

COMPARATIVE INVESTIGATION OF SEMICONDUCTOR AND ELECTROCHEMICAL CELL SENSORS PERFORMANCE FOR CARBON MONOXIDE EMISSIONS MONITORING FROM COMBUSTION PROCESSES

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Abstract. The work described in this paper is concerned with the implementation of semiconductor sensors for the continuous monitoring of carbon monoxide emissions from combustion devices with the emphasis on the comparative investigation of semiconductor and electrochemical cell sensors performance. The mechanisms of operation of both sensors are briefly explained. The calibration results and the measurements of CO concentrations in the flue gases of a purposefully built propane/air burner are given in order to compare the sensors performance. The CO sensor requirements for flue gas analysis are considered and compared with the sensors technical characteristics. It was found that both types of sensors satisfy CO monitoring requirements. The outstanding advantage of the semiconductor sensor is its low cost.

Keywords: flue gas monitoring, carbon monoxide, semiconductor sensors, electrochemical cell.

AIMS AND BACKGROUND

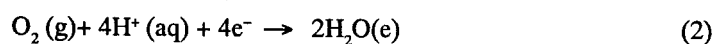
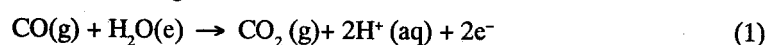
Pollutant emissions from combustion devices have been of environmental concern for many years. As far as CO and NO_x are concerned, the mechanism of CO oxidation is far better known due to its relative simplicity¹. Therefore, research on the reduction of NO_x emissions has dominated in literature over the last decade. Combustion techniques that can result in reducing CO and NO_x emissions to legal limits are well developed and widely applied. Unfortunately, combustion techniques, which are beneficial in NO_x emissions reduction generally, have an adverse effect on CO and particulate emissions levels. On the other hand, combustion efficiency should be maximized and consequently the overall excess oxygen level should be low. This may in turn cause a significant rise of CO emissions if the flue gas monitoring devices are absent or if control is poor, particularly for

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smaller combustion units. In addition, malfunctioning of the components of the burner systems and poor maintenance can severely affect CO and soot emissions. Thus, optimum use of a combustion device may be achieved by real time monitoring and controlling the significant relevant parameters. As far as CO monitoring is concerned, the relatively high cost of standardized instrumentation, e.g. infra-red analyzers, and the legislative requirements for smaller combustion units, which do not include CO monitoring, are clearly discouraging factors. In order to overcome this problem a possible solution is to turn to novel, non-expensive, gas sensors which yet have good measurement accuracy. This paper deals with a SnO₂ semiconductor CO sensor (SCS) and its flue gas monitoring performance compared with a typical electrochemical-cell CO sensor (ECS).

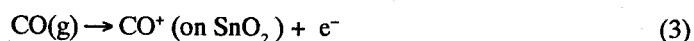
EXPERIMENTAL

Mechanism of operation. The mechanism of operation of ECS, when detecting CO, is based on the following reactions:

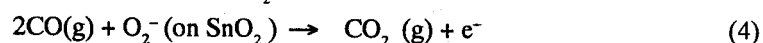


CO and H₂O are being fed to and react at the sensing electrode to form hydrogen ions. These ions are transported through the electrolyte and at the counter electrode react with electrons to form H₂O, thus affecting the current in the counter electrode electric circuit. The magnitude of this effect is a function of CO concentration in the surrounding gas, as explained in more details by Nylander². SCS detection of gases is a physical (physico-chemical) process based on the reaction of a gas molecule with the solid surface of the sensor employing the semiconducting properties of some ceramics. SCSs, based on SnO₂, are being widely used nowadays. This type of sensors is characterized by gas absorption at the sensor surface and chemical bond forming. Two main processes take place during the interaction of CO and the SCS surface, described by equations (3) and (4), as given by Cooper, Advani, Jordan³ and Dramlić⁴:

(i) dissociation of CO



(ii) interaction of CO and the absorbed O₂⁻ at the SCS surface



Comparative investigation and analysis. To compare the performance of SCS and ECS two sets of experiments with two commercially available sensors were conducted: (i) calibration with calibration gases having nominal concentrations of CO, and (ii) simultaneous measurements with a non-premixed flame propane

burner as the flue gas source. The sensors were SCS, Thaguchi gas sensors (TGS) of Figaro Engineering Inc., and ESC, MSI 2000 of MSI Elektronik GmbH (Draeger Group) gas analyzer.

