KRAJOWA KONFERENCJA ELEKTRONIKI
Darłówko Wschodnie 02 - 06.06.2019

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Selectivity of amperometric gas sensors in multicomponenent gas mixtures

Keywords: gas sensor, amperometric sensor, selectivity, cross-sensitivity

ABSTRACT

In recent years smog and poor air quality became a growing environmental problem. There is a need to continuously monitor the quality of air. The lack of selectivity is one of the most important problems limiting the use of gas sensors for this purpose. In this study, a selectivity of the six amperometric gas sensors is being investigated. Calibration of sensors has been performed in order to find a correlation between concentration level and sensor output. The responses of each sensor to the concentrations from 50 ppb to 1 ppm of selected gases have been measured. Usually, sensors responses are measured only in the presence of one gas. The main goal was to study different interactions between sensors and gases in multicomponent gas mixtures. Sensors were studied under controlled conditions, a constant gas flow rate of 100 mL/min and 50 % relative humidity.

1. INTRODUCTION

Poor air quality has not only a significant impact on the health of the human population, particularly in urban areas, but also on the economy, increasing medical costs, cutting lives short and reducing productivity. Air pollution is also very dangerous to vegetation and ecosystems. It has a devastating effect on water and soil contributing to the destruction of fauna and flora. The most harmful air pollutants for ecosystem are ozone, ammonia and nitrogen oxides which introduce an excess of nutrient nitrogen. Nitrogen oxides and sulphur dioxide lead to soil, rivers and lake acidification and acid rain, resulting in biodiversity loss.

Despite reductions in emissions and ambient concentrations, air quality still remains poor in multiple areas, when it comes to Europe. According to the European Environment Agency, the premature deaths attributed to $PM_{2.5}$, NO_2 and O_3 were 422 000, 79 000 and 17 700, respectively in 2015. The countries with the highest numbers of premature deaths and years of life lost are Germany, Italy, Poland, France, Spain and the United Kingdom [1].

For environmental protection, it is very important to measure the level of pollution in the air. On the market, there is a wide range of commercial gas sensors. The most popular are metal oxide semiconductor sensors which output signal is based on a change of conductivity of the oxide that is caused by the reaction with volatile compounds. Unfortunately, this type of sensor has poor selectivity and is sensitive to almost any volatile substances. Due to its low cost and availability, however, they are often in multisensor arrays, so-called electronic noses (e-nose) [2-4]. It has been revealed that multisensor array in combination with machine

learning algorithms is a promising way to get a fast analysis of e.g. air contaminants or flavours and odours of food, so it can be used to verify its quality [3, 5-8].

Amperometric sensors are more selective, stable and have fast recovery time. This type of gas sensor consists of electrolyte and three electrodes. The gas molecules are reduced or oxidised at the working electrode, while the opposite reaction takes place at the counter electrode. The output signal is measured as a current generated by a reaction between the gas and an analyte.

The very important parameter of gas sensors is cross-sensitivity caused by interfering gases. Information provided by manufacturers in data sheets is declared only for selected conditions and often differ from the real-life properties of sensors. Cross-interference is often a cause of negative sensor readings. That is why a laboratory evaluation of sensor properties is needed. The objective of this study is to determine how gas sensors react to the presence of the gases they are constructed to detect and in other gases including multicomponent gas mixtures. The text contains exemplary results for SO_2 and NO_2.

2. EXPERIMENTAL

The measurements were performed in the chamber of our design having a volume of 240 cm^3. In this chamber, six commercially available amperometric gas sensors have been placed. Results for sensor manufactured by Alphasense, namely H2S-B4, OX-B431, NO-B4 SO2-B4, NO2-A43F and CO-A4 that detect H_2S, O_3 and NO_2, NO, SO_2, NO_2 and CO, respectively are described in this text. Amperometric sensors require to be controlled by a potentiostatic circuit to work properly at a fixed potential. Ten of our own design electronic modules forming measuring system have been used for sensor response acquisition. More details of the developed systems were presented elsewhere [9, 10]. Sensors response was measured by PC software once per minute and saved it to a text file.

