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Power Scaling of Chemiresistive Sensor Array Data for Odor Classification

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Abstract

The steady state responses of chemical sensors like the tin-oxide and composite conducting polymer sensors exhibit power law dependency on the vapor concentration. In this research, it is shown that linearization of measured (raw) sensor signals by an inverse power scaling improves class separability in feature space, hence the classification efficiency of electronic noses based on these sensors. The follow up data processing is done by dimensional autoscaling, principal component analysis and backpropagation neural network. The data from three tin-oxide sensor array and one CPC sensor array collected from published sources are utilized. It is found that by preprocessing the data according to the suggested power law improves class separability and classification efficiency. An improvement of 14% to 16% is obtained for tin-oxide sensor array and of 33% for conducting polymer sensor array are obtained. The approximate values of the scaling exponents were first deduced as prompted by the sensor response models, and then one adjust were done empirically.

Keywords: Metal-oxide sensor, composite conducting polymer sensor, electronic nose, power law scaling, sensor array data preprocessing.

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1. Introduction

An electronic nose system mimics working paradigm of mammalian smell sensing organ by using an array of chemical sensors along with pattern recognition analysis. Electronic nose systems and applications in wide ranging areas from detection of hazardous chemicals in environment and detection of explosives for security purposes to various industrial and commercial applications such as monitoring food quality, health hazards, workplace environment, cosmetics and fragrance. The most commonly used sensors technologies for electronic nose development are the surface acoustic wave (SAW) and bulk acoustic wave (BAW) crystal oscillators, metal-oxide-semiconductor (MOS) and composite conducting polymer (CCP) chemiresistors, and fiber optic chemical sensors [1, 2, 3, 4]. The chemoresistive metal-oxide and conducting polymer sensors (MOS and CCP) are most suited for large volume low cost applications because of their small size combined with their high sensitivity and selectivity, and easy manufacturability. Under exposure to target vapor samples, the sensor array in electronic nose system generates response patterns (sets of sensors output) which can be analyzed by pattern recognition methods to determine vapor class identities.

The pattern recognition system finds discriminating information about vapor samples through preprocessing and feature extraction, and then declares class identities by employing a classifier. The preprocessing is to prepare the measured sensor signal by denoising, normalization and transformation in suitable form for efficient and reliable feature extraction. A good preprocessor is crucial for efficient working of an electronic nose system, as it always reduces the burden of feature extractor

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and classifier algorithms, and enhances classification rate. Most of reported works on sensor array based vapor identification assume linear dependence of sensor outputs on analyte (vapor), and employ linear data transformation and feature extraction methods [5, 6, 7]. For example, a most commonly used method for sensor array data preprocessing is autoscaling [5]. The method performs mean-centering and variance-normalization with respect to samples for each sensor output by assuming linear dependence of the sensor signal on vapor concentration. The responses of most chemical sensors are however nonlinear to varying degrees. The tin-oxide gas sensors exhibit power law nonlinearity with respect to analyte concentration of the form $\Delta R/R_0 \approx P_A^x$. This is established through several experimental and theoretical studies [8, 9]. SnO_2 thin film sensor shows dependence on vapor pressure (P_A) of exposed analyte as $\Delta R/R_0 \approx P_A^x$ where $\Delta R/R_0$ represents fractional change in sensor resistance under exposure analyte gas having partial pressure (P_A) and the power x assumes values over 0.33 - 0.9 depending on the redox nature of sensor surface and analyte gas [1, 9, 10]. The CCP gas sensors also exhibit similar nonlinear responses with power exponent $x = 1/n$ where n denotes the Freundlich parameter for gas adsorption isotherms [11,12,13].

Linearization of input data can be expected to yield more accurate features by application linear feature extraction methods such as principal component analysis (PCA) or linear discriminant analysis (LDA). However, to linearize the input data one needs to have insight about the sensor behavior. This comes only through detailed experimental studies and theoretical models. An earlier study on SAW sensors revealed logarithmic dependence of the measured responses on analyte concentration [14]. Prompted by this, a logarithmic scaling of the measured SAW sensor array data was implemented before feature extraction by PCA and ICA (independent component analysis), and markedly improved results were obtained in feature space projections and neural network classification [14, 15]. In this paper, we analyze the tin-oxide and the composite conducting polymer gas sensor array data for determining influence of the above mentioned power law nonlinearity on the class separability in feature space and the classification rate.

2. Data

Four data sets collected from three published sources are analyzed. These are, i) two sets of coffee data generated by thin tin-oxide sensor array [16], ii) one set of 3 volatile organic compounds (VOCs) data generated by 16-element composite conducting polymer (CCP) sensor array [17], and iii) one set of 3 VOCs data generated by a thick tin-oxide sensor array [18]. A summary of these datasets is given in Table 1.

