

Standardization of metal oxide sensor array using artificial neural networks through experimental design

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ABSTRACT

The shift in sensor signal measured by identical gas sensor array system (commonly called an electronic nose) makes the analysis of merged measurement data difficult. This would grossly affect the gas quantification accuracy of such electronic nose (E-nose) instruments. Thus, a real-time calibration transfer based on reference alcohol projection transfer model (RAPT) was designed in this paper which aims to project onto the hazardous gas and set up a “bridge” to transfer from instrument to instrument through three artificial neural networks (ANN), and attempt to solve the problem of signal shift between E-nose instruments of identical sensor array. Besides, principal component analysis (PCA) is also used for validation of different models in component space. For comparison, previous four models including univariate direct standardization (UDS), partial least square (PLS), neural, and global affine transformation based on robust weighted least square (GAT-RWLS) are also presented. Qualitative and quantitative results demonstrate that the proposed RAPT model is competitive in E-nose signal shift standardization.

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1. Introduction

Sensor array system or commonly called an electronic nose (E-nose), has already been proved to be effective in air quality monitoring applications. Gardner and Bartlett gave a comprehensive overview of such systems, which also contains a concise definition of an electronic nose: “an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition algorithm” [1]. Conventional gas detection methods use mass spectrometers that identify molecules through the characteristic variable deflection from a magnetic field, or Fourier transform infrared instruments that utilize the infrared spectral characteristics of gases [2,3]. These instruments are usually expensive, bulky, high maintenance, slow in terms of response time and require skilled operators, making them impractical for air quality monitoring applications. Recently, great advancement has also been made in the field of gas sensor array systems [4,5].

A gas sensor is a miniature transducer that detects gas molecules and produces the electrical signal associated with the gas concentration [6]. Due to attractive features such as high sensitivity, fast response time, long life, low cost and simple circuit design, metal oxide semi-conducting sensors are found to be the most widely used in sensor array systems [7]. However, due to the inherent

sensor variability (e.g. sensitivity) during the manufacturing process, and the environment (e.g. temperature, humidity and pressure), gas sensors generally reflect diverse selectivity, baseline difference (signal shift) and nonlinearity with respect to gas concentration. Consequently, signal shift occurs in the measurement data from one instrument to another when using these sensors. Signal shift may also occur within the same instrument because of sensor replacement or some temporal change. This instrumental signal shift would result in false recognition and concentration estimation of analytes because the associated classification and estimation algorithms were commonly developed on one E-nose instrument (commonly called “master instrument”) off-line. Then incorrect discrimination of analytes and concentrations would be given when using the well developed prediction parameters on other E-nose instruments (commonly called “slave instruments”). The problem of sensor drift, which also often disturbs the classification accuracy, has been fully studied [8–13]. Besides, background noise reduction algorithms in electronic nose signal were also given full studies [14–17] for improving the precision of an E-nose. However, baseline and sensitivity difference caused by signal shift of identical sensors was still a key problem. Related research about sensor array calibration for baseline compensation have been presented, such as univariate direct standardization (UDS) [18], partial least square (PLS) [18], neural methods [19,20], and global affine transformation based on robust weighted least square (GAT-RWLS) [21]. UDS and GAT-RWLS are straightforward methods based on linear least square regression, where signal shift compensation

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models are created for each unique sensor; PLS can be used for standardization in a principal component space; neural method is a nonlinear based method, which designs shift standardization on sensor array but not unique sensor. Neural method, PLS and UDS methods need a large number of experimental calibration transfer samples of target contaminants for a high calibration accuracy so that the calibration complexity would increase significantly. So, these three methods will become very difficult to be implemented for standardization in mass production of instruments in this way. GAT-RWLS method built with only several calibration transfer samples in on-line use was proposed by our team. Although this method overcomes the common flaw exists in the first three methods, the transfer samples were still obtained from poisonous contaminants. Thus, it inspires us to do this research further on instrument standardization of electronic nose.

In this paper, a real-time RAPT model was proposed for electronic nose instrument standardizations in our project. The applied methodology of RAPT model is artificial neural network, which is simple to be applied in electronic nose with the well-trained hyper-parameters (e.g. weights and biases). Through comparisons with a neural method (direct calibration using ANN), UDS method, PLS method, and GAT-RWLS method, the presented RAPT model is more competitive relatively.