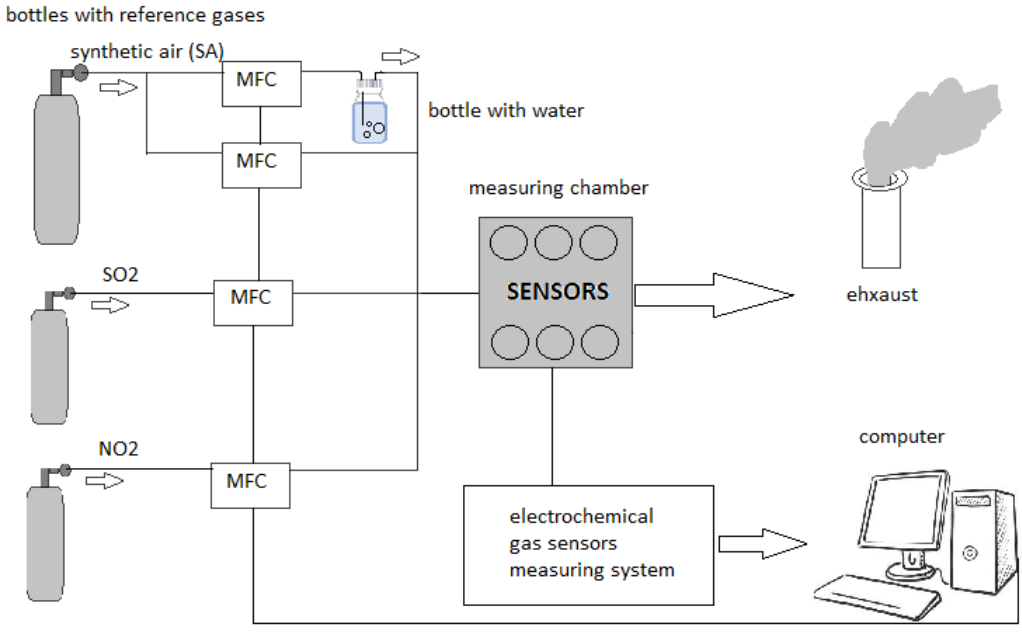

Fig. 1. Structure of the measuring stand

The gas-delivery system consist of four Brooks GF Series mass flow controllers (MFC) connected to the computer via RS-485 interface (Fig. 1). The flow of gas was programmed with Medson software. The desired gas mixture was obtained by mixing and diluting gases

from reference cylinders with synthetic air. The measurements were carried out under controlled gas concentrations, constant air flow rate 100 ml/min and 50% relative humidity conditions. For the sensitivity calculation, the synthetic air gas was used for about 3 hours, then the sensors were flushed alternately with synthetic air and a fixed value of specific toxic gas concentration (from 50 ppb to 1 ppm) for 4 hours. In case of gas multicomponent measurements, toxic gases were used with the following order: 1 ppm of SO_2, 1 ppm of NO_2 and a mixture of 1 ppm of SO_2 and 1 ppm of NO_2. Between changes of toxic gases type, the sensors were flushed with synthetic air to clean up the measurement chamber from the toxic gas.

3. RESULTS

The sensitivity of sensors was investigated by measurement their response with gradually increased concentration of detected gases. Fig. 2 presents time courses of sensors response to different SO_2 concentrations. Usually, for most sensors, an increased presence of each gas causes increased response of all sensors. For example, the presence of SO_2 results in a significant response of SO_2, as well as, H_2S sensor. Such behaviour confirms the lack of selectivity of this kind of sensors.

The 15-minute averages of the curve parts once the response stabilized (i.e. before the new gas concentration was introduced into the chamber) were used to calculate the response of the sensors in a given concentration of SO_2, what is graphically presented in Fig. 3. The experiment was repeated for all toxic gases (not shown here). The sensors' response almost linearly depended on the concentration of the measured gases. The slope of the response was used for the calculation sensor's sensitivity (Table 1). Generally, obtained numbers are within range declared by the manufacturer. As it can be seen, measured sensitivity of H2S-B4 and NO2-A43F slightly differs from datasheets information.

