

Effects of interfering gases in electrochemical sensors NH₃ and NO₂

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Abstract. Electrochemical sensors used for toxic gas measurement. In this paper construction EC sensor and principle of operation has been described. The results of research on the influence of interfering gases on the readings of detectors containing ammonia and nitric oxide (IV) electrochemical sensors are presented. Span gases were used in the tests: 100 ppm CO, 25 ppm H₂S, 25 ppm NH₃, 10 ppm NO, 25 ppm NO₂, 10 ppm Cl₂, 10 ppm HCN, 10 ppm HCl, 2% vol. H₂, 2.5% by volume CH₄, 0.35% by volume of C₅H₁₂. The conducted research indicates that the presence of chlorine, hydrogen chloride, hydrogen cyanide, carbon monoxide and saturated hydrocarbons in the atmosphere does not affect the work of the ammonia electrochemical sensor. In the case of this sensor, there was a significant cross effect in relation to hydrogen sulphide and hydrogen. The administration of these substances indicated the presence of ammonia outside the measuring range (200 ppm). In the measurements using the NO₂ sensor, in most cases negative interference was found. The test results indicate that the measurements made with electrochemical sensors may be subject to error in the presence of interfering gases. The results obtained may be both understated and overstated.

1 Introduction

The first electrochemical sensors were created over half a century ago and were used to measure the oxygen concentration [1-3]. Over time, sensors for monitoring other substances, such as: chlorine, ammonia, hydrogen chloride, hydrogen cyanide, hydrogen sulfide, ozone, carbon monoxide, nitrogen oxides (II, IV), sulfur oxide (IV) have been developed [4-7]. The progressive miniaturization of the EC has resulted in their common usage [8]. Currently, due to sensors' advantages, i.e. sensitivity up to approx. 0.1 ppm, the possibility of using it in a wide temperature range (-40 °C to 50 °C), low supply voltage, they are used in portable gas detectors [9-11]. They are used by emergency services for qualitative and quantitative analysis during events involving hazardous substances [12]. Due to the frequent inability to use instrumental methods to identify substances, the results obtained by electrochemical sensors form the basis of tactics of rescue operations [13-17].

A typical electrochemical sensor consists of a sensing electrode, counter electrode and a housing containing acidic electrolyte and a hydrophobic membrane (Fig. 1).

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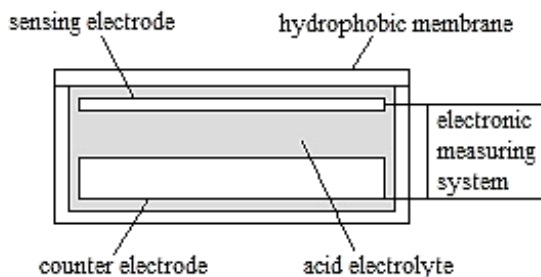
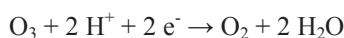
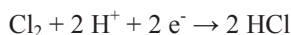
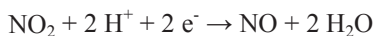


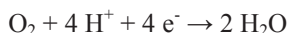
Fig.1. Construction of an electrochemical sensor.

The hydrophobic membrane is permeable to gases and impermeable to liquids. In some sensors, additional electrodes - reference electrodes - are used to increase sensitivity [18-21].

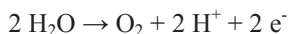
The principle of operation of the electrochemical sensor is based on the measurement of potential change on the working and compensating electrodes - the counter electrode, where the oxidation and reduction processes take place simultaneously. Gases are oxidized or reduced by striking the surface of the working electrode [22-23].



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



The appropriate amount of oxygen is therefore a condition for the proper functioning of the sensor. In the case when reduction processes occur on the working electrode, the water reacts on the counter-electrode according to the equation:



Reactions on the electrodes cause the current to flow. The intensity of this current is a function of the number of oxidized / reduced molecules. The dependence in a given range of concentrations is linear [1,2].

Because other substances present in the analyzed air may influence the measurement value, it poses the limitation in the use of electrochemical sensors. Such gas interference is called crossover effect [23]. This effect can be observed when measuring the potential of reduction / oxidation of undesired substances by the sensor and falseness of the measurement result of the test substance (e.g. in a room, there may be no gas to be tested at all, while the sensor detects its presence) [24]. Due to the fact that the sensor is not able to distinguish what substance has undergone an oxidation or reduction reaction, it can only measure the value of flowing current [2, 25-27].

Specific electrochemical sensors should react to the presence of only those gases for which they are intended. In order to increase the selectivity of the sensor, additional electrodes and a suitable electrolyte are used, as well as selective filters that eliminate unwanted substances from the sample being tested. It is practically impossible to build an electrochemical sensor, which will be perfectly selective, and will not react to any gas except the one being tested. Interference can be positive or negative. In the case of positive interference, the readings are greater than the actual values, while during negative interference the results are understated [22].