2. Experimental design

2.1. Electronic nose sensor array system

Four electronic nose instruments designed with sensors of the same types and other associated electronic components were used in this work. The electronic nose module in this paper has been introduced in detail in our previous work [22]. The sensor array in each instrument consists of two auxiliary sensors for the temperature and humidity embedded in one module (SHT2230 of Sensirion in Switzerland), four Taguchi semiconductor sensors (TGS2602, TGS2620, and TGS2201 dual sensor), an oxygen sensor (O_2A_2 , type of electrochemical), and one GSBT11 sensor (Ogam Technology in Korea). The sensing material in TGS gas sensors is metal oxide, most typically SnO_2 . When a metal oxide crystal such as SnO_2 is heated at a certain high temperature in air, oxygen is adsorbed on the crystal surface with a negative charge and the crystal surface is formed to serve as a potential barrier against electron flow. The electrical resistance of the sensor is attributed to this potential barrier. The sensing element type of GSBT11 is also semiconductor and it has similar sensing principle with TGS sensors.

2.2. Samples measurements

2.2.1. Hazardous gas measurements

The measurements were carried out on five target gases (five data sets), separately. They are carbon monoxide (CO), benzene (C_6H_6), toluene (C_7H_8), ammonia (NH_3), and nitrogen dioxide (NO_2). Moreover, these dataset are made up of variables in R^8 space in which each row denotes one observation, that is, the extracted steady state response vector of the sensor array in one experiment. The four instruments were placed into a constant temperature and humidity chamber wherein both the temperature and humidity are controlled. The experimental platform for sample collection has been clearly illustrated in reference [22]. For all the measurements, target temperature (T) values ($^{\circ}C$) of 15, 20, 25, 30, and 35 and relative humidity (RH) values of 40%, 60%, and 80% were considered. Thus, the measurements were carried out in 15 different combinations of target temperature and humidity. To create a concentration in the chamber, high-precision chromatography syringes were used to inject the volume of analyte. The total

measurement cycle time for a single measurement was set to 20 min, i.e. 2 min for reference air (baseline), 8 min for sampling and 10 min for chamber cleaning phase. It is worth noting that clean air is used for the cleaning phase by an air pump and an extra fan.

2.2.2. Reference alcohol measurements

The analytical pure alcohol (99.99%) is used as reference gas which aims to replace the contaminants in preparing of calibration transfer samples. For the reference alcohol, the same 15 temperature–humidity conditions as the target gases were still selected for projection building between alcohol and target gases. We carried out the alcohol experiments through injecting alcohol into the chamber with 10-ml and 20-ml, respectively. Therefore, 30 alcohol gas samples were prepared to build up a relation between target gases and the reference alcohol gas. Considering the necessity of calibration simplicity and 60% RH is around the constant value in air, a total of 6 alcohol samples which were carried out by injecting alcohol into the chamber with 10-ml and 20-ml under three temperature–humidity combinations (15–60, 25–60, and 35–60), were used as transfer samples for the bridge. Note that the concentrations of the 6 alcohol samples can be arbitrary at the beginning, but they should be fixed once the calibration transfer has been well-designed.

2.3. Measured target dataset

This section presents five data sets which were measured in the constant temperature and humidity chamber within one month using the target gases. Notice that the reproducibility of sensors in our project is good, and the short-term sensor drift can also be neglected. To each sample, only one point at the steady state response of each sensor is extracted as a feature or an observation in each measurement. All the measurements are carried out at the 15 combinations of target temperature and humidity. Table 1 presents the detailed test sample sets of five gases. Note that the “ T ” denotes temperature, “ RH ” denotes relative humidity and “ C ” denotes concentration for each measurement in Table 1. The first data set (set-I) including 42 training samples and 16 test samples is collected in the chamber by injecting CO. The second data set (set-II) including 50 training samples and 22 test samples is measured using benzene in the chamber. The third data set (set-III) including 45 training samples and 21 test samples is measured using toluene in the chamber. The fourth data set (set-IV) including 20 training samples and 9 test samples is measured by injecting NH_3 into the chamber. The fifth data set (set-V) including 20 training samples and 10 test samples is collected by injecting NO_2 into the chamber. Note that the training and test samples are randomly chosen and ordered.

