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The Influence of Hydrogen on the Indications of the Electrochemical Carbon Monoxide Sensors

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Abstract: This article examines electrochemical carbon monoxide (CO) sensors used as mobile devices by rescue and firefighting units in Poland. The conducted research indicates that the presence of chlorine (Cl₂), ammonia (NH₃), hydrogen sulfide (H₂S), hydrogen chloride (HCl), hydrogen cyanide (HCN), nitrogen (IV) oxide (NO₂), and sulfur (IV) oxide (SO₂) in the atmosphere does not affect the functioning of the electrochemical CO sensor. In the case of this sensor, there was a significant cross effect in relation to hydrogen (H₂). It was found that the time and manner of using the sensor affects the behavior in relation to H₂. Such a relationship was not recorded for CO. Measurements in a mixture of CO and H₂ confirm the effect of hydrogen on the changes taking place inside the sensor. Independently of the ratio of H₂ to CO, readings of CO were flawed. All analyses showed a significant difference between the electrochemical CO sensor readings and the expected values. Only in experiments with a 1:3 mixture of CO and H₂ was the relative error less than 15%. The relative error in the analyzed concentration range for a sensor with an additional compensation electrode ranged from 7% to 38%; for a sensor without this electrode, it ranged from 23% to 55%. It was ascertained that in the cases of measurements for tests carried out at higher concentrations of H₂ in relation to CO, a sensor with an additional electrode is significantly better (more accurate) than a sensor without such an electrode. Differences at the significance level $p = 0.01$ for measurements made in the CO:H₂ mixture at a ratio of 1:3 were ascertained.

Keywords: electrochemical sensor (EC), crossing effect; measurement carbon monoxide; interfering gases; hydrogen

1. Introduction

To identify hazardous substances, rescue units around the world use different measurement techniques, including gas chromatography, infrared spectroscopy, ion mobility spectrometry, and electrochemical methods [1–3]. Due to the low price, small size, and the possibility of their use in mobile instruments, electrochemical sensors have found wide application and are used for monitoring, including for carbon (II) oxide (CO), hydrogen sulfide (H₂S) [4], ozone (O₃) [5], nitrogen (II) oxide (NO), nitrogen (IV) oxide (NO₂) [6], ammonia (NH₃) [7], chlorine (Cl₂), hydrogen chloride (HCl), hydrogen cyanide (HCN), and sulfur (IV) oxide (SO₂) [8].

A typical electrochemical sensor consists of a sensing electrode, counter electrode, and a housing containing an acid electrolyte. One of the housing walls is made of a hydrophobic membrane that is permeable to gases and impermeable to liquids. A hydrophobic membrane is used to control the amount of gas molecules reaching the electrode surface. It is mainly made of thin, low-porosity Teflon

membranes [2,9,10]. The electrodes can be made of various materials. Many kinds of nanoparticles, such as metal, oxide, and semiconductor nanoparticles, have been used for constructing electrochemical sensors [11–15].

The electrochemical sensor market is expected to register a Compound Annual Growth Rate of 11.4% over the forecast period 2019–2024. The emergence of nanotechnology-based sensors will drive the market during the forecast period [16].

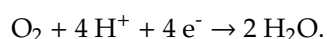
Statistical data indicate that the most common reason for the intervention of emergency services is the suspected release of carbon monoxide. CO is formed as a result of incomplete combustion of carbon and organic substances. As CO is an odorless, tasteless, and colorless gas, it is known as the silent killer. CO poisoning is the most common type of deadly air poisoning in many countries [17]. CO enters the body mainly through the respiratory system, and the amount that enters the body depends on the concentration of CO in the air and the amount of time for which a person breathes polluted air. The most common symptoms include headache, nausea and vomiting, dizziness, lethargy, and a feeling of weakness [18,19]. Health effects associated with exposure to CO range from the more subtle cardiovascular and neurobehavioral effects at low concentrations to unconsciousness and death after acute or chronic exposure to higher concentrations of CO [20].

Carbon monoxide combines with hemoglobin to produce carboxyhemoglobin (COHb). About 80%–90% of carbon monoxide in the human body is reversibly bound to hemoglobin. CO has over 200 times greater affinity for binding to hemoglobin than to oxygen [21]. A small environmental concentration will thus cause toxic levels of COHb [19]. Different people may have different carbon monoxide tolerance levels [20]. Exposures of CO at 100 ppm or higher is assumed to be hazardous to human health [22].

