the latest development trends. Performance and applications options for carbon monoxide measurements in the process using calorimetric catalytic, mixed potential electrochemical CO-sensor with zirconia solid electrolyte and tunable diode laser (TDL) or quantum cascade lasers (QCL) spectroscopy for CO measurements are discussed for the applications in power generation, chemicals production, heating, process control, safety, and quality. Special attention is given to the technologies application limits and analyzer’s system requirements.

Keywords: Combustion analysis, Flue gas, Carbon monoxide gas sensing, Calorimetric catalytic CO sensor, Mixed potential CO-sensor, Tunable Diode Laser Spectroscopy (TDLS), Quantum Cascade Laser Spectroscopy (QCLS).

1. Introduction

In the regular combustion process, hydrocarbon fuel (C_{x}H_{y}) would react with oxygen (O_{2}) producing primarily two major products, carbon dioxide (CO_{2}) and water (H_{2}O) with traces of other gases, e.g., sulfur dioxide (SO_{2}), and nitrogen oxides (NOx) formed from nitrogen oxidation and fuel impurities. The oxygen is measured to optimize the combustion process efficiency, to control the product formation and quality, and to minimize runaway combustion leading to an explosion. Oxygen excess in the combustion is measured in the flue gas to control the ideal safe minimum of oxygen and process efficiency. Zirconia oxygen potentiometric technology was applied with very good success in the combustion control of power generation boilers, hot stoves for steelmaking, heating and combustion exhaust gas control of coke ovens for steelmaking, lime and cement kilns combustion control, incinerator combustion control, combustion control of heating furnaces for oil refinery and petrochemical industry and many other applications.

After 45 years, zirconia potentiometric oxygen gas sensing technology is still dominating the combustion market with high reliability, accuracy in the majority of applications and relative low price compared to other technologies [1-3]. Combustion control is mostly accomplished with O_{2} measurement alone and an improved combustion efficiency and stability can be achieved with the concurrent measurement of carbon monoxide, CO. Operation at ~100...200 ppm CO levels and ~1-2 % of oxygen depending on the fuel type would indicate conditions near the stoichiometric point with the highest efficiency in safe operation.
mode (Figs. 1-2). An in-situ, part per millions (ppm) combustible gas measurement in the real process environment with significant temperature and pressure variation would be highly challenging and often not quite reliable limiting most of the combustion analyzers available on the market to the extractive systems employing a flue gas sampling using an eductor driven with compressed air [4]. Some flue gas conditioning, like particle filtering and temperature/flow stabilization, would benefit these measurements reliability in the challenging combustion process flue gas environment.

There are three comprehensive carbon monoxide gas sensing technologies implemented so far in combustion analyzers on the market: calorimetric catalytic, mixed potential electrochemical with oxygen ion conducting zirconia solid electrolyte, and Tunable Diode (TD) or Quantum Cascade (QC) Laser Spectroscopies.

![Figure 1](image1.png)

**Fig. 1.** Combustion control with CO breakthrough scenario at coal fired power plant using O₂ & CO regulation.

![Figure 2](image2.png)

**Fig. 2.** Coal fired power plant flue gas diagram with O₂ or O₂ & CO regulations.
2. Calorimetric Catalytic CO Gas Sensing Technology

For the extractive type combustion analyzers, an advanced calorimetric CO-sensor was developed by several analytical corporations utilizing combustible reaction heat on a special selective catalyst film over the resistance temperature detector (RTD) implemented for the temperature measurements [5-6]. The catalyst material in calorimetric CO-sensor was initially based on Hopcalite®, a commercial catalyst mixture of copper and manganese oxides for CO catalytic oxidation. Unfortunately, this catalyst was showing very short life in severe combustion process environment and was replaced by more reliable platinum group catalyst using a glass coating for protection in processes containing sulfur oxides. The catalyst film was merged with RTD using highly thermally conductive packaging oxide materials to utilize more efficiently the heat transfer of the carbon monoxide combustion reaction in the flue gas to RTD. Catalyst film can be attached to metallic (Fig. 3) or ceramic substrate that is thermally connected to the RTD.