Table 1: Summary of the datasets used in the present analysis.

Data Sets	Vapor Class	No. of Classes	No. and Type of Sensors in Array	Signal	No. of Samples	Remark
1	Coffee (blend)	7	5, tin-oxide	$\Delta R/R_0$	249	(15)[a]
2	Coffee (mono)	7	4, tin-oxide	$\Delta R/R_0$	210	(15)[a]
3	VOCs	3	16, CCP	$\Delta R_{max}/R_0$	22	Table 3 in (16)[b]
4	VOCs	3	4 Taguchi	$\Delta G(\infty)$	9	Table 2 in (17)[c]

[a] The classes are aroma of the two groups of coffee (blend and monovariety). The sensor signal is the relative change in sensor resistance. [b] The vapor samples are methanol, ethanol, and their mixtures at different concentration. Signal is differential change in sensor resistance. [c] The vapor samples are ethanol, toluene and o-xylene at 3 concentrations. The signal is change in conductance in steady state.

3. Data Preprocessing and Classification

3.1 Power Scaling Prompted by Tin-Oxide Sensor Behavior

The electrical conductance of tin-oxide sensors in equilibrium to an analyte vapor is described by

$$G = G_0 + AP_A^x \tag{1}$$

where G_0 denotes the sensor conductance in presence of reference gas (usually oxygen rich air ambience), (P_A^x) denotes partial pressure of the test vapor, (A) is an empirical constant that depends on dominant surface adsorption and electrical conduction processes in the sensor film, and the power exponent (x) assumes values in the range of 0.33 to 2.4 depending on the sensor fabrication condition (film preparation method, grain size, porosity, thickness), ambient oxygen and humidity, operating temperature, and nature of analyte gas (reducing or oxidizing) [9]. The Sensor signal $\Delta R/R_0$ can thus be defined as: $\Delta R/R0 = \Delta G/G_0 = (A/G_0)P_A^x$, that is

$$\Delta R/R_0 \approx P_A^x \tag{2}$$

This relation suggests that by scaling of the raw sensor signal by appropriate inverse power law will linearize the sensor output with respect to analyte partial pressure. Keeping this in view the raw sensor signal in the present analysis are transformed according to

$$\Delta R/R_0 \rightarrow (\Delta R/R_0)^y = S_{ij} \tag{3}$$

where $y = 1/x$ and Sij represents the transformed signal of j_{th} sensor for i_{th} sample. An approximate value of the power exponent was first chosen in accordance with the sensor models described in cite9 vis–vis sensor construction and operation parameters. The description of the tin-oxide sensor film morphology (porous, nano-sized agglomerates) and the operation temperature (near 400°C), as given in the coffee data paper [16] and in other related works [19, 20] were matched, and an approximate value of x=1.25 was arrived at. The final adjustment of x was then made empirically by observing the effect of power law scaling on the classification rates as described in the following.

3.2 Power Scaling Prompted by CCP Sensor Behavior

The response modeling of conducting composite polymer (CCP) sensor involves combining application of general effective medium theory and thermodynamics to describe electrical conduction along conducting percolation network embedded in polymer matrix [21]. The thermodynamic behavior of polymer matrix in CCP film in presence of chemical interaction with vapor analytes has been explored with Flory-Huggins theory and Freundlich isotherm [22, 23]. The Flory-Huggins theory explains chemical vapor induced swelling of the host polymer matrix while the Freundlich isotherm depicts the surface adsorption of chemical vapor in the polymer composite. The theoretical models suggest a nonlinear dependence on vapor concentrations as [13, 24, 25].

$$Q_t = \Delta m/m = (R_{max-R_0})/R_0 = KC^{1/n} \tag{4}$$

where R_0 represents the initial resistance of sensor, R_{max} is the maximum resistance under vapor exposure, C denotes the target vapor concentration, and K, $1/n$ are Freundlich parameters which depend on characteristics of polymer composite and interacting vapor. Dong et al. [13] reported $n \approx 0.24 - 0.64$ for CCP sensors fabricated with carbon black/poly(butylmethacrylate) composites and exposed to seven chemical species. In some other studies [17, 26] also similar power law dependencies were reported. In view of this, we adapted a power law scaling transformation of the same kind as indicated by Eq.(3) for the analysis of CCP sensor array data. An approximate value of the power exponent was selected $y = 0.4$ in view of the reported value of Freundlich parameter

in [13]. The final adjustments were however made empirically by observing the effect of power scaling on classification rate.

