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EFFICIENCY OF LINEAR AND NON-LINEAR CLASSIFIERS FOR GAS IDENTIFICATION FROM ELECTROCATALYTIC GAS SENSOR

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Abstract

Electrocatalytic gas sensors belong to the family of electrochemical solid state sensors. Their responses are acquired in the form of I-V plots as a result of application of cyclic voltammetry technique. In order to obtain information about the type of measured gas the multivariate data analysis and pattern classification techniques can be employed. However, there is a lack of information in literature about application of such techniques in case of standalone chemical sensors which are able to recognize more than one volatile compound. In this article we present the results of application of these techniques to the determination from a single electrocatalytic gas sensor of single concentrations of nitrogen dioxide, ammonia, sulfur dioxide and hydrogen sulfide. Two types of classifiers were evaluated, i.e. linear Partial Least Squares Discriminant Analysis (PLS-DA) and nonlinear Support Vector Machine (SVM). The efficiency of using PLS-DA and SVM methods are shown on both the raw voltammetric sensor responses and pre-processed responses using normalization and auto-scaling.

Keywords: electrocatalytic sensor, cyclic voltammetry, data pre-processing, Support Vector Machine, Partial Least Squares Discriminant Analysis.

1. Introduction

Gas-analyzing systems based on gas sensors or gas sensor arrays are the practical implementation of an artificial olfaction concept proposed by Persaud in 1982 [1]. Since then, a variety of electronic noses were proposed for qualitative and quantitative characterization of different volatile compounds. Such systems usually consist of an array of chemical sensors combined with specific data analysis and pattern-recognition methods [2]. The electronic nose systems are still of scientific and commercial interest due to their ability of fast, reliable and even on-line measurements in a working environment. One of the areas of application of such devices is the field of air quality monitoring.

Electrocatalytic gas sensors belong to the group of solid-state electrochemical gas sensors [3, 4]. Such sensors are operating in the cyclic voltammetry mode. With proper excitation and in suitable operating conditions they are able to detect different gases with a single and simple sensor structure [5, 6]. The electrocatalytic sensors are still under development. Our previous research activities were connected with investigation of different sensor structures and operating conditions and with elucidating their sensing mechanism [7-11]. On the other hand, efficient ways of electrocatalytic gas sensor response analysis in order to predict the gas type and estimate its concentration are sought. So far, only a few methods have been proposed. One method utilizes the fact that concentration of the measured compound is related to the area under the I-V peak. This assumption is based on the fact that there is a relation between

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the amount of the charge taking part in electrochemical electrode reactions and the area under the peak [8]. Another approach has been proposed by analogy to the wet chemistry, where the height of the peak at a specific excitation voltage can be used as an indicator of the type and concentration of the measured gas [12]. Our recent studies are related to response analysis from a single electrocatalytic gas sensor using multivariate data analysis and pattern recognition techniques. These techniques are commonly used in the field of gas-sensing [2, 13]. Although, there were also reported attempts of using noise measurements and simpler algorithms for gas detection with single commercial TGS gas sensors [14].

This study is focused on the examination of the classification efficiency of linear and nonlinear classifiers, namely Partial Least Squares Discriminant Analysis (PLS-DA) and Support Vector Machine (SVM), which are performed on data from the single electrocatalytic gas sensor. Both methods are applied for the first time for the analysis of the electrocatalytic gas sensor responses. Four different environmental gases of single concentration (20 ppm), i.e. nitrogen dioxide, ammonia, sulfur dioxide and hydrogen sulfide, were investigated. The ability of determination of the type of measured gas was examined using raw data and processed with two popular pre-processing methods – data normalization and auto-scaling. Additionally, the results of using PCA as the feature extraction method and SVM as classifier for improving the determination efficiency are shown.