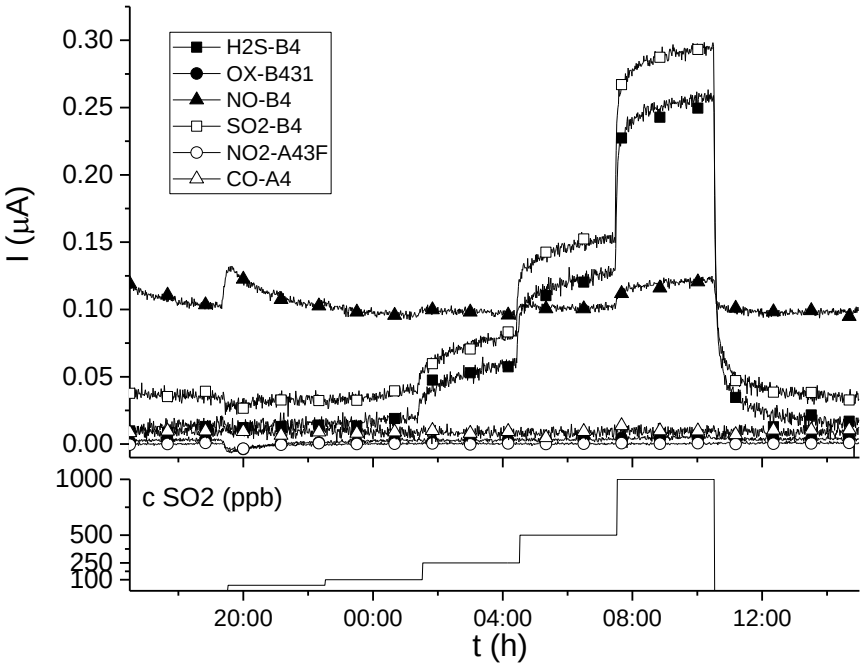

Fig. 2. Sensors response to different concentrations of SO_2

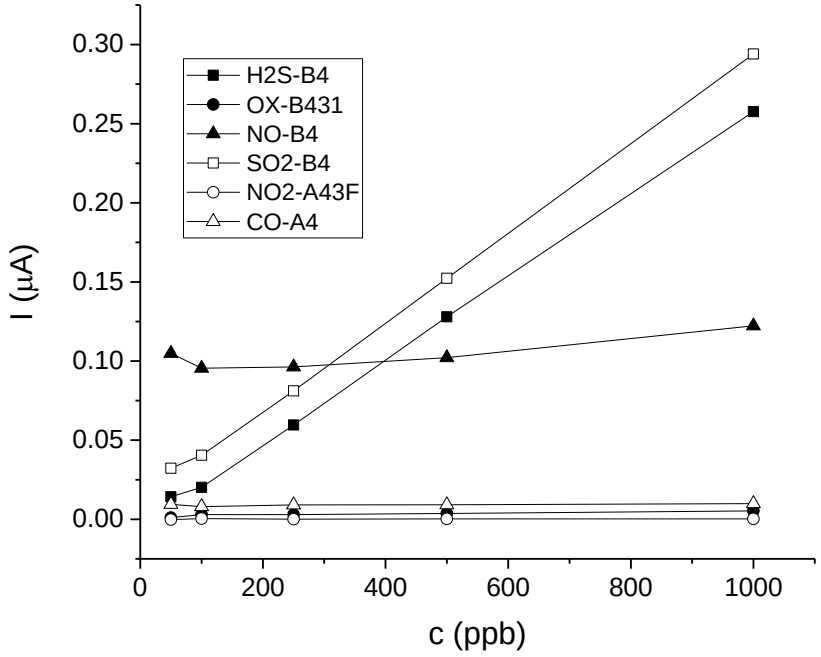

Fig. 3. Sensors stability in given concentrations of SO_2

Table 1. Comparison of calculated sensors' sensitivity values and sensitivities provided by datasheets.

Sensor model	Calculated sensitivity [nA/ppm]	Datasheet sensitivity [nA/ppm]
H2S-B4	1123.8	1450 ÷ 2150
OX-B431	-322.1	-650 ÷ -225
NO-B4	528.2	500 ÷ 850
SO2-B4	275.5	275 ÷ 475
NO2-A43F	-160.9	-450 ÷ -175
CO-A4	276.1	220 ÷ 375