The principle of operation of the electrochemical sensor for carbon monoxide is based on the measurement of potential change on the working and the counter electrode, where the oxidation and reduction processes take place simultaneously [2,23]. Gases are oxidized by striking the surface of the working electrode [24]:



In the case of oxidation of the substance on the working electrode, there is oxygen (O₂) reduction on the counter electrode (cathode) according to the equation:



Reactions on the electrodes cause the flow current to flow. The intensity of this current is a function of the number of reduced/oxidized molecules. The dependence in a given range of concentrations is linear [10].

The use of electrochemical sensors is limited by the fact that the measurement value may be affected by other substances present in the analyzed air [25]. This gas interference is called the crossing effect. This effect is based on the measurement of the reduction/oxidation potential of undesirable substances and distorts the measurement results of the test substance. Interference can be positive or negative. In the case of positive interference, the readings are higher than the actual values, while in the case of negative interference, the results are underestimated [26].

Some electrochemical CO sensors are susceptible to the presence of hydrogen in the atmosphere. In order to minimize the H₂ influence in such sensors, an additional electrode is installed—a compensating one. During the measurement, all CO and a portion of the H₂ oxidize on the working electrode, while the rest of the hydrogen goes to the compensating electrode, where it is oxidized. After the measurement, when the voltages on all electrodes are known, a compensating signal is emitted according to the current on the compensating electrode, by which the measured concentration of CO is corrected [8,27].

Not only interfering substances, but also the conditions under which measurements are carried out may affect the work of the electrochemical sensor. Research conducted by Popoola et al. and

Wu et al. indicates that meteorological conditions (temperature and humidity) also have a great influence on measurement [28,29].

This paper presents the results of measurements made with an electrochemical CO sensor. Calibration gases were used in the tests. Particular attention was paid to the behavior of the electrochemical CO sensor in a hydrogen (H₂) atmosphere. In order to determine the impact of the use of an additional electrode on the accuracy of measurements, the content of CO was measured with two sensors in samples that contained a mixture of carbon monoxide and hydrogen. One contained a working electrode and counter electrode, and the other also had a third electrode—an electrode compensating for the outflow of hydrogen per measurement. The tests were carried out under the same ambient conditions.

The obtained results were used to:

1. Investigate the effect of selected substances on the electrochemical CO sensor readings.
2. Determine the kinetics of the oxidation and reduction processes taking place in the electrochemical CO sensor under the influence of 100 ppm CO and 500 ppm H₂ for 1 minute at a rate of 1L/min.
3. Determine the influence of H₂ content in the analyzed sample according to the indications of electrochemical CO sensors.

The tests were carried out on sensors used in mobile CO measuring instruments commonly used by rescue units.

2. Materials and Methods

2.1. Materials

To measure the influence of gases on the electrochemical CO sensor indications, the following gases were used: 100 ppm CO, 25 ppm H₂S, 10 ppm SO₂, 25 ppm NH₃, 25 ppm NO, 25 ppm NO₂, 10 ppm Cl₂, 10 ppm HCN, 10 ppm HCl, 500 ppm, 2% vol. H₂, and 2.5% vol. methane (CH₄). Mixtures of CO and H₂ in synthetic air were obtained using gas mixers (LAT, Poland).

Electrochemical CO sensors with a measuring range of 0–999 ppm (Industrial Scientific Corporation, USA) were tested. These were commercial sensors, commonly used by rescue units in Poland. MX4 detectors were utilized with electrochemical CO sensors with different lifetimes. These detectors were made of only two electrodes: a sensing electrode and a counter electrode. In tests with CO and H₂ mixtures, an iTX multi-gas detector with two electrochemical CO sensors was used. One of them had an additional electrode compensating the influence of H₂ on the measurement of CO.