2. Experimental

The electrochemical gas sensor was fabricated using solid state Nasicon electrolyte (chemical formula $Na_{2.8}Zr_2Si_{1.8}P_{1.2}O_{12}$). A description of the sensor's preparation procedure is described in detail in [7]. Briefly, the Nasicon powder was prepared by the conventional solid-state ball milling method using stoichiometric mixtures of chemically pure $NaHCO_3$, ZrO_2, SiO_2 and $NH_4PO_4 \bullet 3H_2O$ [15]. Pellets in the form of discs of 12 mm in diameter and 1 mm thick were prepared by powder iso-axial pressing and sintering at 1200°C. Electrodes were made by coating opposite pellet sides with a platinum paste (ESL 5542) and firing at 900°C. The measurements were conducted in synthetic air and in 20 ppm of ammonia, sulfur dioxide, nitrogen dioxide and hydrogen sulfide. All toxic gases were obtained premixed with synthetic air (Linde Gas). Precision mass flow controllers were used for obtaining the desired concentration of each gas. During measurements a constant gas flow of 100 cm^3 min^{-1} was maintained. The sensor was placed in a tube furnace. For electrical measurements the Solartron SI 1287 electrochemical interface was used. The sensor was excited with a symmetrical triangular voltage of 5 V amplitude and sweep rate of 50 mV s^{-1}. All results presented in this work were obtained for a single sensor at an operating temperature of 300ºC. The measurements were conducted according to the following procedure.

Before the measurements, the sensor was regenerated by cycling (40 cycles, ±5 V, 50 mV s^{-1}) in synthetic air (SA) at the temperature of 500ºC [16]. When the process of regeneration was completed, the operating temperature was decreased to 300ºC and the measurements in synthetic air were conducted until the sensor response was stable (~20 cycles). After that, the sensor was exposed to 20 ppm of the selected gas (in the following order – H_2S, NH_3, NO_2, SO_2), and when the response has been stabilized (after ~10 cycles), the measurements were performed and I-V responses were collected for further analysis. After the measurements, the procedure of regeneration was repeated and the following gas was measured as described above.

3. Data analysis

In order to utilize the possibility of determining the gas type using pattern recognition algorithms, the measured data have been treated in a systematic way. The analysis consisted of procedures of feature selection from the measurements, data pre-processing, feature extraction, dimensionality reduction and finally classification.

The analysis of electrocatalytic sensor responses is based on the assumption that the whole I-V curve could give useful information. Thus, the values of current from the whole range of voltage excitation are treated as features for the classifiers. They are frequently pre-processed using such methods as normalization or auto-scaling [17]. The pre-processing often improves the classification results [18]. Though, the pre-processing step is not always used [19]. In this work, we investigate the influence of utilizing pre-processing techniques on the efficiency of linear and nonlinear classifiers. We also present the results for raw (untreated) data. In fact, the good performance using untreated data would also be desirable because of data processing simplification. The next step in multidimensional analysis is feature extraction. The goal for this step is to remove the redundancy from data and present them in a more suitable form for the classifier. In the field of gas sensor analysis and voltammetric data analysis in liquid electrochemistry, the Principal Component Analysis is often used at this step [20 - 22]. In this work we demonstrate the influence of application of the PCA feature extraction procedure on the efficiency of classification. The classifiers used in this work, PLS-DA and SVM, are the supervised analysis methods based on learning by example. This means that they need to be trained using a training dataset to perform the task of classification. The efficiency of the classifier is tested through the use of the test set, which contain a different dataset than used during training. All analysis presented in this study has been performed using Toolboxes (Statistics Toolbox) provided in Matlab (Mathwork, Inc). For SVM classification, the library LIBSVM was used [23].

3.1. Dataset – feature selection procedure

The measured and collected I-V responses were used to create a dataset for the analysis. The resulting multidimensional set contained a total of 158 observations (acquisitions) for four toxic gases and synthetic air. Each I-V curve (a single acquisition) taken for analysis was treated as a vector of selected values of current corresponding to the values of voltage excitation in the range from -5 V to 5 V with a 0.1 V step. As a result, a single acquisition vector length was equal to 200 current responses. The dataset which contained all acquisitions was divided into 2 sets, which were used for different purposes. The initial 73% of the acquisitions for each of measured gas was used for training the classifiers (training dataset), while the last 27% of the acquisitions for testing efficiency of classifiers (testing dataset). Additionally, the whole dataset was used for PCA analysis in order to visualize classes representing each volatile compound: synthetic air, ammonia, nitrogen dioxide, sulfur dioxide and hydrogen sulfide.