Calibration of sensors. Calibration gases were carefully prepared by mixing measured volumes of dry air and carbon monoxide. The mixture of gases was introduced into a cylinder and further fed to both sensors and then analyzed, following the procedure proposed by Jelenkovic, Tasic and Dramlic⁵.

Flue gas comparative measurements. The experimental set-up consisted of a 15 kW gaseous propane/air non-premixed burner, used as the flue gas source, flue gas settling chamber, sampling train, both sensors connected in series and the data acquisition system. The burner air/fuel ratio was varied in order to cover a range of CO concentration from 0 to 1000 ppm. The flue gas sampling system consisted of an uncooled stainless steel sampling probe, connected to a flue gas cooler, drier and CO sensors. The sampling gas flow rate was constant at 0.5 l/min. The sampling probe was positioned in the axis of the settling chamber, 0.4 m downstream of the burner exit. The time lag of the sensors response was minimized by making the sampling line between the sensors as short as possible. The sensors signals were transferred to a 12-bit acquisition board and further to a laboratory computer. The mean flue gas velocity in the sampling section was near 8 m/s. Besides CO the other relevant flue gas component concentrations and temperature were measured continuously.

RESULTS AND DISCUSSION

Typical results of CO concentration measurements are given in Figs 1 and 2, respectively. Both plots show higher values of CO concentrations as measured by SCS, in the region of lower [CO] runs (< 120 ppm).

The difference was around 40 ppm. It must be emphasized that the calibration of ESC showed constant negative error in CO concentration measurements of the order of 10 ppm, thus, one may conclude that the measurement error of SCS, was around 30 ppm. This measurement error could be attributed to the interference of oxygen molecules in the process of CO chemisorption at the sensor surface, but further analysis of this behaviour should be carried out. Figure 2 also shows

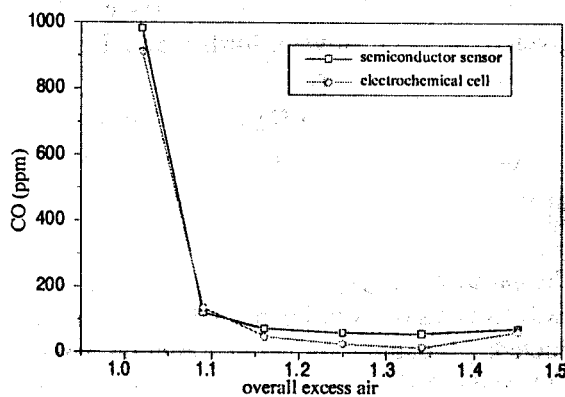


Fig. 1. Steady state output of CO sensors

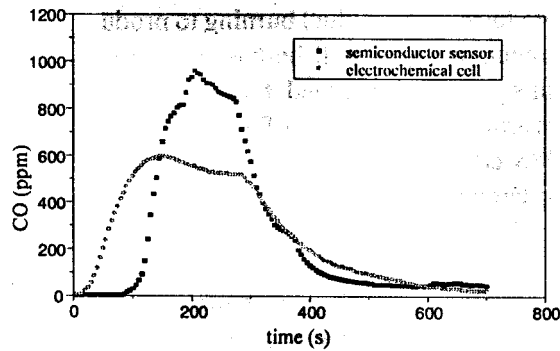


Fig. 2. Dynamic output of CO sensors

that the dynamic response of SCS was around 10 ppm/s which is more than twice that of ECS. It should be mentioned that the accepted reference values of CO were those which were simultaneously measured by the infrared analyzer H&B Uras 10 E.