2.2. Methods

The tests were carried out in three measurement series:

- I) First series: Calibration gases (substances interfering with the measurement) were supplied with intensity of 1 L/min directly from the cylinder to the MX4 multi-gas detector (Industrial Scientific Corporation, USA). The electrochemical CO sensor in the analyzer was new, and never used in rescue operations. Gas was supplied for 2 minutes. The gas introduced through the hydrophobic membrane into the sensor on the surface of the electrodes caused a reaction, which led to a change in current intensity, and the detector showed different concentration values.
- II) Second series: Calibration gases CO (100 ppm) and H₂ (500ppm) were supplied directly from the bottle to three MX4 detectors (Industrial Scientific Corporation, USA). The electrochemical CO sensors installed in the detectors differed in their time of usage. A new sensor and 4 and 8 year old sensors were used in the research. The kinetics of the redox reaction process were determined by recording sensor indications as a function of time.
- III) Third series: Mixtures CO and H₂ were supplied through the sensors. Samples containing CO and H₂ were prepared in a gas mixer in 1:3; 1:2; 1:1; and 2:1 ratios, respectively. They were then introduced into the FTIR spectrophotometer GASMET Dx-4010 (Temet Instruments Oy,

Finland) and the iTX multi-gas detector (Industrial Scientific Corporation, USA). Tests for each electrochemical CO sensor were carried out for five CO concentration values. Three measurements were made with each sensor for each concentration value. The results obtained from the GASMET Dx-4010 spectrophotometer were taken as real (expected) values of CO concentration in the analyzed sample, and C_{CO} was determined. The differences between the C_{CO} value and the C concentration value read from the iTX instrument were assumed to be the effect of hydrogen. Two electrochemical CO sensors were tested. One of the sensors had—in addition to the working and counter electrode—a compensating electrode limiting the influence of H_2 on the measurement of CO.

2.3. Statistical Analysis

Data are presented as mean \pm standard error of the mean (SEM). The relative error of measurement was calculated from the following formula:

$$\delta = \frac{C - C_{CO}}{C_{CO}} 100\%,$$

where:

C—measurement result with an electrochemical sensor, [ppm]

C_{CO} —expected concentration value (concentration measured by spectrophotometer GASMET Dx-4010), [ppm].

A comparison between groups was performed using a t-Student test after verification of normality was calculated with Statistica 12.0 software. Statistical analysis was also carried out based on the unloaded estimator of variance of result–expected value using the F-Snedecor test. Data were considered statistically different when $p < 0.05$.

3. Results and Discussion

3.1. Impact of Selected Gases on CO Sensor Readings

The conducted tests of the influence of selected gases on indications of the electrochemical sensor readings show that only two of the tested substances caused positive interference of readings—NO and H_2 . The test results are shown in Table 1.

Table 1. The interfering gases affecting the electrochemical CO sensor readings.

No.	Interfering Gas	Concentration of Interfering Gas	Display of the Electrochemical CO Sensor
1	CO	100 ppm	100 ppm
2	H_2S	25 ppm	0 ppm
3	SO_2	10 ppm	0 ppm
4	NH_3	25 ppm	0 ppm
5	NO	25ppm	8 ppm
6	NO_2	25 ppm	0 ppm
7	Cl_2	10 ppm	0 ppm
8	HCN	10 ppm	0 ppm
9	HCl	10 ppm	0 ppm
10	H_2	2% of volume	out of range
11	H_2	500 ppm	100 ppm
12	CH_4	2.5% of volume	0 ppm

The test results indicate that the electrochemical CO sensor does not respond to the presence of CH₄ and toxic gases, such as: H₂S, SO₂, NH₃, NO₂, Cl₂, HCN, or HCl. The obtained results confirm that the electrochemical CO sensor in the presence of H₂ may indicate the presence of CO. Wojnowski et al. [24] point to the above disturbance. In [30], it was pointed out that measurement in an atmosphere containing 100 ppm H₂ may cause the CO sensor to be displayed at 40 ppm.

3.2. Impact of Electrochemical CO Sensor Usage Time on Redox Kinetics

The experiments showed that during the sampling of 100 ppm CO, the sensors showed a maximum value at similar times. A steady state was obtained after up to 34 seconds of measurement. The time to reach 50% and 90% of the final value in measurements with a new sensor was 3 seconds shorter than for other sensors (Table 2). The tests were repeated three times for each condition and converging results were received. There was no decrease in sensor efficiency during carbon monoxide measurement. Mead et al. also observed good reproducibility of results and stability of measurements made with an electrochemical CO sensor [10]. The indications of the sensors as a function of time when supplying the calibration gases are presented in Figure 1.

Table 2. Parameters obtained when supplied with 100 ppm CO or 500 ppm H₂. EC-0—new sensor, EC-4—4 year old sensor, EC-8—8 year old sensor, C max—maximum concentration, T50—time after which the signal reaches 50% of the maximum concentration value, T90—time after which the signal reaches 90% of the maximum concentration value.