2.4. Standardization models

2.4.1. Objective of standardization

Generally, for a given two instruments, a decision that who will be used as the slave instrument and who will be declared as the master instrument needs to be made in study of a standardization model between the two instruments. So, for easy illustrations, these four instruments used in this work are labeled as master instrument, slave instrument 1 (slave 1), slave instrument 2 (slave 2) and slave instrument 3 (slave 3), respectively. For visibility of the signal shift, the raw data of sensor TGS2620, TGS2602, TGS2201A and TGS2201B in one measurement are shown in Fig. 1, respectively. Fig. 1 illustrates the gas sensor response differences and inherent variability of the raw measured test set using the four instruments. This figure shows signal shift in the responses of sensors from one instrument to another, which is an inherent characteristic of semi-conducting metal oxide sensors. From Fig. 1, we can see that, both

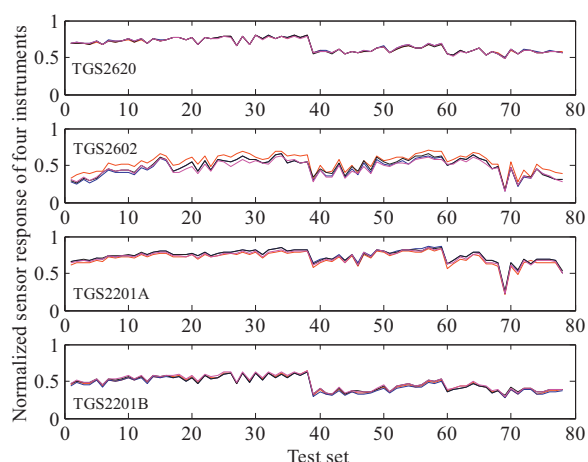
Table 1Experimental environments of temperature (T , °C), relative humidity (RH, %) and concentrations (C, ppm).

Sample	CO			Benzene			Toluene			NH ₃			NO ₂		
	T	RH	C	T	RH	C	T	RH	C	T	RH	C	T	RH	C
1	15	60	23	15	60	0.7056	15	60	0.0668	15	60	0.2466	15	60	0.66
2	15	80	12	15	80	0.7056	15	60	0.0865	20	40	0.8014	20	40	0.77
3	20	40	22	20	40	0.7056	15	80	0.0516	20	60	0.7991	20	60	0.28
4	20	60	11	20	40	0.9112	20	40	0.0668	25	40	0.1232	20	80	0.18
5	20	80	12	20	60	0.1721	20	40	0.0865	25	60	0.5528	20	80	0.30
6	25	40	14	20	60	0.7056	20	60	0.0516	25	60	0.7914	25	40	0.20
7	25	60	21	20	80	0.7056	20	60	0.0865	30	60	1.1767	25	60	0.03
8	25	60	33	25	40	0.7056	20	80	0.0516	35	60	0.2662	25	80	0.07
9	25	60	37	25	60	0.7056	25	40	0.1425	35	60	2.1481	25	80	0.17
10	25	60	55	25	80	0.7056	25	60	0.0516	---	---	---	30	60	1.36
11	25	80	13	30	40	0.1721	25	60	0.1425	---	---	---	---	---	---
12	30	40	48	30	40	0.9112	25	80	0.1425	---	---	---	---	---	---
13	30	60	6	30	60	0.1721	30	40	0.0516	---	---	---	---	---	---
14	30	80	25	30	60	0.9112	30	40	0.0668	---	---	---	---	---	---
15	35	40	16	30	80	0.4999	30	60	0.1425	---	---	---	---	---	---
16	35	60	29	30	80	0.7056	30	80	0.1425	---	---	---	---	---	---
17	---	---	---	35	40	0.4999	35	40	0.0516	---	---	---	---	---	---
18	---	---	---	35	40	0.7056	35	40	0.0668	---	---	---	---	---	---
19	---	---	---	35	60	0.4999	35	60	0.1425	---	---	---	---	---	---
20	---	---	---	35	60	0.7056	35	80	0.0516	---	---	---	---	---	---
21	---	---	---	35	80	0.4999	35	80	0.1425	---	---	---	---	---	---
22	---	---	---	35	80	0.7056	---	---	---	---	---	---	---	---	---

TGS2620 and TGS2201B have smaller signal shift compared with TGS2602 and TGS2201A. The mean relative absolute errors (MRAE) calculated by Eq. (4) between slave 1 and master instrument in the test set are 0.87%, 12.99%, 5.08% and 2.71% for TGS2620, TGS2602, TGS2201A and TGS2201B, respectively. Similarly, 0.47%, 10.65%, 5.14% and 3.04% were obtained between slave 2 and master; 0.85%, 14.07%, 2.62%, and 3.15% were obtained between slave 3 and master. We can find that TGS2620 and TGS2201B have smaller signal shift ($\leq 5\%$), thus only TGS2602 and TGS2201A are calibrated in this paper. It is worth noting that the normalization is that sensor responses were directly divided by 4095, and the digit of 4095 (that is, $2^{12}-1$) is the maximum value of the 12-bit A/D output for each sensor.