3.2. Principal Component Analysis – feature extraction procedure

Principal Component Analysis is a linear technique that can be used for feature extraction and input data reduction. The goal is to obtain new features that provide information in a more compact way in comparison with the original data. It is a mathematical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated

variables into a set of values of linearly uncorrelated variables called principal components (PCs). The number of PCs is equal to the number of original variables, but often the first few components explain the most variance of the original variables. This fact frequently implies a reduction in the number of features used for the classification procedure because the dimension of the feature space is now reduced. The PCA can also be utilized to visualize the multidimensionality of data. Namely, it helps establishing whether the classes can be distinguished. The PCA method converts the input data **X** into the product of two matrices – scores **Q** and loading **P**, according to the rule:

$$X = QP^T . \tag{1}$$

The score matrix contains vectors which describe the direction of the principal components in relation to the observations, while the loading matrix is a set of loading vectors which describe the direction of the principal components in relation to the original variables [2, 24, 25]. In this paper the PCA is used for two purposes: for feature extraction and to visualize the multidimensionality of data. For the former, the PCA is performed on the train set, so the initial acquisition vector can be reduced for the further classification task. For the latter, the PCA is performed on the whole dataset to visualize the effect of application of the pre-processing procedure and repeatability of the sensor responses.

3.3. Data pre-processing

In the analysis of sensor output signals, the choice of the appropriate pre-processing technique is crucial for the performance of the pattern classifier [26]. However, there is still no rigid guideline which pre-processing technique is the best to maximize the classification efficiency [17]. Here, two pre-processing methods are applied, i.e. normalization (range-scaling) and auto-scaling. Normalization is used to rescale the values of the measurements to a level which is more suitable for classifiers. Especially in the case of the Support Vector Machine classifier its performance might be decreased dramatically, if the input data are not rescaled to the appropriate level, such as [0, 1] or [-1, 1] [27]. The formula of the normalization technique for values from the matrix with acquisitions $\boldsymbol{X}$ is presented below:

$$x_{ij}^{norm} = \frac{x_{ij} - \min(x_j)}{\max(x_j) - \min(x_j)}, \tag{2}$$

where $\boldsymbol{X}^{\boldsymbol{norm}}$ is the normalized matrix, index i is the number of rows (one row is one acquisition) and j indicates the number of columns (corresponding to a set of current values related to the selected excitation voltage for all acquisitions).

The auto-scaling method provides the mean-centering of data from $\boldsymbol{X}$ matrix and sets the variance within the data to 1. In this procedure, the mean value of the j^{th} column is subtracted from the original matrix, and then it is divided by the standard deviation of the j^{th} column. The formula for calculation the auto-scaled matrix $\boldsymbol{X}^{\boldsymbol{scal}}$ is shown below:

$$x_{ij}^{scal} = \frac{x_{ij} - mean(x_j)}{std(x_j)} . \tag{3}$$

To present the auto-scaled data in a form more suitable for classifiers, the third pre-processing technique is based on the combination of the two previously described methods. Namely, the acquisitions are in the first step auto-scaled and then normalized in order to obtain the data in the range between 0 and 1.

Beside the utilization of pre-processing techniques, we also demonstrate the efficiency of classification using only raw data, i.e. without any mathematical operations. In fact, if it is possible to achieve satisfactory results on the raw (untreated) data, it would be an advantage for the gas detecting system based on the electrocatalytic gas sensor.

3.3. PLS-DA and SVM classifiers

A Partial Least Squares analysis have been originally developed as a regression method [28], commonly used for modeling and analysis of multidimensional data, i.e. data from electrochemical sensors. The PLS can be also utilized as a classifier (PLS-DA). This linear supervised method requires two datasets – a matrix of measured samples $\boldsymbol{X}$ (i.e. a set of acquisitions) and corresponding to them vector $\boldsymbol{Y}$ containing classes for specific compound. The PLS-DA models the relationship between those two datasets. It determines a set of latent variables (LVs) in a similar way to the principal components for the PCA. However, in case of PLS-DA, the LVs explain both the variance of $\boldsymbol{X}$ as well as the correlation with the $\boldsymbol{Y}$. As a result of using the PLS-DA method, a matrix of predictors is achieved, which estimates class affiliation [18, 29]. In this study we present the results of creating PLS-DA models with various numbers of latent variables used to train the classifier.