The catalytic film oxidizes carbon monoxide selectively in presence of other flue gas species. Developed calorimetric catalytic CO-sensors on the market are quite selective and cross sensitivity of a typical CO-sensor is summarized in Table 1.

Oxidation reaction occurs between combustible species and oxygen with defined heat released depending highly on the combustible concentration. Calorimetric catalytic CO-sensor can measure CO-concentration down to ppm level with detection limit ~5…10 ppm CO. This technology is employed in Rosemount Measurement and Analytical (USA), Servomex (GB), Ametek (USA) and ABB (Swiss) extractive combustion analyzers permitting fast and precise <±25 ppm CO (Fig. 4) or 5 % of the reading measurements in flue gas up to ~1750°C temperature.

Calorimetric catalytic CO-sensor has good >99.9 % linearity in a wide CO concentration range up to 2.5 % CO concentration (Fig. 5) but to improve accuracy a calibration would be always recommended using upper limit of CO concentration measurement range. Calorimetric catalytic CO-sensor is highly flow sensitive and gas flow stabilization and a flow sensor should be implemented to improve CO-sensor reliability in extractive combustion analyzer.

However calorimetric catalytic CO sensor also has sensitivity to other combustible gases, especially to hydrogen, H₂ (see Table 1) and unsaturated hydrocarbons. An industrial combustion analyzer is always measuring carbon monoxide equivalent, COₐ proven to be sufficient for the combustion process control. Considering the flow and temperature sensitivity of the catalytic CO-sensor, gas temperature conditioning of incoming flue gas and precise internal flow and temperature control in the analyzer should be implemented. An in-situ process application for this type of sensor was proven to be much less precise and should be avoided because of the flow and temperature fluctuation in the process affecting catalytic CO combustion reaction speed and compromising sensor reading.

Calorimetric catalytic CO-sensor has shown a good reproducibility (Fig. 6), stability in modulated combustion flue gas (Fig. 7) and was evaluated with some good success even in dusty high sulfur (up to 0.4 % SO₂) combustion flue gas environment at a coal fired power plant (Fig. 8).


Mixed-potential gas sensing technology employing oxygen ion conducting zirconia solid electrolyte and two different activity electrodes was invented by Sandler in 1976 [7] and was proposed for the detection of combustible gases. The presence of CO or any other combustible species effects well known zirconia oxygen sensor signal and two competing reactions on electrodes.

Table 1. Calorimetric catalytic CO-sensor typical cross-sensitivity.

<table>
<thead>
<tr>
<th>Gas of interest</th>
<th>CO-sensor cross sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2 : 1</td>
</tr>
<tr>
<td>O₂</td>
<td>1 : &gt;10,000</td>
</tr>
<tr>
<td>SO₂</td>
<td>1 : &gt;1000</td>
</tr>
<tr>
<td>NOₓ</td>
<td>1 : &gt;1000</td>
</tr>
<tr>
<td>CH₄</td>
<td>1 : &gt;20,000</td>
</tr>
<tr>
<td>H₂O</td>
<td>1 : &gt;1000</td>
</tr>
</tbody>
</table>
Fig. 4. Rosemount calorimetric catalytic CO-sensor response and stability.

Fig. 5. Rosemount calorimetric catalytic CO-sensor linearity.

Fig. 6. Calorimetric catalytic CO-sensor reproducibility.
Oxygen reduction and CO or other combustible species oxidation would establish mixed potential highly depending on CO concentration (Fig. 9). This developed mixed potential depends mostly on the electrodes electrochemical and catalytic activity, film morphology, and temperature. Various metals and metal oxide materials were investigated for sensitive electrodes in the mixed potential sensors in the past [8] and the gold metal was one of the most promising sensitive electrodes because of its low catalytic activity for the combustion and chemical stability in hazardous chemicals environment.

Mixed potential value depends on two competing reduction/oxidation reactions on catalytically inactive Au-electrode:

\[
\frac{1}{2}O_2(g) + V_O (SE) + 2e^-(Au) \leftrightarrow O^{2-}(SE), \quad (1)
\]

\[
CO(g) + O^{2-}(SE) \leftrightarrow CO_2(g) + V_O (SE) + 2e^- (Au) \quad (2)
\]

with \( V_O \) oxygen vacancy, \( O^{2-} \) oxygen ions in zirconia solid electrolyte (SE) and \( e^- \) electrons in Au-electrode.