Electrochemical CO Sensors	Gas supply—100 ppm CO			Gas supply—500 ppm H ₂		
	T50 [s]	T90 [s]	C max [ppm]	T50 [s]	T90 [s]	C max [ppm]
EC-0	3	10	99 (33 s)	4	10	100 (33 s)
EC-4	6	13	98 (34 s)	6	12	149 (26 s)
EC-8	6	13	99 (34 s)	5	10	122 (39 s)

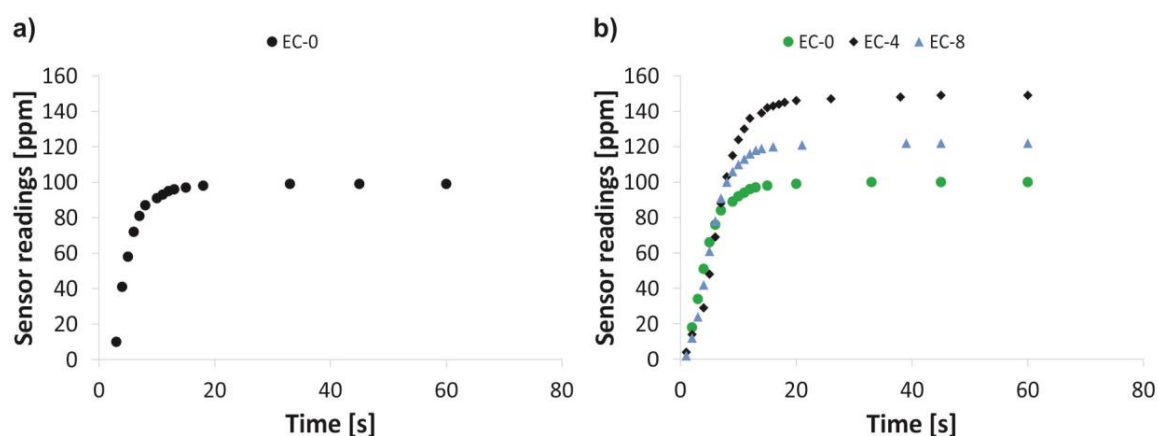


Figure 1. Electrochemical CO sensor readings as a function of time when supplying: a) 100 ppm CO or b) 500 ppm H₂.

The electrochemical CO sensor response time was shorter than its characteristics describe. Similar times were reported in the studies of Yan and Liu, where the time for a response to a step change of CO equaled ca. 3 s [31]. This is due to the way that gas is supplied directly from the cylinder.

The conducted research indicates that the sensors used significantly affected the behavior of the electrochemical CO sensor in relation to hydrogen. Measurements carried out with a 4 year old sensor showed almost 50% higher readings than in the case of a new sensor. No such changes were found for CO measurements (Figure 2).

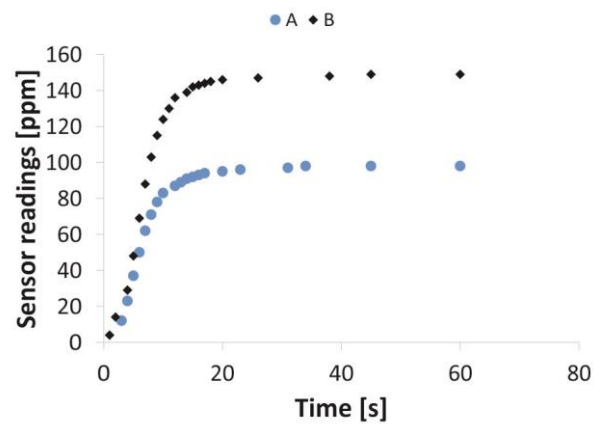


Figure 2. Electrochemical CO sensor EC-4 readings as a function of time when supplying A) 100 ppm CO and B) 500 ppm H₂.

3.3. The Influence of Hydrogen on the Indications of the Electrochemical CO Sensor

The tests were carried out using two sensors; one of them had an electrode compensating for the influence of hydrogen, and the other did not. The gas samples tested contained CO and H₂. Test results for the mixtures are presented in Tables 3–6.

Table 3. Test results for the mixture of CO:H₂ in a 1:3 volume ratio.