A second classifier examined in this study was the Support Vector Machine. The SVM method, proposed by Vapnik [30], has proved to be an useful tool in case of analyzing data from gas sensors [31, 32, 33]. The SVM maps the input data onto a higher dimensional feature space, which is non-linearly related to the input space. The goal for this method is to achieve a maximal margin between target classes. The SVM was primarily proposed as a binary classifier, however, by utilizing kernel functions and strategies one-against-one or one-against-all the SVM can be applied to the multi-class problems. For the analysis presented in this study, a strategy one-against-one for determining five volatile compounds was used. It means, that the SVM classifier creates k(k-1)/2 different binary classifiers, where k is the number of different classes. A great advantage of the SVM method is the fact that using kernel functions it provides non-linear classification or regression. The most popular kernel functions are linear, Gaussian radial basis or polynomial functions. In this work, the Gaussian radial basis function was selected as a kernel function (4):

$$k(x_i, x_i^{'}) = \exp(-\gamma \left\| x_i - x_i^{'} \right\|^2), \tag{4}$$

where, x_i and $x_i^{'}$ are the row vectors from the matrix of acquisitions $\boldsymbol{X}$.

The procedure of applying SVM for a specific classification problem requires estimating optimal parameters, like the penalty-constant C or parameter γ. For a large value of C, a large penalty is assigned to margin errors. A smaller value of C allows ignoring points which are too close to the decision boundary, and allows increasing the margin between classes. The parameter γ is used to estimate the properties of Gaussian kernel function. The larger the parameter γ, the greater the curvature of the decision boundary. The optimal parameters C and γ can be obtained using a cross-validation technique. In the presented study, to train the SVM classifier, a 10-fold cross-validation was performed [23, 27].

3.4. Procedure of the classification

A flow diagram of the performed analysis is presented in Fig. 1. The raw data from the training set, and the data transformed using pre-processing techniques were treated as inputs for the PLS-DA and SVM classifiers. Additionally, the SVM classifier was employed with dimensionally reduced data using the PCA feature extraction method. The results of classification are presented in the form of percentage efficiency *CC* of successful classification, represented by formula:

$$CC = \frac{N_{CC}}{N_{ALL}} \times 100\%, \tag{5}$$

where the N_{CC} represents correctly classified data, while the N_{ALL} is the total number of testing data.

4. Results and discussion

Fig. 2 presents raw sensor responses at 300°C for 20 ppm of sulfur dioxide, 20 ppm of hydrogen sulfide and 20 ppm of nitrogen dioxide. It can be seen that responses for SO_2 and H_2S look similar, what is manifested by the similar excitation voltage for the position of the peak. Moreover, the responses for sulfur-containing compounds (SCC) are also not very repetitive (see Fig. 3a) in comparison with the responses for non-sulfur containing compounds. For example, the nitrogen dioxide acquisitions (see Fig.3b) are very repetitive.

