Extraction and evaluation of gas-flow-dependent features from dynamic measurements of gas sensors array

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ABSTRACT

Gas analyzers based on gas sensors are the devices which enable recognition of various kinds of volatile compounds. They have continuously been developed and investigated for over three decades, however there are still limitations which slow down the implementation of those devices in many applications. For example, the main drawbacks are the lack of selectivity, sensitivity and long term stability of those devices caused by the drift of the sensors. This implies the necessity of investigations not only in the field of development of gas sensors construction, but also the development of measurement procedures or methods of analysis of sensor responses which compensate the limitations of sensors devices. One of the fields of investigations covers the dynamic measurements of sensors or sensor-arrays response with the utilization of flow modulation techniques. Different gas delivery patterns enable the possibility of extraction of unique features which improves the stability and selectivity of gas detecting systems. In this article an overview of three utilized flow modulation techniques is presented, together with the proposition of the evaluation method of their usefulness and robustness in environmental pollutants detecting systems. The preliminary results of dynamic measurements of an commercially available TGS sensor array in the presence of nitrogen dioxide and ammonia are shown.

Keywords: TGS sensors, dynamic measurements, electronic nose

1. INTRODUCTION

The studies on the development of an instrument, which is able to perform quality and quantity analysis of measured volatile compound are conducted since 1982 [1], when the concept of utilization of an array of partially selective gas sensors and proper data analysis software for the purpose of measured gases recognition was presented. Since then, such devices, in literature commonly referred to as electronic noses, have found a wide range of potential applications, e.g. in medicine for detection of diseases [2, 3], in industry for monitoring food or drinks quality [4] or for environmental pollutants monitoring [5, 6, 7]. Their advantages, e.g. the possibility of working in real-time operation mode, compact size or low cost caused that electronic gas-analyzing systems became an attractive alternative for other gas-analyzing systems, like gas chromatographs. However, those devices still have limitations, which need to be investigated.

The main drawback of electronic gas-analyzing systems is connected with the gas sensors properties [8]. Currently, commercially available gas sensors are having poor selectivity and sensitivity. Additionally, their metrological properties vary in time – sensors tend to drift [9]. This fact implies the need for the investigations on the new better construction of gas sensors, but also in the field of the development of advanced measurement procedures or data-analysis algorithms for mitigation the negative effects of sensors properties. One of the fields of investigations in the artificial olfaction covers the data analysis methods for recognition and quantification of measured compounds. There is a variety of statistical and machine learning algorithms employed for this purpose [10, 11]. In general, all methods require two-stage procedure to perform the task of the recognition or quantification – the stage of training and validation. This cause the need for creation representative training and validation datasets, which contain the informative features obtained from sensor responses. The problem of features extraction and selection from measurements is a crucial stage, which implies the general performance of data analysis software. The way of obtaining informative features is directly connected with the types of sensors, measurements procedure as well as utilized gas-delivery system. In this article we present the procedures of dynamic measurements of sensor array responses, and we propose the assessment method for evaluation the usefulness of obtained in this way features.

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2. GAS-DELIVERY SYSTEMS IN ELECTRONIC GAS-ANALYZERS

2.1 Features connected with electronic gas-analyzer’s subsystems

The typical electronic gas-analyzing device, schematically presented in Figure 1 consists of four main elements, namely, gas delivery subsystem, an array of gas sensors, data acquisition and power supply circuits and data analysis software. The feature vectors, which are given as inputs for pattern recognition algorithms, are formed based on the measured responses. Thus, they depend strongly on all components of the system. There are many reports [e.g. 12, 13] in which features connected with sensors power supply system are utilized. This technique is called temperature modulation, because the voltage waveform given on the sensors heater causes the changes in operation temperature of the sensor, which often improves the selectivity and sensitivity of the sensor. With proper preprocessing (e.g. FFT, DWT), temperature modulation enables an efficient gas recognition. There are also reports in which the features for gas recognition are connected with the data acquisition system, e.g. fluctuation-enhanced gas sensing [14, 15]. One of the approaches for obtaining additional information about the type and the concentration of measured gas results uses gas-delivery subsystem and is connected with the changes of gas flow rate in measurement chamber.