2.4.2. UDS method

The UDS method [18] treats the signal of each sensor separately and employs signal shift calibration models of each unique sensor. The shift calibration model for sensor i is designed by performing linear regression from the training sets of the slave instruments to the training set of the master instrument, respectively. Applying regression of higher order than 3 is not recommendable because of the risk of the data overfitting [18]. Through the linear regression

**Fig. 1.** Raw data of four electronic nose instruments without standardization.

operation, two regression coefficients (intercept and slope of the regression line) would be obtained in standardization process. However, it will need a number of training samples for calibration, and this would provide a model that is not robust and therefore not suitable for the calibration of new measurements or new instruments.

2.4.3. PLS method

PLS is a multivariate standardization method which has been presented for instrument standardization in [18]. PLS is operated for projecting the data set of the slave instruments onto the data set of the master instrument in a principal component space which is different from UDS. Note that principal component analysis is an internally embedded step in PLS algorithm, thus, a reconstruction step is also contained for transformation from principal component space to original data space. However, PLS method also needs a number of training samples for an accurate calibration.

2.4.4. Neural method

Neural method [20] is presented for instrument standardization through artificial neural network training from data set of slave instrument to the data set of master instrument, and hyperparameters (weights and biases) which represent the nonlinear relation between instruments would be obtained for signal shift reduction. Neural method is a nonlinear method which treats sensor array's signal non-linearly but not a unique sensor and it is different from other methods. That is, the sensor array will be standardized in the whole by a neural method. As we know, a good robustness of one ANN should be based on a large number of experimental samples so that the standardization can traverse environmental conditions as many as possible and will work in standardization. However, preparations of a large number of samples are very complex for each target gas being analyzed, and the experimental burden is also heavy. Especially, when a new instrument comes, repetitive experiments of the same amount of work would be employed further which is similar with UDS and PLS method, it would increase the experimental burden in large scale of instruments standardization.

2.4.5. GAT-RWLS method

To overcome the common flaw of UDS, PLS and neural methods that a large number experimental calibration samples should be

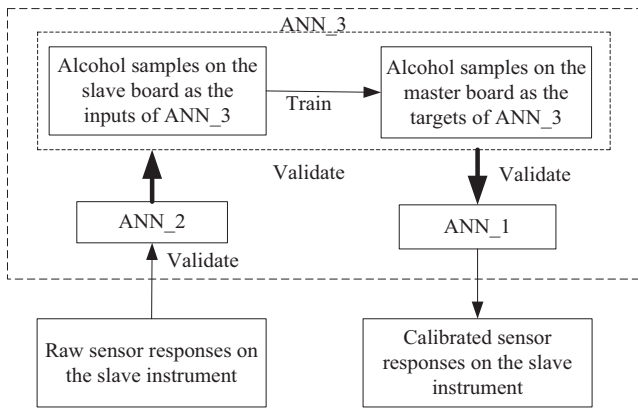


Fig. 2. Block diagram of RAPT model (validation) in real-time instrument standardization.

needed in standardization, a GAT-RWLS method was proposed in [21]. This method is realized using robust weighted least square algorithm based on global affine theory. The calibration sample set was selected as the most representative transfer samples. This method needs less calibration samples, and performs well with a good robustness in electronic nose instruments standardizations.

2.4.6. Reference alcohol projection and transfer model (RAPT)

Artificial neural network (ANN) is a widely used nonlinear regression method such as curve regression and approximation [23]. Consider its strong ability of nonlinear regression, ANN methodology is used in the proposed RAPT standardization model. To avoid the heavy work for experimental gas samples and the harmfulness when preparing for the gas samples, a RAPT method to project onto hazardous gases and construct the “bridge” to transfer between two instruments is presented based on ANN methodology in this section. For this calibration task, experiments using alcohol as analyte were carried out because alcohol is nontoxic and metal oxide sensors generally exhibit fast response to it. Data sets from these experiments were then used to build up projection relations between alcohol and the target gases. Besides, they were also used to set up the transfer bridge between slave instruments and the master instrument. Because of the bridge construction, three neural networks were created and trained on a PC to realize the standardization including projections (ANN_1 and ANN_2) and transfer (ANN_3) for each gas calibration. Three networks denote three projections: from gas to alcohol, from alcohol to gas and from alcohol to alcohol. Therefore, the input and target of ANN_1 should be target gas and alcohol, respectively; the input and target of ANN_2 should be alcohol and target gas, respectively. Then ANN_1 and 2 would be embedded into other instruments for real-time gas quantification. A rationale assumption behind the proposed calibration method is that the nonlinear projection between the reference alcohol gas and the target gas is consistent for each instrument. It means that the signal shift between instruments does not influence the relation of alcohol and target gas. The detailed RAPT model shown in Fig. 2 illustrates the specific calibration block diagram and denotes the whole process of standardization and validation when an e-nose is exposed to real-time scenario.