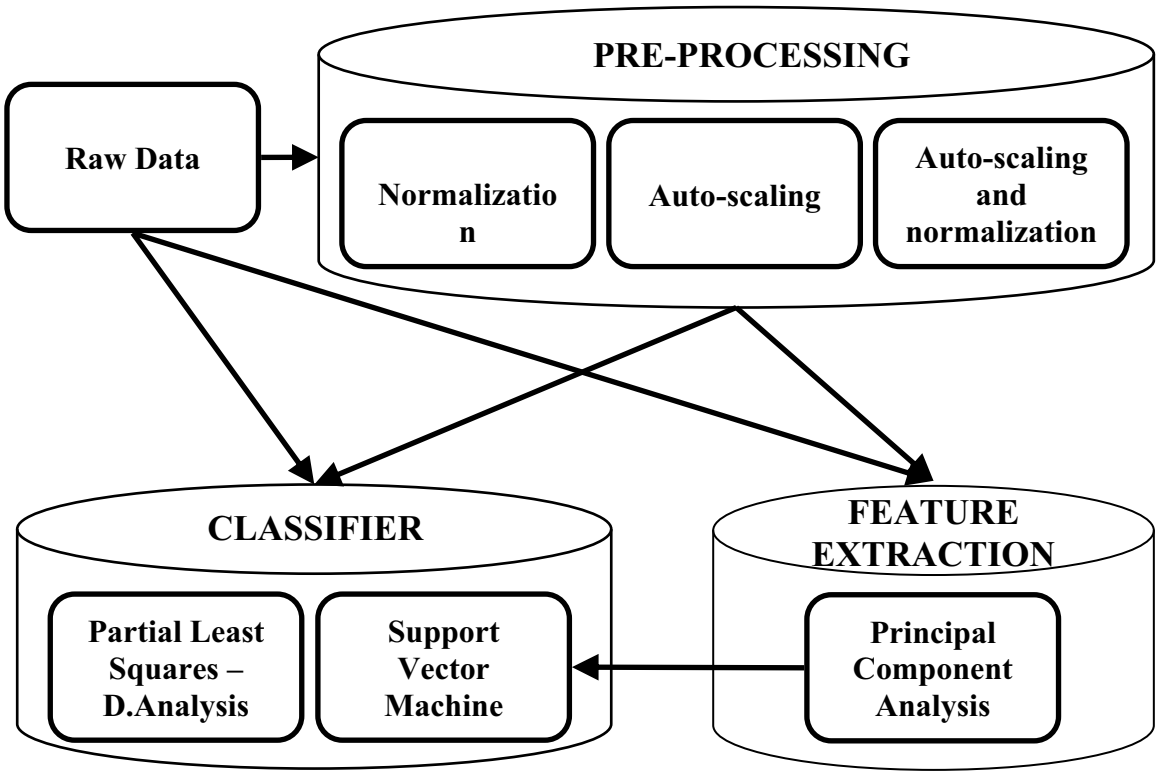

Fig. 1. Analysis flow diagram.

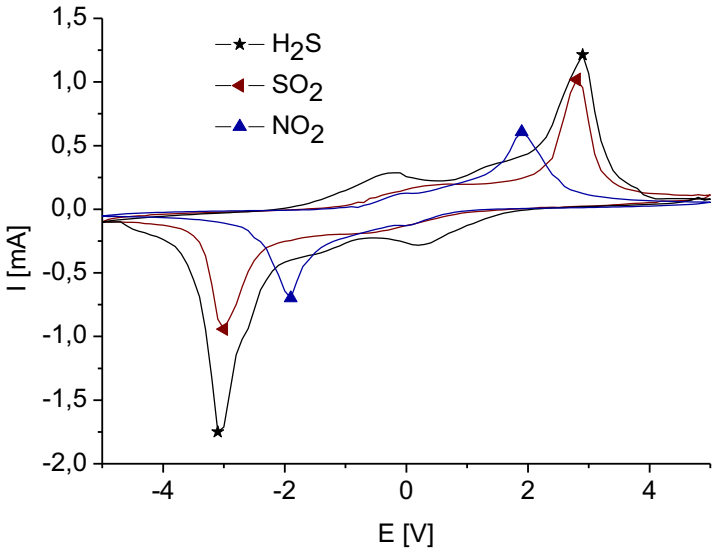

Fig. 2. Typical I-V plots obtained for 20 ppm SO_2, 20 ppm NO_2 and 20 ppm H_2S for the sensor operated at 300°C.

In order to perform analysis and classification using PCA, PLS-DA and SVM methods, the measured sensor responses were organized in the form of vectors containing 200 values of measured currents. The acquisition vectors were arranged into a training dataset matrix and then pre-processed. In Fig. 4a a sample acquisition for 20 ppm of ammonia is shown to visualize one acquisition vector. The effects of using auto-scaling and normalization can be observed in Fig. 4a right axis and Fig. 4b. It can be observed that the normalization procedure is rescaling the dataset values into a range from 0 to 1, while the shape of the original plot is retained. The response transformed using auto-scaling reveals more potentially useful features for classification, i.e. additional peaks, which can help to improve the classification efficiency.