Mixed potential will be affected by changes in electrode triple phase boundary (TPB) area, limited diffusion in the gas phase or electrode, limited absorption and interference of other gases in combustion process like H_2O, CO_2, SO_2, NO_x and O_2. Mixed potential CO-sensor with catalytically inactive electrode based on Au-alloy produces a repeatable signal (Fig. 10) with significant \( \pm 100 \) ppm CO impact by oxygen variation between 3 and 20 % O_2 (Figs. 11-12).

The gold film electrode re-crystallization and coarsening by temperatures over 500 °C will affect electrochemical triple phase boundary and sensitivity of the sensor, liming this electrode application at higher, over 500 °C temperature [9].
### Fig. 9. Mixed potential CO-sensor with two different activities electrodes.

<table>
<thead>
<tr>
<th>Models</th>
<th>Catalytically Active Equilibrium Electrode (Pt)</th>
<th>Catalytically Inactive Mixed potential Electrode (Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactions</td>
<td>$\Delta G(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$</td>
<td>$O_2(g) + O^{2-}(YSZ) \rightarrow CO_2(g) + V_{YSZ}^{2+} + 2e^-(Au)$</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}O_2(g) + V_{YSZ}^{2+}(YSZ) + 2e^-(Au) \rightarrow O^{2-}(YSZ)$</td>
<td>$E_{eq} = \frac{RT}{4F} \ln \frac{p(O_2)<em>{process}}{p(O_2)</em>{ref}}$</td>
</tr>
<tr>
<td>Equations</td>
<td>$E_{mix} = E_{eq} = C \ln (\phi(O_2))$</td>
<td>$E_{mix} = E_{eq} = C \ln (\phi(O_2))$</td>
</tr>
</tbody>
</table>

### Fig. 10. Mixed potential CO-sensor response and reproducibility.

### Fig. 11. Mixed potential CO-sensor response to 1000 ppm CO at different O2 concentrations.
CO-sensor with gold composite electrode (Fig. 13) especially with gallium oxide exhibits higher sensitivity to CO and long-term stability in combustion process environment even at higher temperature [10].

Unfortunately, mixed potential CO sensor signal is not linearly depending on CO concentration (Fig. 14) and a special polynomial calibration algorithm should be developed based on evaluation in different combustion processes. An oxygen correction algorithm applied to mixed potential CO-sensor signal using an extra oxygen concentration measurement input would improve CO measurement reliability in challenging oxygen concentration environment (Figs. 15-16).

Investigation with different catalytically inactive electrodes based on Au-alloy or Au-composite has shown that sulfur dioxide (SO2) and methane (CH4) can highly compromise the mixed potential CO sensor reading (Figs. 17-18).

**Fig. 12.** Mixed potential CO-sensor step response at 3 and 20 % O2.

**Fig. 13.** Scanning electron micrograph of Au-composite electrode film.

**Fig. 14.** Optimized mixed potential Au-composite electrode based CO-sensor signal dependence on CO concentration.
Fig. 15. Mixed potential CO-sensor signal dependence on oxygen concentration.

Fig. 16. Mixed potential CO-sensor with Au-composite electrode response and stability with oxygen correction.

Fig. 17. Au-alloy based mixed potential CO-sensor typical cross-sensitivity.
In many practical combustion applications, a removal of these interference gases using special chemicals, like lime for SO$_2$, would be required in sensor packaging or special gas filtering membranes or molecular sieves like zeolites [11-14] should be employed to reduce the interference. These membranes or molecular sieves would require an evaluation in combustion flue gas for their performance reliability and chemical stability in the challenging temperature and chemicals environment.

In some applications to reduce SO$_2$ cross interference a correction algorithm based on measured or known stable SO$_2$ concentration might be applied for more precise CO measurement.