Let X and Y denote the alcohol gas measurement dataset and the target gases measurement dataset on the master instrument, respectively. Then the ANN_1 and ANN_2 can be represented as:

$$X \xrightarrow{\text{ANN}_1} Y = f_1(X) \tag{1}$$

$$Y \xrightarrow{\text{ANN}_2} X = f_2(Y) \tag{2}$$

Modules labeled ANN_1 and ANN_2 in Fig. 3 denote the well trained networks. ANN_3 plays an important role in the calibration

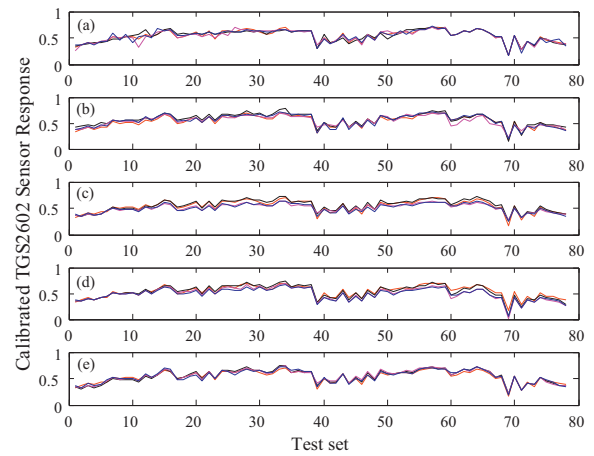


Fig. 3. TGS2602 sensor response after standardization of four e-nose instruments using RAPT (a) Neural (b), UDS (c), PLS (d) and GAT-RWLS (e), respectively.

transfer as a bridge. The mapping is built up using alcohol data sets from both the slave instrument and the master instrument. For instance, suppose that Z_{slave} represents the alcohol dataset from a slave instrument and Z_{master} indicates the alcohol dataset from the slave instrument, then the following relation for signal shift compensation, between a master instrument and any slave instrument, can be elaborated.

$$Z_{\text{slave}} \xrightarrow{\text{ANN}_3} Z_{\text{master}}, Z_{\text{master}} = f_3(Z_{\text{slave}}) \tag{3}$$

In the calibration transfer, we define the dataset of a new slave instrument as S , and target dataset M of the master instrument. In this work, the neural networks contain three layers (input layer, hidden layer and output layer). The number of input layer and output layer is 6 (the number of sensors); the hidden layer contains 10 neurons. A neural network was trained using “trainlm” learning algorithm in Matlab for its fast convergence velocity. The activation functions in the hidden layer and the output layer are the “log-sigmoid” and “pure-linear” functions, respectively. The convergence goal and the maximum number of iterations (training epochs) for each train were set to 0.05 and 2000, respectively.

2.5. Performance analysis of standardization

In this paper, the mean relative absolute error (MRAE), root mean square error (RMSE), standard deviation of residual and correlation coefficient between gas sensor responses of the slave and master instruments are used to evaluate the calibration transfer system. MRAE can show the relative standardization performance from s to m because there is a division in calculation $|s - m|/m$. RMSE is a direct way to calculate the difference $|s - m|$ between two vectors s and m . The MRAE and RMSE are calculated as follows

$$\text{MRAE} = \frac{1}{n \cdot N_1} \sum_{i=1}^n \sum_{j=1}^{N_1} \left| \frac{S_{i,j} - M_{i,j}}{M_{i,j}} \right| \times 100 \tag{4}$$

$$\text{RMSE} = \sqrt{\frac{1}{n \cdot N_1} \sum_{i=1}^n \sum_{j=1}^{N_1} (S_{i,j} - M_{i,j})^2} \tag{5}$$

where N_1 denotes the number of test samples, n denotes the number of calibrated sensors.