2.2 Influence of the gas flow velocity on the TGS sensor responses

Gas sensors responses, especially in the case of commercially available and widely used in numerous applications TGS sensors, are strongly dependent on the gas flow rate. In Figure 2 this phenomenon is shown on the example of two TGS sensors – TGS 825 and TGS 880. Figure 2 presents the changes in sensors responses in the presence of synthetic air which does not flow, and flows with constant rate of 50 cm$^3$ min$^{-1}$ and 100 cm$^3$ min$^{-1}$. Both sensors responses change noticeably with the change of gas flow. Additionally, it is shown that sensors react differently for the changes of flow rate. This property of the sensors gives the background for utilization the dynamic measurements, e.g. gas flow rate modulation for obtaining the additional information from sensors responses in electronic gas-analyzing systems.

<table>
<thead>
<tr>
<th>R/Ω</th>
<th>t/min</th>
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<tbody>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>100 cm$^3$ min$^{-1}$</td>
<td>12</td>
</tr>
<tr>
<td>50 cm$^3$ min$^{-1}$</td>
<td>12</td>
</tr>
<tr>
<td>0 cm$^3$ min$^{-1}$</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 2. Gas flow dependence on the TGS sensors responses. On the left – the responses of TGS 825 sensor, on the right – the responses of TGS 880.
2.3 Dynamic measurements

In general, the response obtained from the sensor during dynamic measurements forms the characteristic fingerprint, which contains the information about the type and the concentration of measured gas. This differs from e.g. static characteristics measurements, where only single value is measured. The TGS sensors responses are dependent on many factors. Namely, beside the gas concentration and gas flow rate, it includes temperature, humidity and drift caused by poisoning or aging. Thus, static measurements can be insufficient for detection and cannot provide the long-term stability of metrological instrument. There are several techniques of the dynamic measurements that are reported to be utilized. The implemented measurement procedures are always based on at least one stage of target gas delivering to the measurement cell and the stage of cleaning, most commonly with the use of synthetic air or N₂. The stage of delivering the target gas to measurement cell can be performed using flow controllers, where the gas flow velocity can be maintained at the demanded level, but it can also be done with the use of e.g. syringe, where the established amount of gas is injected into the measurement cell. There are no established guidelines for the time of exposure to the target gases and cleaning phase, i.e. these times differ in various reports [16-19].

2.4 Standard protocol

![Diagram of standard protocol for dynamic measurements.](image)

Figure 3. Standard protocol for dynamic measurements.

The diagram of the standard protocol for the dynamic measurements is presented in Figure 3. Single acquisition of the sensor response contains measurements in the presence of target gas. The target gas is delivered to the measurement cell at time \( t_1 \), then, during \( t_2 \) time, the cleaning stage is conducted. From the obtained curve, which represents the response for specific target gas, characteristic features can be calculated [18, 19].

2.5 Short period gas delivery pattern

![Diagram of short period gas delivery pattern.](image)

Figure 4. Short period gas delivery pattern.

The modification of the standard protocol, presented in [20], called short period gas delivery pattern, is based on the sequential delivering during shorter periods \( t_1 \) and \( t_2 \) of the target gas to the measurement cell. This implies the different sensors response acquisition shape, where additional features for the further recognition can be observed and utilized. The diagram of standard protocol for short period gas delivery pattern is shown in Figure 4.
2.6 Stop flow mode of operation

Another procedure of dynamic measurements of sensors array, called, the stop flow mode of operation \([21, 22, 23]\) consist of three stages. During \(t_1\) period, the target gas is delivered to the measurement cell, then, for the \(t_2\) the gas flow is stopped and finally, in the last stage of measurement, the cell is cleaned with the reference gas, e.g. the synthetic air. The diagram for this mode of gas delivering is shown in Figure 5. This technique also enables obtaining the additional information hidden in the unique shape of acquisition.