A mixed potential CO-sensor prototype with Au-Ga$_2$O$_3$-composite electrode was packaged like Lambda sensor (Fig. 19) using CO-sensor chip and mechanical electrical contact.

This CO-sensor was installed in the Lambda sensor spot in the manifold of automotive engine Cummins ISF 109-167 PS with temperature recording and emission monitoring just next to the sensor. Extractive 5 channel Horiba MEXA 7500 CEMS analyzer was used for O$_2$, CO, CO$_2$, NO$_x$, C$_x$H$_y$ emission monitoring and the mixed potential CO-sensor output showed quite good agreement with an extractive CO measurement (Fig. 20).

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**Fig. 18.** Au-composite based mixed potential CO-sensor typical cross-sensitivity.

**Fig. 19.** Mixed potential CO-sensor prototype with Au-composite electrode.

**Fig. 20.** Au-composite based mixed potential CO-sensor evaluation in automotive engine.
After ~5h emission test in diesel engine, running in high concentration CO environment, mixed potential CO sensor was completely coated with the soot (Fig. 21) might be affecting CO-sensor reading in long term running, considering soot (carbon) oxidation to CO/CO\textsubscript{2} in with oxygen excess fuel lean running engine.

Based on evaluation results, mixed potential CO-sensor has practically negligible cross-interference to CO\textsubscript{2} or H\textsubscript{2}O and quite low interference with O\textsubscript{2} considering combustion flue gas oxygen concentration range to be between 2 and 5 % O\textsubscript{2}, depending on the fuel type used for combustion. Based on O\textsubscript{2}-sensor input signal, a correction related to the oxygen concentration using special algorithm could be implemented, improving the reliability of CO-sensor. Cross-sensitivity to SO\textsubscript{2} and CH\textsubscript{4} can be reduced by materials and microstructure optimization but this interference is still quite high to provide very reliable CO measurements in high concentration SO\textsubscript{2} environment. An algorithm related to SO\textsubscript{2} and H\textsubscript{2}O interference based on laboratory investigation was developed and with some success was evaluated at coal fired power plant with up to 0.2 % SO\textsubscript{2} concentration (Fig. 22).

There are two combustion analyzers on the market from Enotec GmbH (Germany) and Lamtec GmbH (Germany) with implemented mixed potential CO-sensor providing ~ ±25 % of the reading or ±5 % of full range, in-situ carbon monoxide equivalent, CO\textsubscript{eq}, measurements in very clean gas or light oil combustion applications.

4. Tunable Diode Laser (TDL) and Quantum Cascade Laser (QCL) Spectroscopies

Tunable Diode Laser Spectroscopy (TDLS) and Quantum Cascade Laser Spectroscopy (QCLS) are innovative optical measurement techniques utilizing semiconductor lasers to detect a variety of gases in the near infrared (IR) range [15] for the combustion measurements in (Fig. 23).

TDLS is highly distinguished from the conventional process photometry by the ability of the laser to be scanned across the narrow CO absorption peaks many times per second by trimming the current through the laser. With a typical scan in the range of 0.2...0.3 nm laser would provide much better resolution and selectivity.

Wavelength-modulation spectroscopy (WMS) has been increasingly applied to the measurements improving sensitivity and selectivity [17-18]. Sensitivity can be also improved using specific microstructures such as Hollow-Core Photonic Bandgap Fibres (HC- PBFs) or high Q cavities that provide longer absorption path lengths for the gases.

The second overtone band of CO near ~ 1.57 μm has been utilized commonly for measurements using inexpensive telecommunication type diode lasers. However, because of the weak line strengths and interference to carbon dioxide (CO\textsubscript{2}) and moisture
(H2O), always present in combustion process, the first overtone ro-vibrational band of CO near ~2.3 µm would provide a better detection limit free of interference. Specialty TDLs and Quantum Cascade Lasers (QCLs) have been utilized for CO-measurements. The IR absorption spectrum of carbon monoxide (CO) is like a fingerprint, providing CO identification at 1.57 µ, 2.33 µ (TDL) or 4.8 µ (QCL) and measurements in a wide concentration range down to ~0.5 ppm CO (TDL) or even ~10 ppb CO (QCL) as a detection limit.