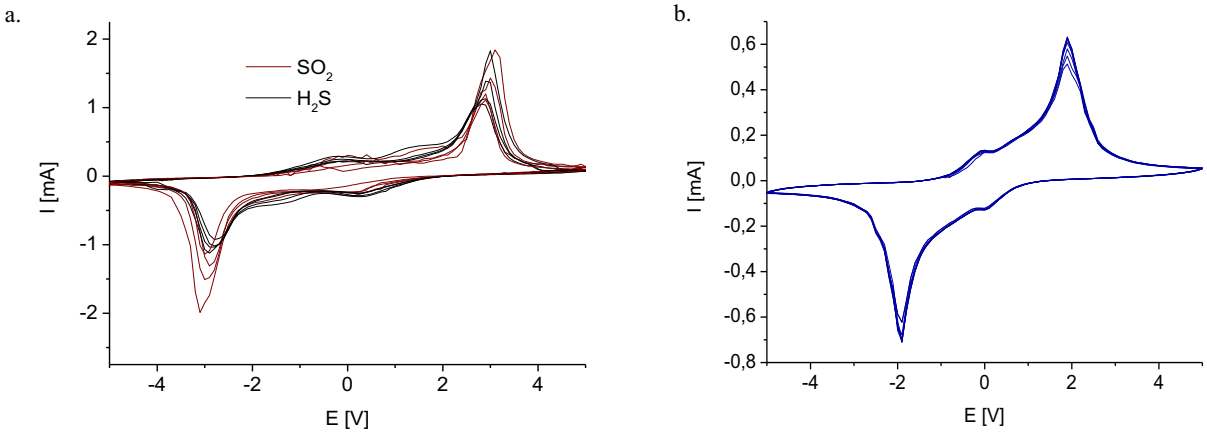

Fig. 3. Reproducibility of sensor responses for sulfur containing compounds - 4 acquisitions for H_2S and 4 acquisitions for SO_2 (a) and nitrogen dioxide - 8 acquisitions (b).

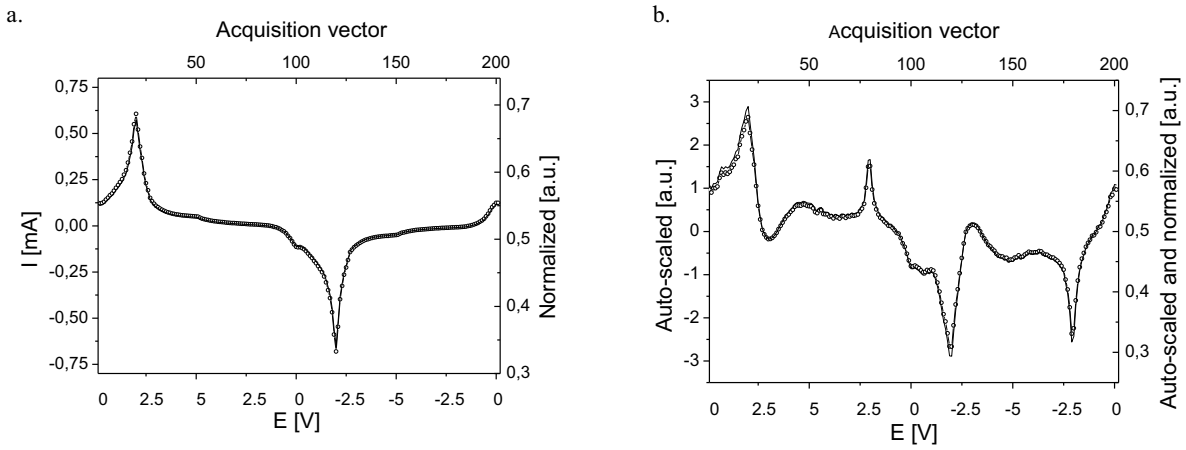

Fig. 4. Single acquisition for 20 ppm of ammonia in the form of a vector suitable for classifier: raw data and normalized (a) and auto-scaled and normalized (b).

In order to visualize the effects of using pre-processing methods, the PCA was performed on the whole dataset. The PCA score plots for normalized and auto-scaled data are presented in Fig. 5a and 5b, respectively. In both cases, data represented in the PC space show distinct clusters for each compound. The clusters for the SA, NO_2 and NH_3 are very compact, so one may expect that the sensor responses for those compounds were reproducible and the efficiency of the classifiers should be very high. The PCA scores plot for normalized data shows also that sensor responses for SCC were not very reproducible. The boundary between SO_2 and H_2S is not sharp.

However, the PCA performed on the auto-scaled data shows (see Fig. 5b) that the pre-processing method improves the ability of class separation for the SCC compounds. Namely, the auto-scaling procedure forms two clearly separable clusters in the PC space for H_2S and SO_2.