2.7 Features from the dynamic measurements

Various different features can be extracted from the response curve obtained during measurements \([19]\). Some of them are taken directly from the acquisition, e.g. minimum or maximum value of sensor response, based on which the parameter of amplitude or relative amplitude can be calculated. There are also features connected with dynamic properties of the sensors – quasi time-constants (the selected part of initial exposure to the target gas) or the features which represent the total information about reaction on the sensors – the surface under the measured curve. Another approach for obtaining informative features is based on additional calculation of the statistical parameters such as kurtosis or skewness \([18]\). Skewness and kurtosis are the measures which describe the shape of measured curve. Skewness is the indicator of the asymmetry of the curve, while kurtosis describes the flatness of the acquisition. Thus, these parameters can be utilized as a features for the gas concentration recognition.

2.8 Statistical evaluation

The statistical evaluation of the informative role of features extracted from dynamic measurements is not currently available in literature. The comparative study on that problem could be the useful guide in the process of the development of the electronic gas-analyzing systems and supports the choice of the most suitable data processing. A statistical evaluation of measurement data can be used for this purpose. In \([24]\), the statistical assessment was utilized for evaluation of quantification methods in gas sensor system. The McNemar’s test was applied for the investigation of significant differences between selected methods for prediction of toluene concentration.

The aim of statistical evaluation of the influence of the selected features from dynamic measurements is to indicate, whether there is a significant difference between utilized gas-delivering procedures. For this task, the McNemar’s test could be used \([24]\). Using this test, the sets of features from various dynamic measurement techniques can be compared. In the first step, the analysis of the usefulness of the extracted parameters is performed for the purpose of creation the optimal feature set. The statistical analysis in this case covers the evaluation of the distribution of individual features (the test depends on the size of the dataset – for the smaller set, the Shapiro-Wilks test can be applied). The Spearman’s rank correlation coefficient can be utilized as a indicator of the features, which should be selected for composition of features vector for further classification or regression analysis. Then, with the established sets of features the evaluation of the efficiency of the individual gas-delivering procedures can be performed. In this work, a set-up for experiment for conducting dynamic measurements of sensor array and preliminary results obtained for further statistical assessment described above are shown.
3. EXPERIMENT SETUP

3.1 Measurement stand

The measurements are conducted on the prepared measurement stand. The gas sensor array consists of two measurement cells serially connected with in total eight commercially available semiconductor TGS sensors (four sensors in each cell) and two temperature sensors (one for each cell). The temperature inside the one of the chambers can be adjusted by a heating cable wrapped around a measurement chamber, which temperature is controlled by the temperature controller Fuji PXR4. This enable conducting measurements in varying temperature profiles inside the cell. The types of sensors utilized in an array are shown in Table 1. Sensors heaters were supplied with a constant voltage of 5 V or 6.2 V (TGS 2106) using programmable power supply HAMEG 8040. The sensors responses are automatically measured using multimeter Keithley 2700 and designed software for data acquisition. The resistance was measured using 4-probe method.

Table 1. Composition of an array.

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Target gases</th>
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<tbody>
<tr>
<td>TGS 826 (2x)</td>
<td>NH₃</td>
</tr>
<tr>
<td>TGS 825 (2x)</td>
<td>H₂S</td>
</tr>
<tr>
<td>TGS 2106 (2x)</td>
<td>NO₂</td>
</tr>
<tr>
<td>TGS 880</td>
<td>Air pollutants</td>
</tr>
<tr>
<td>TGS 2600</td>
<td>Air pollutants</td>
</tr>
<tr>
<td>Pt 100, Pt 1000</td>
<td>Temperature monitors</td>
</tr>
</tbody>
</table>

The gas-delivery system, the crucial system for conducting the dynamic measurements, consists of two Brooks GF Series mass flow controllers connected to the PC with RS 485 interface. This system is easily scalable, there is a possibility of adding more flow controllers (e.g. for the purpose of conducting measurements with changing humidity levels). The gas profiles are programmed with the MEDSON software. The gas flow in the measurement cell is set to 100 cm³ min⁻¹.