Temperature and pressure variation in the process can introduce an extra error in the measurement and requires compensation. There are challenges with in-situ calibration for the systems employing internal reference cell because this reference cell is short and at different temperature compared to varying process temperature. IR light reflection at high temperature combined with wide background radiation from the fire box combined with process windows fouling might bring additional challenge in the application and might reduce the service life of the analyzer.

There are many quite accurate TDL/QCL Analyzers (Table 2) developed by Yokogawa (Japan), NEO Monitors (Norway), Focused Photonics Inc. (China), Rosemount Measurement and Analytical (USA), Mettler-Toledo (USA), Fuji Electric (Japan), Siemens (Germany), Servomex (GB) and Sick Maihak (Germany) with ~±1 % (2 % for in-situ) error for CO measurements. These analyzers are providing often dual CO and O₂ measurements in combustion environment across the duct or in-situ with CO detection limit being <1 ppm CO.

However, TDL Analyzers are very expensive and considering combustion process highly challenging temperature, pressure variation and flue gas turbulent flow, an in-situ CO calibration or validation would be highly recommended for all these analyzers.

5. Conclusions

Three major carbon monoxide gas sensing technologies, calorimetric catalytic, mixed potential with zirconia solid electrolyte and tunable diode laser (TDL) and quantum cascade laser (QCL) spectroscopies were employed in analytical instrumentation with some good success on the combustion market (Table 3).
Table 2. TDL and QCL CO Analyzers on the market.

<table>
<thead>
<tr>
<th>Company</th>
<th>Products</th>
<th>Detection limit</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yokogawa (Japan)</td>
<td>TDL8000</td>
<td>Application dependent</td>
<td>Across duct or extractive</td>
</tr>
<tr>
<td>Siemens (Germany)</td>
<td>SITRANS SL</td>
<td>0.6 ppm</td>
<td>Across duct or extractive</td>
</tr>
<tr>
<td>Focused Photonics Inc. (China)</td>
<td>LGA-4100, LGA-4500, LGA-3500</td>
<td>0.6 ppm</td>
<td>Across duct or extractive</td>
</tr>
<tr>
<td>NEO Monitors (Norway)</td>
<td>LaserGas II SP, LaserGas III SP</td>
<td>0.3 ppm</td>
<td>Across duct or extractive</td>
</tr>
<tr>
<td>Servomek (GB)</td>
<td>SERVOTOU GH LaserSP</td>
<td>0.3 ppm</td>
<td>Across duct or extractive</td>
</tr>
<tr>
<td>Sick Maihak (Germany)</td>
<td>GM901 CO</td>
<td>N/A</td>
<td>In-situ (&lt;430°C)</td>
</tr>
<tr>
<td>Mettler-Toledo (USA-Swiss)</td>
<td>TDLs GPro 500</td>
<td>1 ppm</td>
<td>In-situ (&lt;250°C)</td>
</tr>
<tr>
<td>Rosemount Measurement and Analytical (USA)</td>
<td>CT5800</td>
<td>0.05 ppm</td>
<td>Extractive</td>
</tr>
</tbody>
</table>

Table 3. Performance and application summary of major carbon monoxide gas sensing technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Temperature (T) and Pressure (P) effect</th>
<th>Major applications</th>
<th>Cost with installation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorimetric catalytic, Extractive</td>
<td>Fixed temperature, Minor P effect, Flow sensitive</td>
<td>Power generation, Middle to large boilers, Petrochemical industry</td>
<td>~$20 k for CO and O2 Analyzer</td>
</tr>
<tr>
<td>Mixed potential zirconia, In-situ</td>
<td>Temperature &amp; Pressure sensitive</td>
<td>Natural gas and light oil application mostly</td>
<td>~$5-10 k for CO Analyzer</td>
</tr>
<tr>
<td>TDLs/QCL Extractive, across the duct, in-situ</td>
<td>T &amp; P algorithms T &amp; P fluctuation effect?</td>
<td>Petrochemical industry, High temperature furnaces</td>
<td>~$100 k for CO and O2 Analyzer</td>
</tr>
</tbody>
</table>

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