2 Material and Methods

The test place designed to measure the influence of gaseous pollutants in the air analyzed on the operation of a specific electrochemical sensor consists of:

1. The iTX multi-gas detector with exchangeable electrochemical sensors, with the possibility of continuous or periodic recording of measurements.
2. A set of calibration gases.
3. Data recorder.

Electrochemical sensors were tested in which the electrolyte was in the gel form. The influence of selected gases on the behavior of electrochemical sensors - NH₃ ammonia, nitrogen dioxide NO₂ was investigated. Sensors with the following measuring ranges were examined: ammonia (0-200 ppm), nitrogen dioxide (0-100 ppm).

Calibration gases were used for the test: 100 ppm of carbon monoxide, 25 ppm of hydrogen sulphide, 10 ppm of sulfur dioxide, 25 ppm of ammonia, 10 ppm of nitric oxide, 25 ppm of nitrogen dioxide, 10 ppm of chlorine, 10 ppm of hydrogen cyanide, 10 ppm of hydrogen chloride, 2% of volume hydrogen, 2.5% by volume methane, 0.35% by volume pentane.

The measurements were carried out in the following way. Calibration gases (interfering substances) were fed at a rate of 1 l/min directly from the bottle to the iTX multi-gas detector (Industrial Scientific Corporation, USA). The gas introduced through the hydrophobic membrane into the sensor on the surface of the electrodes, underwent reactions, which caused a change in the current intensity and the display of different concentration values on the detector's display.

3 Results and discussion

The test results are shown in Tables 1-2.

The following gases do not affect the operation of the ammonia sensor - carbon monoxide, chlorine, hydrogen cyanide, hydrogen chloride and saturated hydrocarbons, while hydrogen sulphide and hydrogen have a very big influence. The ammonia sensor exposed to these gases in a consecutive 25 ppm and 2% vol. within a few seconds it indicated exceeding the measuring range of 200 ppm. The research also indicates that the presence of sulfur dioxide and nitrogen oxides in the analyzed air affects the work of the NH₃ sensor, i.e. the value of the ammonia concentration measurement.

Table 1. The interfering gases affecting in the NH₃ sensor readings.

No.	Interfering gas	Concentration of interfering gas	Display of the NH ₃ sensor with a measuring range of 0-200 ppm
1	Carbon monoxide CO	100 ppm	0 ppm
2	Hydrogen sulfide H ₂ S	25 ppm	out of range
3	Sulfur dioxide SO ₂	10 ppm	13 ppm
4	Nitric oxide (II) NO	10 ppm	25 ppm
5	Nitrogen (IV) NO ₂	25 ppm	7 ppm
6	Chlorine Cl ₂	10 ppm	0 ppm
7	Hydrogen cyanide HCN	10 ppm	0 ppm
8	Hydrogen chloride HCl	10 ppm	0 ppm
9	Hydrogen H ₂	2 % of volume	out of range
10	Methane CH ₄	2.5% of volume	0 ppm
11	pentane C ₅ H ₁₂	0.35% of volume	0 ppm

Table 2. The interfering gases affecting in the NO₂ sensor readings.

No.	Interfering gas	Concentration of interfering gas	Indication of the sensor NO ₂
1	Carbon monoxide CO	100 ppm	- 0.5 ppm
2	Hydrogen sulfide H ₂ S	25 ppm	-14 ppm
3	Sulfur dioxide SO ₂	10 ppm	- 0.7 ppm
4	Nitric oxide (II) NO	10 ppm	1.5 ppm
5	Ammonia NH ₃	25 ppm	- 0.5 ppm
6	Chlorine Cl ₂	10 ppm	- 0.3 ppm
7	Hydrogen cyanide HCN	10 ppm	- 0.6 ppm
8	Hydrogen chloride HCl	10 ppm	0 ppm
9	Hydrogen H ₂	2 % of volume	- 0.9 ppm
10	Methane CH ₄	2.5% of volume	- 0.6 ppm
11	Pentane C ₅ H ₁₂	0.35% of volume	- 0.3 ppm

The operation of the nitrogen dioxide sensor in addition to hydrogen chloride is affected by all the gases tested. Impact on the sensor of the tested substances excluding nitric oxide causes negative interference, the highest in case of hydrogen sulphide 14 ppm. In the case of other gases, the indications did not exceed 1 ppm.

4 Summary

The conducted research indicates that the presence of chlorine, hydrogen chloride, hydrogen cyanide, carbon monoxide and saturated hydrocarbons in the atmosphere does not affect the work of the ammonia electrochemical sensor. In the case of this sensor, there was a significant crossing effect in relation to hydrogen sulphide and hydrogen. The administration of these substances indicated the presence of ammonia outside the measuring range (200 ppm). In the measurements using the NO₂ sensor, in most cases negative interference was found. The test results indicate that the measurements made with electrochemical sensors may be subject to error in the presence of interfering gases. The results obtained may be both understated and overstated.

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