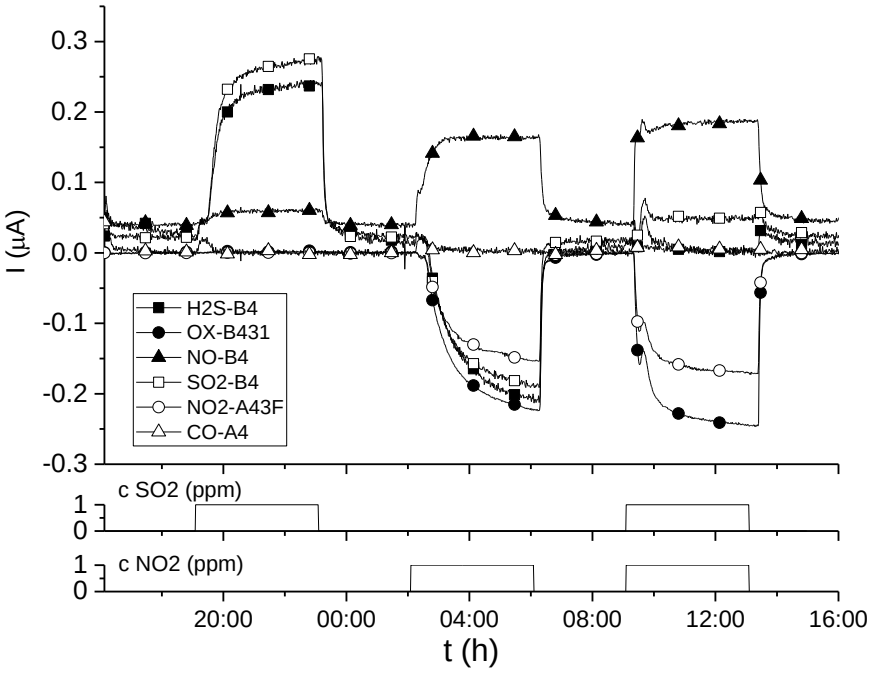

Fig. 4. Sensors response to SO_2 and NO_2 at 50% RH and 100 ml/min flow rate

Fig. 4 represents sensors response to the alternating presence of synthetic air and toxic gases. Calibration of the sensor is necessary to find a correlation between concentration level and sensor output. Calculated sensitivities from Table 1 allowed to convert the current responses of sensors to toxic gas concentration levels, what is illustrated in Fig. 5. The obtained curves show cross-sensitivity of sensors to the presence of NO_2 or SO_2.

It can be observed that sensors react slower to NO_2 than to SO_2. Every sensor except CO-A4 reacts to toxic gases used in the experiment. The difference between SO2-B4 and NO2-A43F responses to SO_2 and NO_2 gas should be equal to the response of the sensors to a mixture of these gases with identical concentrations, but it is not equivalent as it is presented in Table 2.

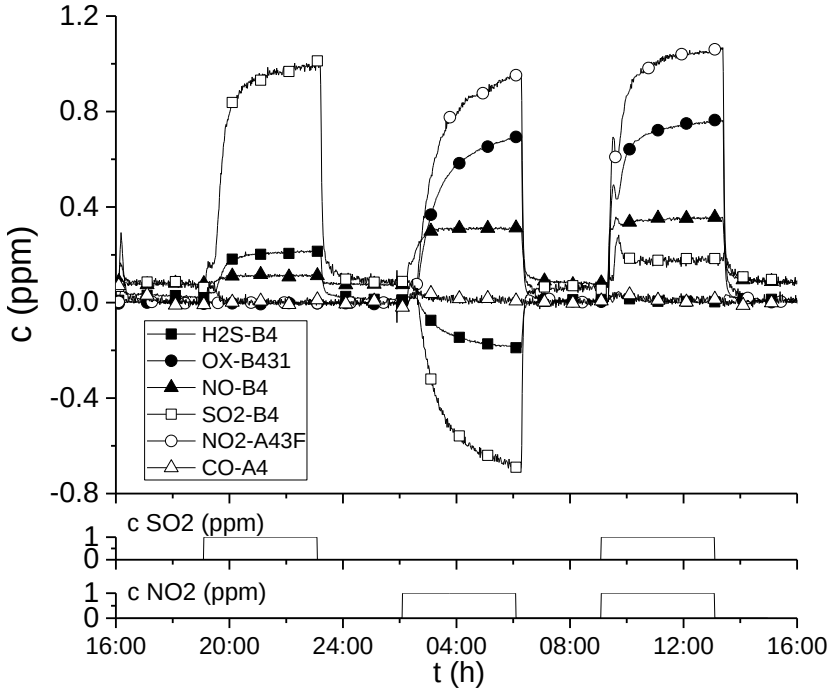

Fig. 5. Sensors response to SO_2 and NO_2 after converting signal to predicted concentrations in ppm using calculated sensitivity (see Table 1)

Table 2. Sensors' responses to SO_2, only NO_2 alone and to mixture of SO_2 and NO_2 gases.