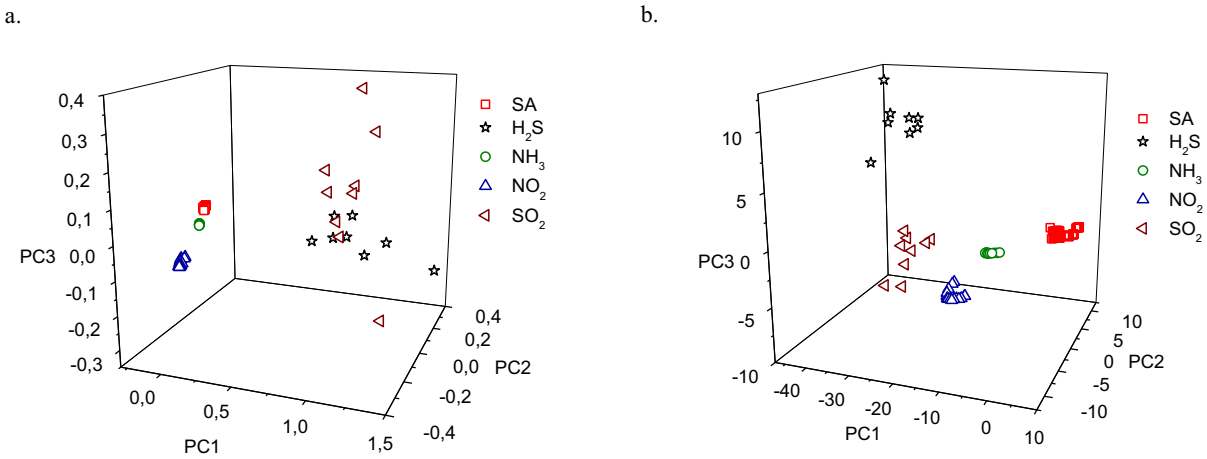

Fig. 5. PCA score plots for normalized data (a) and for auto-scaled data (b).

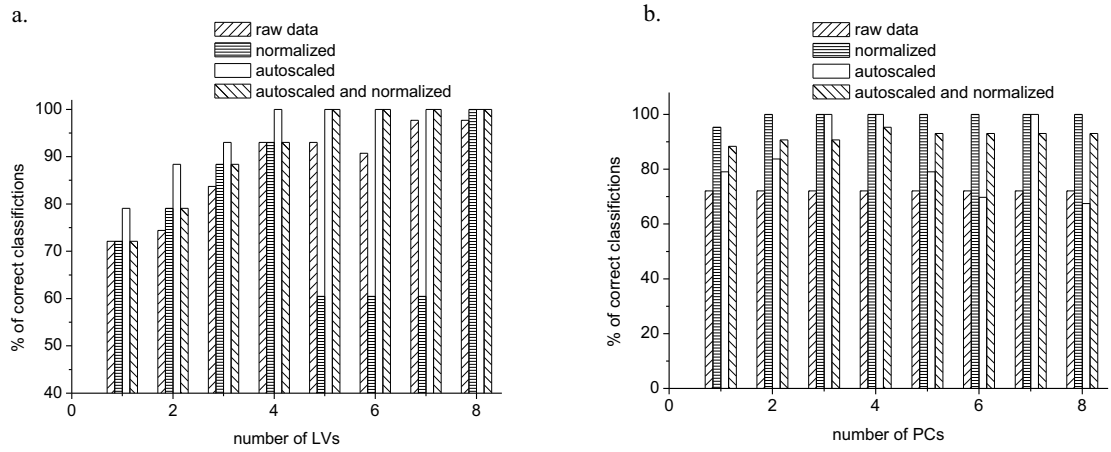

Fig. 6. The classification efficiency for various number of LVs (a) and PCs as inputs for SVM (b).

The linear PLS-DA classifier had to be trained using a train dataset to provide satisfactory results. The complexity of the model was examined by testing its performance with a varying number of latent variables. The number of LVs was altered from 1 to 10 for each: raw, normalized, auto-scaled and auto-scaled and normalized data. The assumed criterion of optimal parameters was the minimal number of LVs which provides 100% of classification efficiency. The results shown in Fig. 6a and Table 1 indicate that using the PLS-DA it was possible to classify correctly all test samples, however, with a different number of LVs for raw and pre-processed data. For the raw data, 10 LVs had to be used to create a model which was able to achieve a 100% correct classification. For normalized data, the same result was obtained with 8 LVs. The best performance provided the model on the auto-scaled data without normalization. In this case only 4 LVs are sufficient to obtain a 100% correct classification. This performance was expected, since the PCA plot presented in Fig. 5b shows distinct clusters for all investigated gases. In case of normalization of the auto-scaled data the number of LVs necessary to obtain 100% of correct classification was not improved. Only 5 LVs were necessary to obtain 100% classification efficiency.