MRAE and RMSE represent the general difference between two dataset which can be used as good performance measures of standardization. Smaller values of MRAE and RMSE prove a better standardization from the slave instruments to the master. However, MRAE and RMSE only calculate the average error of residuals,

and the error distribution, fluctuations, stability and the evident difference can not be reflected. Therefore, the standard deviation and correlation coefficient are calculated. Standard deviation shows the general standardization effectiveness and the deviation rate from each sample's standardization error to the center of all samples' standardization errors. Correlation coefficient shows the standardization from the angle of similarity between two vectors such as Euclidean distance. Smaller standard deviation value demonstrates the better stability of standardization for each sample. Larger correlation coefficients demonstrate the stronger similarity of two vectors, the Euclidean distance will also be smaller and the standardization should be better.

Assume x and y are the average sensor response vectors of slave instrument and master instrument, respectively. Then, the statistical standard deviation of residual and the correlation coefficient are calculated as follows

$$\text{Standard derivation} = \sqrt{\frac{n \cdot \sum_{i=1}^n |x_i - y_i|^2 - (\sum_{i=1}^n |x_i - y_i|)^2}{n^2}} \tag{6}$$

Correlation coefficient

$$= \frac{n \cdot \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i}{\sqrt{(n \cdot \sum_{i=1}^n x_i^2 - (\sum_{i=1}^n x_i)^2)(n \cdot \sum_{i=1}^n y_i^2 - (\sum_{i=1}^n y_i)^2)}} \tag{7}$$

where n denotes the number of data points.

Besides, in order to evaluate the statistical significance of improvement in performance, statistical analysis using Student's t -test performed by Matlab was employed on the $RMSE$ and $MRAE$, respectively. The statistical H value between two cases is calculated with a confidence level of 95%, and statistical difference exists between two cases if $H = 1$.

3. Results and discussion

3.1. Standardization of sensor signal shift

The sensor signal shifts between slave instruments and the master were treated using the presented five standardization models. Fig. 3 illustrates the reduced TGS2602 signal shift of the test set including 78 samples of five target gases. Fig. 3(a)–(e) denotes RAPT, Neural, UDS, PLS and GAT-RWLS standardization method,

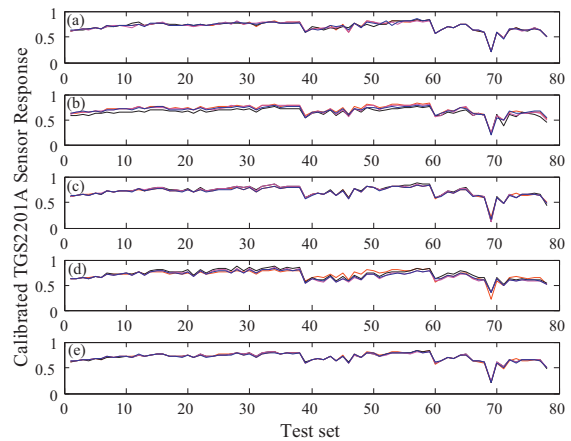


Fig. 4. TGS2201A sensor response after standardization of four e-nose instruments using RAPT (a), Neural (b), UDS (c), PLS (d) and GAT-RWLS (e), respectively.

respectively. In each subfigure of Fig. 3, four curves including the master, calibrated slave 1, calibrated slave 2, and calibrated slave 3 were shown. Similarly, Fig. 4 illustrates the reduced TGS2201A signal shift of the test set. From Figs. 3(a) and (e) and 4(a) and (e), we can see that signal curves of four instruments almost overlap after standardization between the slave instruments and the master instrument. Seemingly, both RAPT and GAT-RWLS methods are superior to other three methods. We may not clearly find out the significant difference among the five methods through the qualitative analysis of Figs. 3 and 4, except for some segments and some obvious points. Therefore, Table 2 presents the quantitative results ($RMSE$ and $MRAE$) of TGS2602 sensor signal shift after standardization between the slave instruments and the master using these five methods. Similarly, Table 3 presents the quantitative results of TGS2201A sensor signal shift after standardization. Table 2 and 3 demonstrate that the proposed RAPT method is competitive to other methods.

Besides, statistical analysis including standard deviations ($std. dev$) and correlation coefficients ($corr. coef$) is also calculated to check the performance of standardization models. Table 4 presents the statistical analysis results of TGS2602 sensor signal shift after standardization between the slave instruments and the master. The statistical results of TGS2201A sensor are illustrated in Table 5.

Table 2
TGS2602 sensor signal shift after standardization between slave instruments and the master.