3.3 Data Processing

After data linearization according to Eq.(3) the sensor responses were further transformed by concentration normalization and autoscaling. The autoscaling is mean-centering and variance normalization of each sensor with respect measurement samples [5]. Further processing is done by principal component analysis (PCA) for feature extraction, and by 3-layer feed forward neural network with error back propagation algorithm for classification. The parameters like the number of neurons in the hidden layer, activation function and training iteration were optimezd empirically to achieve best performance. For datasets I and II a $3 \times 3 \times 7$ network with sigmoidal in hidden and linear activation function in output layer were used. In this case, convergence is reached after 70,000 iterations. For data set-III, $3 \times 7 \times 4$ neural network with same activation functions were employed. The convergence in this case is reached after 5000 epochs. Due to small number of observation data the neural network classification was not implemented on dataset-IV. The implementations are done by using Matlab statistical and neural tools.

4. Results and Discussion

Fig.1 through Fig.4 show the PC score plots for all the datasets in Table 1 under the two conditions for comparison. In one condition, no data linearization by power scaling is done. In the other condition, the data is transformed according to Eq.(3) before autoscaling and PCA. The optimum value of power exponent for each dataset is taken as $y = 0.8$ for datasets I and II, $y = 0.40$ for dataset-III and $y = 0.35$ for dataset-IV. The principal component variances are shown in these figures in percent of the total cumulative variance. The improvement in class compaction and interclass separation is noticeable in each case after power scaling. Even though the enhancements in visual separation of classes in these PC plots appear marginal for some classes, it makes noticeable impact on the class separability measure and the classification rate as shown in Table 2 and Table 3 respectively.

The class separability measure is defined in terms of scatter matrices of the principal components as $J = trace(S)_m/trace(S)_w \equiv B/A$, where S_m is the covariance matrix of PC components defined with respect to global mean, and S_w is the weighted covariance matrix of PC components defined with respect to class means [**?**]. The value of B is a measure of inter-class separation and the value of A is a measure of within-class compaction. High B and low A, therefore, high J value indicates high class discrimination ability of the data processing method. An improvement of 10% to 46% in class separability can be seen across different data sets as a consequence power law scaling, Table 2.

Table 2: Values of class separability measure for all datasets with and without power law scaling.

	Without scaling			**With scaling**		
Data Set	**(A)**	**(B)**	**(C)**	**(A)**	**(B)**	**(C)**
1	0.4208	0.0044	0.0105	0.4119	0.0061	0.0148
2	1.2768	0.0063	0.0049	1.2043	0.0069	0.0057
3	53.366	5.5739	0.1045	51.038	5.8601	0.1147
4	2.1859	0.3210	0.1468	0.0050	0.0010	0.2144

The classification results shown in Table 3 support the expectation based on the improved class separability measure. The numbers in shaded cells are the correctly classified number of samples.

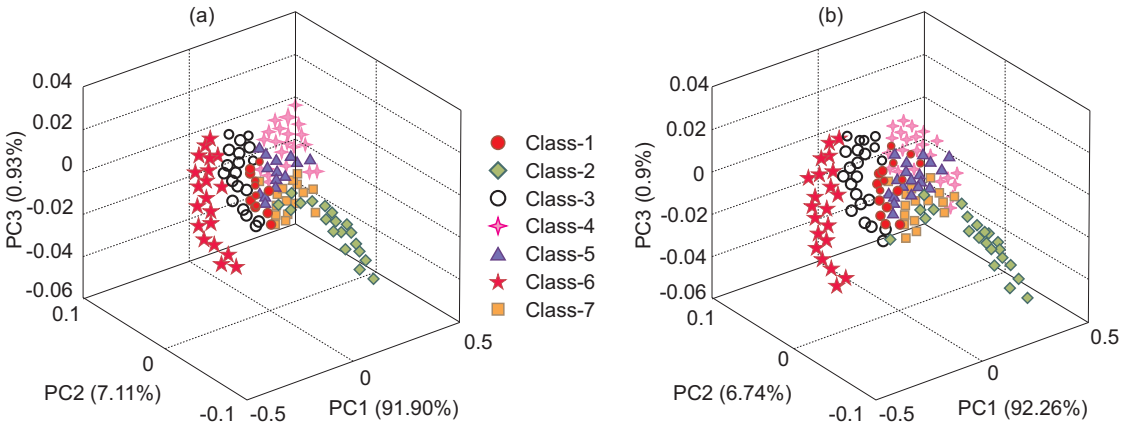

Fig. 1: PCA score plot for Data set-I (a) Without power scaling, (b) Power scaling with scaling factor y = 0.8.