3.2 Gas measurements

For the purpose of conducting statistical analysis described above, three datasets have to be collected, each for the individual gas-delivering technique. Two kinds of air-pollutants were selected as target gases, namely nitrogen dioxide and ammonia. Despite the fact, that selected sensors (TGS 2106 and TGS 826) are designed for detection of those compounds, all utilized sensors change their output resistance in the presence of target gases. For the reference gas, synthetic air was used. All gases were provided by LindeGas. The concentrations of target gases for the measurements are equal to 0 ppm, 25 ppm, 50 ppm, 75 ppm and 100 ppm, for the purpose of further analyses. The measurements are conducted in the dry air, without changing humidity and at constant temperature (47°C in the cell with heating cable and 43°C in the second cell).

3.3 Data processing

The data from acquisition system are further processed using self-written Matlab software. Each measured acquisition forms a vector of resistance responses of individual sensor. A set of vectors are formed into a matrix of samples for each sensor in the presence of individual concentration. The program automatically extracts demanded parameters from a matrix of acquisitions, namely minimum value, maximum value, amplitude, surface under the curve, skewness, kurtosis and the width of the curve that corresponds to the time when the curve reach the half of its maximum height [15]. Data in such a form can be easily processed further with written software that realize various multivariate calibration and pattern recognition methods, like PCA, PLS, k-NN or SVM [25, 26] as well as with the software which realize the statistical analyses.
Figure 6. a) TGS 2106 responses to NO₂ in stop-flow mode of operation. b) TGS 2600 responses to NO₂ in stop-flow mode of operation. c) TGS 880 consecutive responses to 100 ppm of NH₃ in stop-flow mode of operation. d) Features: kurtosis and skewness extracted from TGS 2106 responses.

4. EXEMPLARY RESULTS

The preliminary results are shown in Figure 6. They represent the effects of utilization of stop flow mode of operation. In Figure 6a the exemplary responses of TGS 2106 sensor to 50 ppm and 100 ppm of NO₂ are presented. To show, that each sensors response forms a unique shape, which contain the additional information, in Figure 6b the TGS 2600 sensor responses for the same concentration of NO₂ are presented. The stop flow mode of operation in our study is performed slightly differently than in [21]. The time t₁ was established to last 7 minutes, the same as t₂, but the t₃ (the air-on phase) lasted 46 min, so the whole time of the single measurement was equal to 1 hour. This was caused by the fact, that in reports [21, 22, 23] the gas flow in measurement chamber were equal 2000 cm³min⁻¹ and in our case it was 20 times less – 100 cm³min⁻¹. Due to this fact the air on phase was longer than in reports [e.g. 21], and it lasted till the sensors responses returned to the initial baseline.

In Figure 6c the exemplary results of four measurements of the TGS 880 in the presence of 100 ppm NH₃ are presented to reveal, that in responses to ammonia the drift is observed. The sensors do not achieve their initial baseline resistance. This phenomenon can be managed with proper preprocessing of the sensors data. This task can be done with the normalization procedure which does not reshape the curve, but rescale it to the range of [0:1].
In the Figure 6d the exemplary features calculated from the TGS 2106 response are shown. The skeweness and kurtosis were obtained from the measurements in the presence of synthetic air (four measurements), 50 ppm of NO$_2$ (two measurements) and 50 ppm of NH$_3$ (three measurements). It can be seen, that for different measured compounds, both parameters achieve different values, so they contain information about the kind of measured compound.

5. CONCLUSIONS

In this paper the important part of electronic gas-analyzing systems, namely, the gas-delivery system for dynamic measurements was described and three different approaches which can be utilized to achieve unique features from measurements were shown. The design of the experiment which would indicate the usefulness of the features obtained from the dynamic measurements were presented. The preliminary results from the utilization of the stop flow mode of operation for the measurements of an TGS sensors array in the presence of two air-contaminants – nitrogen dioxide and ammonia were shown. For the purpose of performing the statistical analysis which will indicate the informative role of the obtained features and comparison between three types of gas-delivering procedures, the representative datasets are being collected. The further investigations are connected with the evaluation of the features obtained from the dynamic measurements. The comparison of measurements procedures connected with gas-delivery subsystem in electronic gas-analyzers is being prepared.

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