Sensor Expected Value [ppm]	with Compensating Electrode (EC I)			without Compensating Electrode (EC II)		
	Mean [ppm]	Standard Error	Relative Error [%]	Mean [ppm]	Standard Error	Relative Error [%]
102	124	3.0	22	135	5.9	32
80	87	1.7	9	104	4.4	30
59	67	2.1	14	76	3.0	29
39	42	0.6	7	51	3.2	30
20	19	0.6	7	27	1.5	37

Table 4. Test results for the mixture of CO:H₂ in a 1:2 volume ratio.

Sensor Expected Value [ppm]	with Compensating Electrode (EC I)			without Compensating Electrode (EC II)		
	Mean [ppm]	Standard Error	Relative Error [%]	Mean [ppm]	Standard Error	Relative Error [%]
102	126	1.5	24	140	3.1	38
65	78	2.1	19	86	1.5	32
39	47	1.2	20	51	2.5	30
21	29	2.0	38	29	1.5	40
14	19	1.2	38	20	2.3	45

Table 5. Test results for the mixture of CO:H₂ in a 1:1 volume ratio.

Sensor Expected Value [ppm]	with Compensating Electrode (EC I)			without compensating Electrode (EC ii)		
	Mean [ppm]	Standard Error	Relative Error [%]	Mean [ppm]	Standard Error	Relative Error [%]
102	125	3.8	23	133	5.7	31
75	92	3.1	23	99	2.5	32
39	47	3.5	21	53	3.8	35
21	26	1.0	24	31	2.0	48
14	19	1.0	36	22	2.1	55

Table 6. Test results for the mixture of CO:H₂ in a 2:1 volume ratio.

Sensor	with Compensating Electrode (EC I)			without Compensating Electrode (EC II)		
	Expected Value [ppm]	Mean [ppm]	Standard Error	Relative Error [%]	Mean [ppm]	Standard Error
102	121	3.2	18	130	3.6	27
78	92	3.0	18	96	4.6	23
39	46	1.0	18	51	1.7	31
21	25	1.5	17	28	1.0	33
14	18	1.0	29	21	1.0	50

The conducted tests show that indications of the electrochemical CO sensors are strongly influenced by the presence of H₂ in the analyzed mixture. For the sensor with an additional electrode, the relative error in the H₂ mixture (at CO:H₂ ratios 1:3) for a concentration of <100 ppm CO was less than 15%. In the case of the sensor with an additional electrode, the measurement error ranged from 7% to 38%. Larger errors were obtained in testing the sensors without additional electrodes (from 23% to 55%). The measurement accuracy declared by manufacturers is 15% [32]. The statistical differences for results obtained using an electrochemical CO sensor with and without an additional electrode compared with the expected (real) values are presented in Figures 3–6.

The results depicted in Figures 3–6 indicated that the readings from both sensors were significantly different compared to the C_{CO} set values for all analyzed ratios of CO:H₂. The highest level of significance ($p = 0.0001$) was obtained in both electrochemical CO sensors with measurements made for the CO:H₂ mixture at a ratio of 1:2 when the CO concentration was 102 ppm. Interestingly, the readings from sensor I and sensor II were closest to the lowest values of the set CO concentrations of 39 ppm and 20 ppm for all analyzed ratios of CO:H₂. Therefore, the results showed that both sensors seemed to be the most accurate for the lowest concentrations of CO. Nevertheless, the readings from sensor EC I were closer to the expected value set in the system. The results showed that both sensors seemed to be the most accurate for the lowest concentrations of CO.