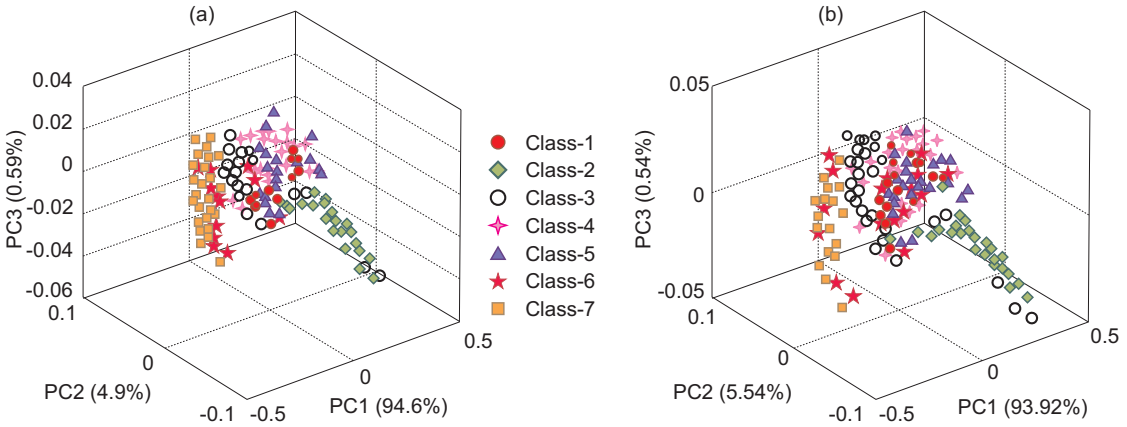

Fig. 2: PCA score plot for Data set-II (a) Without power scaling (b) Power scaling with scaling factor y = 0.8.

After power scaling the number of misclassified samples reduced from 25 to 15 for dataset-I, from 24 to 16 for dataset-II, and from 6 to 3 for dataset-III. This amounts to 14% to 16% improvement in tin-oxide and 33% improvement in CCP electronic noses performance. The confusion matrix in Table 3 shows how improvement in the identity resolution has occurred. The overall success rate in a given classification task depends on a variety of sub processing steps starting from data cleaning for noise and outliers removal, drift correction, averaging and normalization to feature extraction and classification. In effect, these steps produce a number of linear and nonlinear data transformations, and mapping into class labels. The objective of the present work has been to examine the influence of data linearization as suggested by sensor response models. In this respect, the impact of data linearization by power law scaling of the tin-oxide sensors response before any other processing is quite apparent. The classification results can be expected to improve further if combined with more rigorous processing methods, as done by original authors [15].

In [15], the misclassified samples were reported to be 8 and 10 for the data sets I and II, respectively. However, they used a number of customized tools including spike cleaning, denoising, drift correction etc. before PCA feature extraction. Such procedures can be meaningfully applied only with detailed insight of experimental conditions, which is seldom amenable to a data user. In the present analysis, we did not carry out any additional preprocessing except power scaling and dimensional autoscaling. Nevertheless, the PC score plots, particularly those shown in Fig.3 and

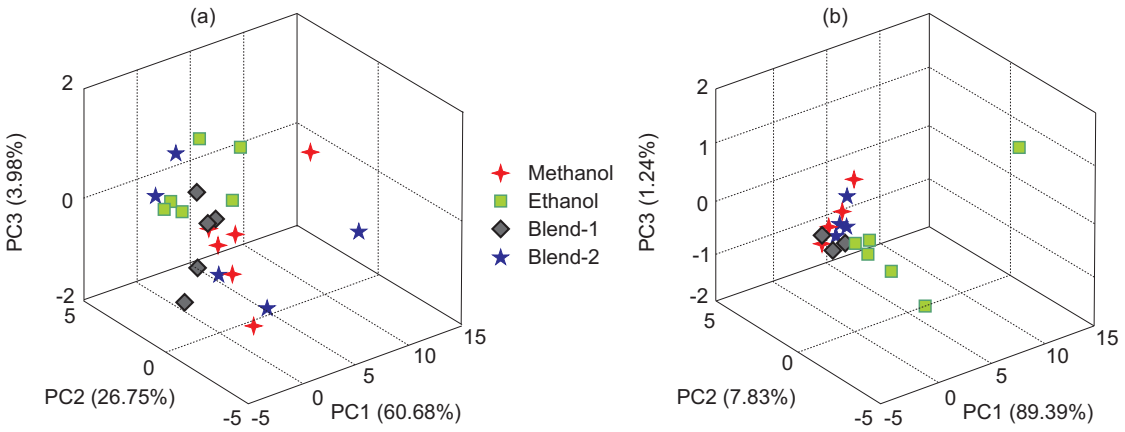

Fig. 3: PCA score plot for Data set-III (a) Without power scaling (b) Power scaling with scaling factor y = 0.4.