Table 1. Technical data and initial cost for infrared, electrochemical and semiconductor CO sensors

	Infrared, Uras 10 E, H&B	ECS, MSI 2000, Draeger Group	SCS, TGS, Figaro Eng. Inc.
Mechanism of operation	IR energy absorption	electrochemical	chemisorption
Response curve	nonlinear	linear	nonlinear
Standard detection range (ppm)	0 - 5000	0 - 4000	5 - 5000
Resolution (ppm)	< 0.5 % of span	< 1	3 - 5
Interferences	nearly none	nearly none	moderate; H ₂ S, H ₂ O ₂ , CH ₄ , H ₂ O
Accuracy ($\pm\%$ of span)	< 0.5	< 1, (0-20% of span); < 5, (20-100% of span)	< 5
Response time (s)	3	\approx 100 (90% of span)	<10 (90% of span)
Stability (%)	< \pm 1 per week	not given	< \pm 2 per week
Flue gas temperature effect	< \pm 1%/10°C	max. allowable 150°C	sensor operating temp. 300 - 400°C
Gas flow rate (l/min)	0.3 - 2	0.8 - 3	1 - 3
Life (years)	5	2	5
Approx. cost (US \$)	10 000 (instrument)	500 (sensor)	20 (sensor)

Technical data for CO sensors. The following analysis is concerned with typical commercially available CO analytical instruments/sensors performance and their characteristics. The data for an infrared instrument, electrochemical (ECS) and semiconductor (SCS) sensors, based on the manufacturers information and found by the authors, are given in Table 1.

CO sensor requirements. The CO sensor requirements depend on the combustion flue gas source and the particular national legal limits for CO emissions. Since the

most common combustion sources are those of fossil fuel burning to produce heat and energy, the CO sensor requirements analysis will be based on the related limits for CO emissions. As far as this paper is concerned, the choice of national legal limits for pollutant emissions is arbitrary, so German Technical Instructions for clean air protection (TA Luft, 1986, ed. 1996), Swiss Fed. Regulations (1985) and DIN EN26 (1981) will be considered here and the legal limits for CO emission will be given.

- Continuous measurements of CO are obligatory for higher than 25 MW power combustion devices. Periodic checks of the flue gas emissions measurement system (once per year) and the calibration (once per 5 years) are also required (TA Luft).

- CO emissions limits (ppm) for higher than 25 MW power (TA Luft), or higher than 1 MW power (Swiss Fed. Reg.) combustion devices:

- solid fuel firing equipment, at $O_2 = 7\%$ vol. < 200;
- liquid fuel firing equipment, at $O_2 = 3\%$ vol. < 135;
- gaseous fuel firing equipment, at $O_2 = 3\%$ vol. < 80.

- For domestic gas fired hot water and central heating appliances and also for low-temperature industrial applications the CO emissions limit is < 1000 ppm (DIN E 26).

It should be noted that in practice the poorly maintained and faulty combustion devices may exhibit much higher CO emissions levels than allowed, as shown by Radovanović, Adzić and Memetović⁶.

According to this analysis, to provide combustion flue gas emission monitoring a CO sensor should meet the following requirements:

- measuring range: 0 – 1000 ppm;
- steady state accuracy: 10 ppm;
- response time: ≈ 1 min;
- minimum operational life: > 1 year;
- interference's: low;
- resistance to poisoning: good;
- initial cost: low.

Based on the given requirements and the sensors performance, the ECS satisfies all the requirements except that of poisoning. On the other hand, the SCS satisfies all the requirements except interference which introduces an error of approximately + 30 ppm. It should be stressed that the initial cost ratio of semiconductor and electrochemical sensors is around 1:25.

Concerning future steps in the field of SCS development it is expected that a new approach to the design and operation of SCSs employing novel materials will significantly improve the interference characteristics and enable multicomponent target gas sensing, as discussed by McGeehin, Moseley and Williams⁷, thus enabling the use of SCSs as both monitoring and control devices.

CONCLUSIONS

This paper discusses the performance of semiconductor and electrochemical CO sensors concerning monitoring of the combustion flue gas sources emission. Experimental comparison of both sensors showed that the semiconductor sensor could satisfy the requirements for CO monitoring. The outstanding advantage of the SCS is the initial low cost.

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