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FFT analysis of temperature modulated semiconductor gas sensor response for the prediction of ammonia concentration under humidity interference

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ABSTRACT

The increasing environmental contamination forces the need to design reliable devices for detecting of the volatile compounds present in the air. For this purpose semiconductor gas sensors, which have been widely used for years, are often utilized. Although they have many advantages such as low price and quite long life time, they still lack of long term stability and selectivity. Namely, environmental conditions have significant effect on the sensing accuracy. That is caused by the fact that sensors also respond to interfering molecules coexisting in ambient gas (e.g. humidity) and their response is highly dependent on the temperature and the gas delivery rate. Among the different strategies used to overcome those shortcomings, the modulation of the sensors' operating temperature has been reported. To perform the interpretation and extraction of useful information from dynamic nonlinear response of temperature modulated sensor, the feature extraction and data processing methods are required. In this article the method of determination the concentration of ammonia in the presence of relative humidity is presented. For this purpose the operating temperature of a single commercial SnO_2 gas sensor is modulated using sinusoidal voltage applied to the heater. The measurements are performed for different concentrations of ammonia at specified levels of relative humidity. The validation data set was obtained 100 days after the set used for the calibration data. Several features from the dynamic measurements are extracted. Qualitative and quantitative analysis of the selection of the signal features containing useful and relevant information for prediction of target gas are performed. The assessment of the impact of the input vector length of the Fast Fourier Transform method on the resulting signal features is examined. The selected features are utilized as an input for Partial Least Squared regression. The calibration is performed and the prediction error of the ammonia concentration is calculated based on the validation data.

1. Introduction

Environmental pollution is one of the most serious problem with which humanity now faces. There is a continuous need to design reliable devices for the detection of the volatile compounds present in the air. Today, sophisticated equipment is available on the market allowing precise gas concentration measurements, e.g. mass spectrometers or gas chromatographs. Those two groups of devices and many others allow performing continuous monitoring, but despite their high accuracy, they have some drawbacks. They are characterized by a very high price, an expensive operation and a need to operate only in the stationary condition. The ever-increasing air pollution forces the need for the continuous monitoring. Therefore, the utilization of semiconductor gas sensors is one of the alternative solutions for the detection and determination of the volatile gas mixtures. First concept of system using an array of gas sensors, allowing to accomplish the task of gas recognition was reported in 1982 [1]. Nowadays, metal oxide semiconductor (MOS) gas sensors are one of the most popular group of gas sensors, widely used in domestic safety, air quality control, automotive, appliance control and industrial safety. Systems composed of MOS gas sensors are applicable in many fields, such as in industry for the purpose of controlling the quality of food [2] or environmental monitoring [3]. Semiconductor gas sensors feature a relatively low price and a quite long life time. Consequently, they have attracted the attention of many users due to large number of possible applications and a great variety of detectable gases. Moreover, the advantages of semiconductor gas sensors are the simplicity of use, uncomplicated design, small size and mechanical strength. On the contrary, the main disadvantages of these sensors concern their lack of long-term stability, high energy consumption and low sensitivity and selectivity [4].

Although gas sensors have been developed to achieve high selectivity for a particular chemical species, their sensing properties are limited, due to the fact that they usually respond also to some interfering molecules coexisting in a ambient gas (e.g. oxygen concentration

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and humidity) [5]. Therefore, semiconductor gas sensors reveal low selectivity and are not able to detect a single chemical species in a mixture. This fact is related to the reactions taking place on a sensing layer. These reactions do not occur only with a specific gas presented in a gaseous mixture, but with every gaseous components of the mixture. Moreover, sensors often respond similarly to different gases. Semiconductor gas sensor have been developed to operate under field conditions, but their response is sensitive to the presence of humidity in the working atmosphere [6,7]. It was reported that the adsorption of water affect and modify the sensor response [8] causing long-term variations in resistance of semiconductor gas sensors [9].

In order, to overcome these drawbacks several approaches have been studied, including certain strategies in material science (doping, catalysts, filters) and the modification and optimization of the structure of the sensor [10]. Furthermore, signal processing algorithms for feature extraction of the data sensor arrays were applied [11]. Over the years promising results were obtained using the analysis of transient sensor responses [12] or changes of sensor temperature [13].

Of the last group of techniques, the most commonly used method includes controlling the temperature of the semiconductor surface in order to gain more information from sensors resistance response. The conventional sensing method based on obtaining information about the gaseous species in form of the conductance under constant applied voltage is limited. That is because sensor also responds to interfering species that exist along with target gas, like e.g. water vapor. On the contrary, by analyzing the dynamic nonlinear response as a result of sensors temperature changes, one can obtain more information about the content of the gas mixture in the presence of the sensor [5,14]. In 1973 Eicker patented a method of carbon monoxide and methane detection using temperature variation of metal oxide semiconductor [15]. This technique, called temperature modulation, was developed for improving the selectivity of gas sensors. It was proven that both, sensitivity characteristics of semiconductor gas sensor and the kinetics of adsorption reactions on the sensing surface, are affected by the operating temperature [14]. It was also reported that using commercial Taguchi Gas Sensors, the amplitudes of the DFT (Discrete Fourier Transform) harmonics obtained from sensor response exhibit characteristic changes depending on the chemical structure and concentration of gases, which enable the distinction among concentration of gases [16]. Moreover, it was possible to quantitatively distinguish propane in the presence of water vapor, by analyzing the response of sinusoidal temperature modulated sensor [5].