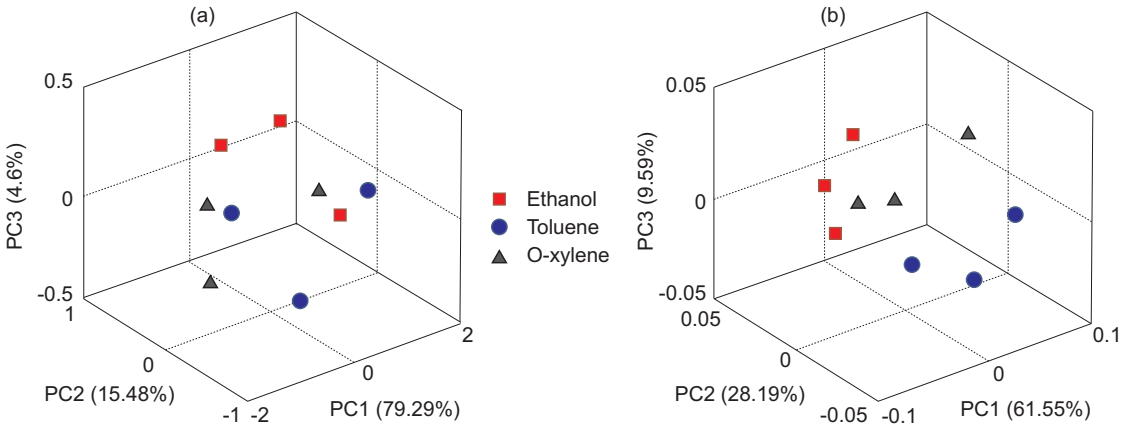

Fig. 4: PCA score plot for Data set-IV (a) Without power scaling (b) Power scaling with scaling factor y = 0.35.

Fig.4, undoubtedly underline the influence of data linearization by power law scaling for both the tin-oxide and composite conducting polymer sensors.

Table 3: Neural network classification results.

Confusion Matrix for Data Set-I

BPNN classification without power scaling							**BPNN classification with power scaling** (scaling exponent y=0.8)						
	True class							True class					
Predicted class	3	0	6	0	0	0	0	7	0	0	0	1	0	0
	3	5	1	0	0	0	0	0	7	0	0	0	0	1
	0	0	7	2	0	0	0	0	1	7	1	0	1	0
	0	0	5	4	0	0	0	1	0	1	7	3	0	0
	0	0	0	5	4	0	0	1	0	0	0	5	0	1
	0	0	0	0	0	9	0	0	0	1	1	0	8	0
	0	0	3	0	0	0	6	0	1	0	0	0	0	7

Confusion Matrix for Data Set-II

BPNN classification without power scaling								**BPNN classification with power scaling** (scaling exponent y=0.8)						
	True class							True class						
Predicted class	7	0	1	0	0	0	0	7	0	0	0	0	0	0
	0	1	0	7	0	0	0	0	7	0	2	0	0	0
	0	0	3	0	0	5	0	0	0	2	0	2	1	0
	0	0	1	3	4	0	0	0	1	0	5	2	0	0
	0	0	3	0	2	3	0	0	0	5	1	4	0	0
	0	0	0	0	0	8	0	1	0	1	0	0	7	0
	0	0	3	0	0	0	8	0	0	0	0	0	0	8

Confusion Matrix for Data Set-III

BPNN classification without power scaling					**BPNN classification with power scaling** (scaling exponent y=0.4)			
	True class				True class			
Predicted class	2	0	0	1	2	0	1	1
	0	1	1	0	0	3	0	0
	1	0	1	1	0	0	1	0
	0	2	0	0	0	1	0	1

5. Conclusion

The analysis presented in this paper demonstrates that data linearization according to power law scaling behavior of the tin-oxide and composite conducting polymer sensors improves the feature extraction capability and classification effciency in electronic nose systems based on the array of these sensors. The value of scaling exponent however depends on the sensor construction and operating conditions, and it should be optimized for specific sensors in application. From the limited data analysis performed in this work, the scaling exponent values of 0.8 for thin film tin-oxide sensors, 0.35 for thick film tin-oxide sensors and 0.4 for composite conducting polymer sensors are obtained. This resulted in improvement of 14% to 33% in various electronic noses.

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