Method	Slave 1-master instrument		Slave 2-master instrument		Slave 3-master instrument	
	RMSE	MRAE (%)	RMSE	MRAE (%)	RMSE	MRAE (%)
Raw	0.0717	12.985	0.0606	10.649	0.0796	14.070
RAPT	0.0352	4.4937	0.0348	4.2496	0.0343	5.0471
Neural	0.0439	7.3751	0.0423	6.6364	0.0309	5.2061
UDS	0.0295	5.1103	0.0509	8.7223	0.0491	8.2925
PLS	0.0339	5.7958	0.0614	9.8336	0.0625	10.397
GAT-RWLS	0.0303	5.0005	0.0321	5.2919	0.0280	4.6997

Table 3
TGS2201A sensor signal shift after standardization between slave instruments and the master.

Method	Slave 1-master instrument		Slave 2-master instrument		Slave 3-master instrument	
	RMSE	MRAE (%)	RMSE	MRAE (%)	RMSE	MRAE (%)
Raw	0.0358	5.0779	0.0357	5.1376	0.0199	2.6196
RAPT	0.0209	1.8150	0.0173	1.6992	0.0179	1.7440
Neural	0.0613	8.1041	0.0225	2.6103	0.0264	3.1363
UDS	0.0260	3.1449	0.0199	2.3178	0.0136	1.2642
PLS	0.0462	5.9412	0.0489	5.9231	0.0461	5.3975
GAT-RWLS	0.0144	1.5675	0.0146	1.6689	0.0126	1.1322

Table 4
Statistical quantization results (standard deviation, correlation coefficient) of TGS2602 using different standardization methods between slave instruments and master instrument on the test samples.

Method	Slave 1-master instrument		Slave 2-master instrument		Slave 3-master instrument	
	<i>std. dev</i>	<i>corr. coef</i>	<i>std. dev</i>	<i>corr. coef</i>	<i>std. dev</i>	<i>corr. coef</i>
Raw	0.0251	0.9756	0.0250	0.9679	0.0263	0.9732
RAPT	0.0258	0.9502	0.0268	0.9532	0.0232	0.9534
Neural	0.0252	0.9658	0.0282	0.9270	0.0169	0.9717
UDS	0.0190	0.9756	0.0253	0.9679	0.0230	0.9732
PLS	0.0214	0.9694	0.0385	0.9333	0.0334	0.9492
GAT-RWLS	0.0175	0.9756	0.0197	0.9679	0.0155	0.9732

Table 5
Statistical quantization results (standard deviation, correlation coefficient) of TGS2201A using different standardization methods between slave instruments and master instrument on the test samples.

Method	Slave 1-master instrument		Slave 2-master instrument		Slave 3-master instrument	
	<i>std. dev</i>	<i>corr. coef</i>	<i>std. dev</i>	<i>corr. coef</i>	<i>std. dev</i>	<i>corr. coef</i>
Raw	0.0106	0.9887	0.0116	0.9900	0.0096	0.9917
RAPT	0.0165	0.9745	0.0123	0.9827	0.0133	0.9815
Neural	0.0214	0.9662	0.0148	0.9800	0.0140	0.9774
UDS	0.0171	0.9887	0.0141	0.9900	0.0115	0.9917
PLS	0.0268	0.8888	0.0304	0.8801	0.0312	0.8879
GAT-RWLS	0.0103	0.9887	0.0101	0.9900	0.0101	0.9917

Through the statistical standard deviation and correlation between signals of the master instrument and calibrated slave instrument, we can see that the RAPT model is slightly weak by comparing the *std. dev* and *corr. coef* after RAPT standardization with the raw value without standardization. However, the phenomena can be understood that RAPT is designed based on ANN which is not very stable globally and therefore affect the standard deviations and correlation coefficients. Technically, the correlation coefficients of calibrated signal remain the same as the raw data using UDS and GAT-RWLS methods, because of their principle of linear least square regression. Statistical significance analysis using *t*-test at a confidence level 95% on the *RMSE* and *MRAE* are illustrated in Tables 6 and 7, respectively. The statistical significance exists between any two cases when *H* value is equal to 1. Both RAPT and GAT-RWLS methods have statistical significance with case of raw data, while other three methods have no statistical significance. RAPT also have significance with cases of neural and PLS methods.

Table 6
Statistical significance analysis on RMSE using *t*-test method with a confidence level 0.95.

<i>H</i>	Raw	RAPT	Neural	UDS	PLS	GAT
Raw	0	1	0	0	0	1
RAPT	1	0	0	0	1	0
Neural	0	0	0	0	0	1
UDS	0	0	0	0	1	0
PLS	0	1	0	1	0	1
GAT	1	0	1	0	1	0

Table 7
Statistical significance analysis on RMAE using *t*-test method.