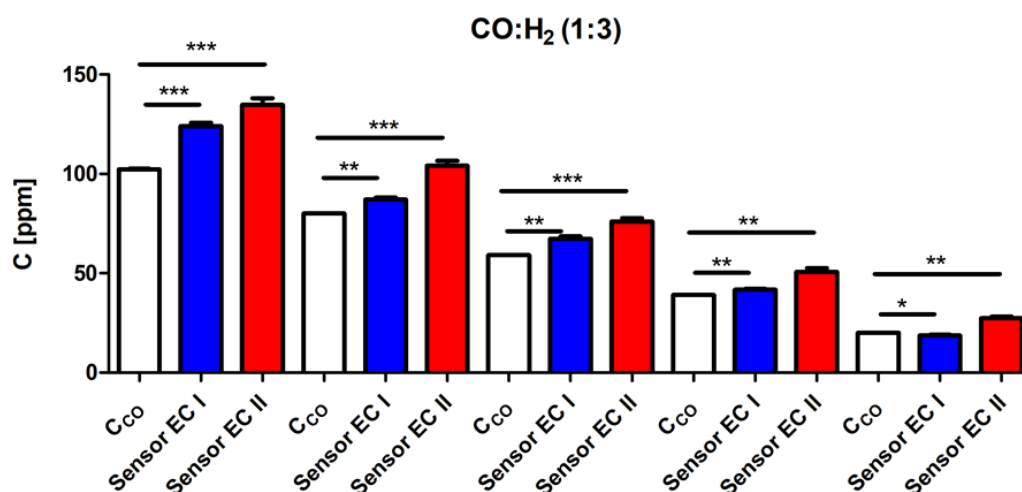


Figure 3. Concentration measured in set conditions (C_{CO}) by sensor I (EC I) and sensor II (EC II) when the CO:H₂ relation was 1:3. Data presented as mean ± standard error, n = 5. T-student test. * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$ vs. C_{CO}.

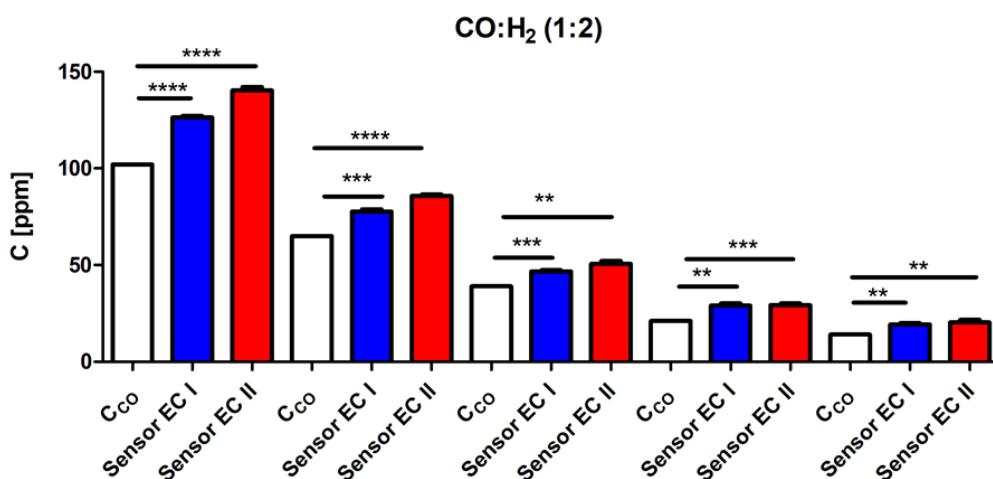


Figure 4. Concentration measured in set conditions (C_{CO}) by sensor I (EC I) and sensor II (EC II) when the CO:H₂ relation was 1:2. Data presented as mean \pm standard error, $n = 5$. T-student test. * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$ vs. C_{CO} .

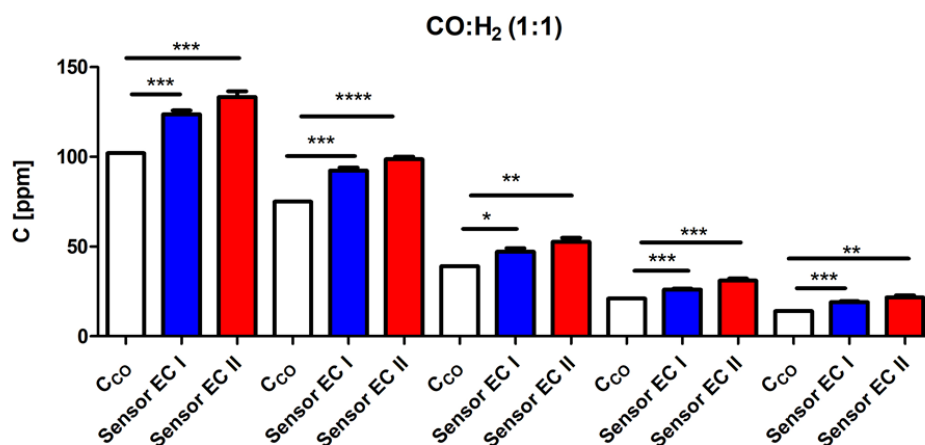


Figure 5. Concentration measured in set conditions (C_{CO}) by sensor I (EC I) and sensor II (EC II) when the CO:H₂ relation was 1:1. Data presented as mean \pm standard error, $n = 5$. T-student test. * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$ vs. C_{CO} .