Sensor model	Response to 1 ppm of SO_2 [ppm]	Response to 1 ppm of NO_2 [ppm]	Response to 1 ppm of SO_2 and 1 ppm of NO_2 [ppm]
H2S-B4	0.19	-0.20	-0.01
OX-B431	0.00	0.70	0.76
NO-B4	0.04	0.24	0.28
SO2-B4	0.92	-0.76	0.12
NO2-A43F	0.00	0.95	1.06
CO-A4	0.00	0.01	0.01

4. CONCLUSIONS

In the present investigation, six electrochemical gas sensors were used in order to reveal its cross-sensitivities. The results presented in the text confirm that electrochemical sensors do not only react to the presence of the gases they are constructed to detect. For each sensor, the current response usually depends on the presence of several gases. Especially, the most

sensitive to other gases were H2S-B4 and NO-B4 sensors' respondings to SO_2 and NO_2.

Cross-sensitivity caused by interfering gases is a very important parameter. It can mislead the user of sensor that there is target gas present or it may reduce the level of target gas when in fact it is not true and the user does not know that can be at risk. There are many ways to achieve cross-sensitivity limitation. It can be limited, for example, by using special filters, surface modifications. The very promising ways that can solve problems with poor sensor selectivity are principal component analysis (PCA), partial least square analysis (PLS) or artificial neural networks (ANN) to recognize the mixed gas patterns, what will be the object of our future investigations.

ACKNOWLEDGEMENTS

This work is a part of the project POIR.01.01.01-0907/16 conducted by PM Ecology sp. z o. o. and supported by National Centre for Research and Development, Operational Programme Smarth Growth (PO IR).

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Badanie selektywności amperometrycznych czujników gazów w wieloskładnikowych mieszaninach gazowych

Słowa kluczowe: czujnik gazu, zanieczyszczenie powietrza, selektywność, czułość skrośna, czujnik amperometryczny

STRESZCZENIE

W ostatnich latach smog i kiepska jakość powietrza stały się ogromnym problemem środowiskowym. Ciągłe monitorowanie jakości powietrza stało się koniecznością. Opracowano 6-czujnikowy system czujników elektrochemicznych w celu prawidłowej identyfikacji i koncentracji gazów zawartych w zanieczyszczonym powietrzu. Kalibracja sensora jest niezbędna w celu znalezienia zależności między jego sygnałem wyjściowym a poziomem stężenia, dlatego najpierw zmierzono odpowiedzi każdego z sensorów na stężenia od 50 ppb do 1 ppm gazu, do którego detekcji zostały skonstruowane. Zazwyczaj odpowiedzi czujników przeprowadzane są w obecności tylko jednego gazu. Głównym celem było zbadanie różnych interakcji pomiędzy czujnikami i gazami w wieloskładnikowych mieszaninach gazów. Sensory zostały przebadane w warunkach kontrolowanych stężeń gazów, stałej prędkości przepływu powietrza wynoszącej 100 ml/min oraz wilgotności względnej równej 50%.

Podpisy pod rysunkami:

Rys. 1. Struktura stanowiska pomiarowego

Rys. 2. Odpowiedź czujników na różne stężenia gazu SO_2

Rys. 3. Stabilność czujników w wybranych stężeniach gazu SO_2

Rys. 4. Odpowiedź czujników na obecność gazu SO_2 i NO_2 dla prędkości przepływu 50 ml/min i wilgotności względnej 50%

Rys. 5. Odpowiedź czujników na obecność SO_2 i NO_2 po przekształceniu sygnału na wyliczone stężenia w ppm z wykorzystaniem obliczonych czułości (patrz Tabela 1)

Podpisy nad tabelami:

Tabela 1. Porównanie obliczonych wartości czułości sensorów i czułości zamieszczonych w notach katalogowych

Tabela 2. Odpowiedzi sensorów na obecność tylko SO_2, tylko NO_2 oraz mieszaniny gazów SO_2 i NO_2