The SVM, the same as the PLS-DA, requires a stage of training and estimating optimal parameters. To do this a 10-fold cross validation was performed on the training data. In the SVM with kernel Gaussian radial basis function, various values of C and γ parameters during the cross validation procedure were examined. In this procedure both parameters were altered to find an optimal pair of C and γ as described in [23]. Namely, each pair of the C and γ from the range $(2^{-6}, 2^{6})$ with a $2^{0.1}$ step were examined to find the one giving the highest cross validation accuracy. The optimal values of C and γ parameters for raw, normalized and auto-scaled data are presented in Table 1. It can be seen that the penalty-constant C validated in the examined range for all preprocessing techniques is obtained the same. Namely, a relatively small value of 29.9 was achieved, what suggest that the boundary margin is relatively wide and independent on the preprocessing method. The value of the kernel parameter γ varies depending on the type of the dataset and achieves the smallest values in case of preprocessed data. Since each acquisition contained 200 features, computationally the classification procedures are rather complex, especially in case of the SVM. Therefore, the PCA method was investigated for feature extraction and data dimension reduction to use it with the SVM classifier. In this case a few initial PC scores obtained on the training dataset were used as the input for the SVM. The procedure of estimating optimal parameters for the classifier was

identical as in case of the SVM analysis with original acquisition dataset as inputs. The classification efficiency as a function of the number of the PC scores used as an input for the SVM was examined The optimal SVM parameters are also summarized in Table 1. The performance of classification with different number of PC inputs for raw and pre-processed data is also shown in Fig 6b.

Table 1. Optimal parameters for the classifiers.

Classifier parameters		Raw data	Normalized	Auto-scaled	Auto-scaled and normalized
SVM	C	29.9	29.9	29.9	29.9
	γ	29.9	0.47	0.058	0.47
PCA+SVM	C	29.9	29.9	29.9	29.9
	γ	29.9	7.5	0.029	3.7
	Number of PCs	2	2	3	4
PLS-DA	Number of LVs	10	8	4	5

For each investigated method the best classification efficiencies are recapitulated in Table 2. The results of classification using the SVM with all 200 features as inputs proved that pre-processing significantly improves the classification performance. The SVM performed on the raw data provided the worst result (*CC*=72.1%). Better results were achieved for normalized data, which proved the literature recommendations for SVM [27]. It says that the SVM efficiency might dramatically decrease when data is not in the range of small values. The best results, i.e. all samples classified correctly, were achieved for the auto-scaled and normalized data. One may note that for small values of γ (Table 1) it was possible to achieve better classification results.

Table 2. Classification efficiencies for all investigated methods.

Method	Raw data	Normalized	Auto-scaled	Auto-scaled and normalized
SVM	72.1%	95.4%	97.7%	100%
PCA+SVM	72.1%	100%	100%	95.3%
PLS-DA	100%	100%	100%	100%

Also the combination of the PCA and SVM methods provided interesting results. The optimal parameters of the SVM and SVM combined with PCA feature extractor can be compared in Table 2. In case of the SVM with PCA feature extractor performed on raw data it was impossible to achieve better classification efficiency than using the standalone SVM. The normalization pre-processing before the PCA enabled to obtain 100% of correct classifications. The same performance was achieved on an auto-scaled dataset. However, for unknown reason, it was impossible to achieve as good classification efficiency on a normalized and auto-scaled dataset.

5. Conclusions

A simple, low-cost device for air-contaminant monitoring with single and simple sensor structure requires a reliable data analysis system. In this paper pattern classification techniques for such a system were investigated. In this study the classification efficiency of two widely used methods in electronic noses and tongues are investigated. Both investigated

methods, the PLS-DA and SVM, allowed achieving satisfactory results with a 100% of successful classification. However, for the linear PLS-DA a 100% efficiency was achieved for both raw and pre-processed data. The SVM, on the other hand, proved to be very sensitive to the pre-processing procedure and its efficiency was low in the case of a raw dataset. The preliminary results presented in this article show that the multivariate analysis and pattern recognition procedures used for determining various air-contaminants with a single electrocatalytic gas sensor provides satisfactory results. Further studies are connected with the examination of methods for prediction of concentrations of different gases and their mixtures, what should lead to the development of a reliable and simple gas-analyzing system.

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