In order to compare the values obtained during measurements of electrochemical CO sensors (with different structures), the F-Snedecor test was performed. It was found that the results obtained with a sensor furnished with an additional electrode are more accurate than those obtained with a sensor without a compensating electrode. The higher the content of H₂ in relation to CO in the tested mixture, the higher the significance level obtained. The highest level of significance ($p = 0.01$) was obtained with measurements made in the CO:H₂ mixture at a ratio of 1:3. In the cases of tests in a mixture in which the ratio of CO to H₂ was 1:2 or 1:1, differences were found with a probability of 94% and 89%, respectively.

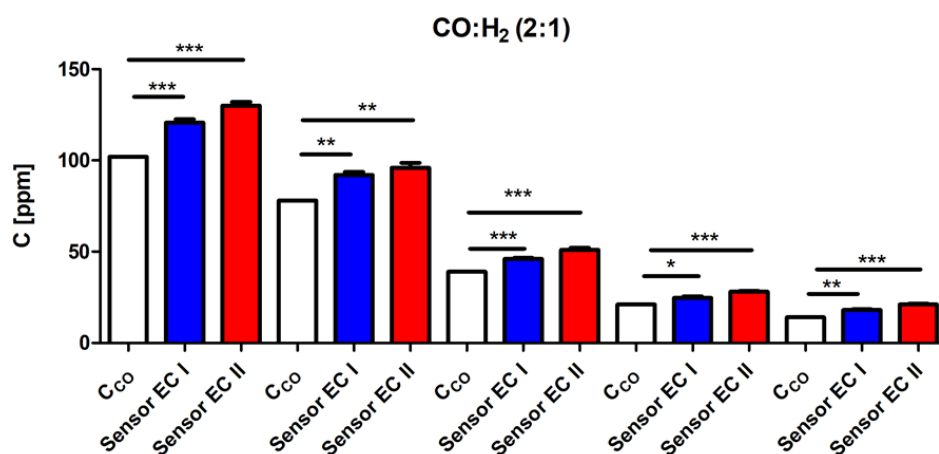


Figure 6. Concentration measured in set conditions (C_{CO}) by sensor I (EC I) and sensor II (EC II) when the CO:H₂ relation was 2:1. Data presented as mean \pm standard error, $n = 5$. T-student test. * $p < 0.05$; ** $p < 0.01$, *** $p < 0.001$ vs. C_{CO} .

4. Conclusions

In rescue operations, mobile detectors with electrochemical sensors are used to determine the content of CO in the air. Measurements performed with the use of those devices do not require any specialist knowledge—the operation is intuitive—yet one should treat the results obtained with some reserve. The values of electrochemical CO sensor indications may be affected by the presence of other substances in the analyzed samples.

This work examined electrochemical CO sensors used by rescue units. The conducted research indicates that the presence of chlorine, ammonia, hydrogen sulfide, hydrogen chloride, hydrogen cyanide, nitrogen (IV) oxide, and sulfur (IV) oxide in the atmosphere does not affect the functioning of the electrochemical CO sensor. In the case of this sensor, there was a significant cross effect in relation to hydrogen. The administration of this substance with a concentration of 2% vol. and 500 ppm indicated the presence of CO at a concentration outside the measuring range (> 999 ppm) and at 100 ppm, respectively.

The lifetime of the electrochemical CO sensor affects the sensor's indications. When supplying 500 ppm H₂ for an EC sensor which was 4 years old, the reading was half as high as for the new sensor. There were no such changes when supplying CO. The time taken to measure steady-states when carbon monoxide is administered does not increase with the electrochemical CO sensor age. Measurements of carbon monoxide concentration in the CO:H₂ mixture indicate that, regardless of the proportions of both substances, the measurements are subject to a large error. All measurement results for mixtures containing H₂ were statistically significantly different from the expected values ($p < 0.05$). The relative measurement error in the analyzed concentration range for the EC I sensor ranged from 7% to 38%; in the case of the EC II sensor, it ranged from 23% to 55%.

It was found that the use of an additional electrode in the sensors limits the influence of hydrogen on the measurement. In the cases of measurements carried out at higher concentrations of hydrogen in relation to carbon monoxide, a sensor equipped with a compensation electrode is much better (more accurate) than a sensor without an additional electrode.

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