Changing (modulating) the operating temperature of the MOS-type sensor affects the desorption and adsorption reactions. That can provide more information from sensor response about the gas species. Moreover, more accurate detection and determination of the composition of atmosphere is possible [16]. Furthermore, it should be emphasized that the interpretation of the dynamic nonlinear response of temperature modulated MOS gas sensor is complex and requires the use of data analysis methods. Such techniques contain a great number of statistical and machine learning algorithms [17,18]. In general, they can be assigned to feature extraction (e.g. Fast Fourier Transform (FFT), Discrete Wavelet Transform (DWT)), and data analysis methods (e.g. Artificial Neural Network (ANN) and Partial Least Squares (PLS)). Also, the Principal Component Analysis (PCA) and Support Vector Machine (SVM) are known as ones of the most efficient tools [19,20].

In this study, a single commercial GGS10331 semiconductor gas sensor in different concentrations of ammonia with humidity interference is examined under the application of a periodic temperature change. The aim of the study was to evaluate whether it is possible to extract the information about the ammonia concentration and build the calibration model able to estimate ammonia concentration despite the humidity level. Moreover, the possibility of shortening the time of the measurements conducted in the temperature modulation mode by comparison of the FFT results performed on different number of periods of sensor responses was investigated. The calibration models composed of sets containing the DC value of the sensor response and relative humidity level and selected features from FFT analysis were compared. It was demonstrated that the approach utilizing FFT features results in a lower prediction error.

The determination of the ammonia concentration was previously investigated using temperature modulated semiconductor gas sensors in humidified atmosphere [21,22]. Also, the FFT analysis, was frequently utilized in the case of the temperature modulated gas sensors e.g. in [23]. However, there is a lack of reports where a single sensor, working in temperature modulation mode combined with FFT analysis and multivariate calibration methods are used for the purpose of prediction of the ammonia concentration despite the presence of humidity. It is also worth emphasizing, that in many literature reports concerning gas recognition and concentration prediction, the data for calibration and validation set are randomly drawn from one data set. That minimizes or even eliminates the aging and other drift causing effects. This is in contrast to our work, in which a strictly defined measurement protocol has been applied and the effects of instability of the sensor response are pronounced.

2. Experimental

2.1. Gas sensor

Single semiconductor gas sensor GGS 10331 produced by Umwelt Sensor Technik (UST) was used in this study. This sensor was design for the detection of air contaminants, making it suitable for the monitoring of the air quality. It is made of a semiconductor sensing layer on Al_2O_3 substrate with a structured Pt-film, consisting of heater channels and electrodes. The measurements were performed under the sinusoidal voltage excitation of the heater. The temperature of the heater in dynamic mode was estimated using Eq. 1 provided by the UST [24]:

$$T_H = -\left(\frac{A}{2B} + \sqrt{\frac{A^2}{4B^2} - \frac{R_{H0} - \frac{U_H}{I_H}}{R_{H0}\cdot B}}\right) \tag{1}$$

where U_H and I_H are the voltage and the current input, $R_{H0} = 10\,\Omega$ denotes the heater resistance at 0 °C and parameters $A = 3.9083\cdot10^{-3}\,°C^{-1}$ and $B = -5.775\cdot10^{-7}\,°C^{-2}$ stands for the linear and the quadratic coefficients, respectively.

2.2. Measurement stand

Schematic diagram of the measurement stand is presented in Fig. 1. A sinusoidal voltage with a frequency f = 0.025 Hz was generated using Arbitrary Power Supply Hameg 8143 and applied to the heater of the semiconductor sensor. The parameters of voltage signal were selected to modulate the temperature of the sensing layer from 300 °C to 500 °C during each period of 40 s. The resistance of the sensing layer was measured using 4-probe method with sampling frequency of $F_{SAM} = 5$ Hz using the digital Multimeter Keithley 2400. The parameters of the voltage signal applied to the sensor's heater were selected to achieve a nonlinear response. For the purpose of conducting measurements with changing relative humidity level, one of the mass flow controllers was connected to air bubbler. The humidity level was controlled by adjusting the flow rate of dry synthetic air and the water saturated synthetic air. Before carrying out the measurements, the humidity level was verified by two commercial humidity sensors SY-HS-220. Maximum deviation of ± 2% RH from desired RH level was obtained. Specific concentrations of ammonia were supplied also by mass flow controllers at a constant flow of 100 $cm^3\,min^{-1}$. Desired concentrations of ammonia were obtained premixed with high purity dry synthetic air (Linde Gas). Gas flow rate was controlled using mass flow controllers Brooks GF Series. Based on technical data provided by the manufacturer, the accuracy of mass flow controllers for the investigated