<i>H</i>	Raw	RAPT	Neural	UDS	PLS	GAT
Raw	0	1	0	0	0	1
RAPT	1	0	1	0	1	0
Neural	0	1	0	0	0	1
UDS	0	0	0	0	0	0
PLS	0	1	0	0	0	1
GAT	1	0	1	0	1	0

3.2. Results of principal component analysis

Principal component analysis (PCA) is an unsupervised method which transforms the original data into the space of the principal components through a linear projection [24]. It is a multi-dimensional signal analysis method in statistical learning by projecting correlated variables into another orthogonal feature space and thus a group of new variables with the largest variance (global variance maximization) were obtained with dimensionality reduction. Although the direct calibration results have been presented, the calibration property in the data space can not be expressed. Therefore, PCA is employed to validate the standardization performance further in a principal component space. The PCA plots of the first two principal components can represent the difference of the whole dataset clearly.

Figs. 5–7 illustrate the PCA plots of the four target gases tested on the slave 1, the slave 2 and the slave 3 instruments, respectively. In each figure, (a)–(f) show the PCA plots with raw data, RAPT, Neural, UDS, PLS and GAT-RWLS corrected data, respectively. Note that the score of PCA is first obtained using the data on the master instrument and it is used to project the data set of the slave instruments onto the PCA space for coefficients. Figs. 5(b)–7(b) show that the cluster of benzene becomes narrow and the separation is clearer after RAPT standardization than other methods.

3.3. Complexity analysis of standardization methods

For an effective standardization model in mass calibration of instruments, calibration complexity should be considered. In terms of the experimental time for one measurement, 10 min are needed in a single measurement. Take the set I as an example, 42 training samples and 15 test samples would totally consume 570 min for experiments. Thus, for UDS, PLS and neural methods, 570 min would be necessary in standardization. In this paper, 30 alcohol samples for projection between harmful gases and alcohol are used in RAPT model. So, 300 min are consumed for building of the projection between harmful gases and alcohol. But in subsequent calibration in mass production, 6 alcohol transfer samples are enough to obtain some information of one new instrument

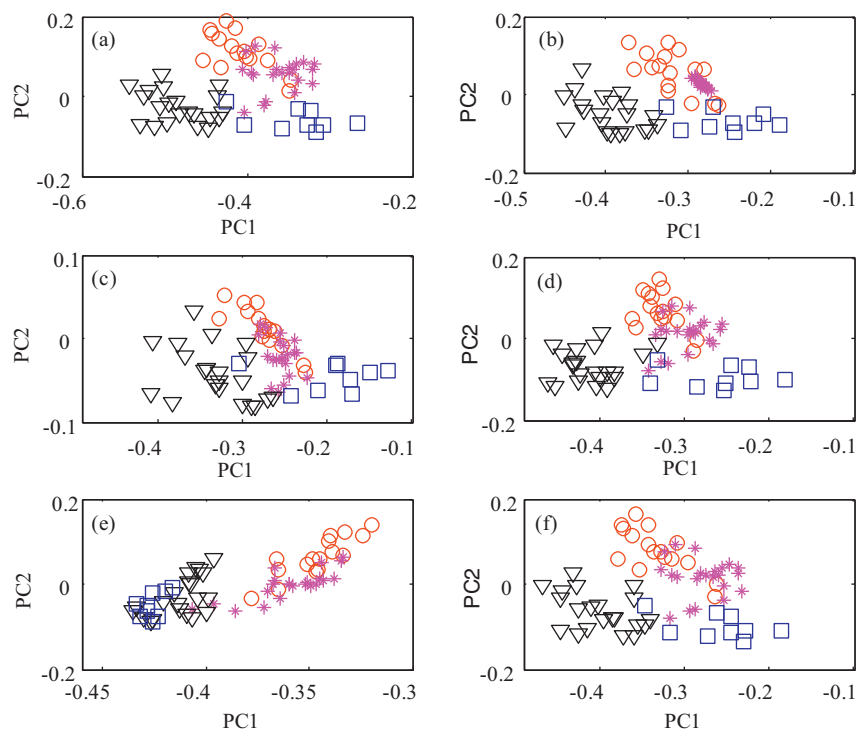


Fig. 5. First two principal components of the data set on the slave 1 instrument with raw data (a), RAPT (b), Neural (c), UDS (d), PLS (e) and GAT-RWLS (f), respectively. 'circle', 'star', 'triangle' and 'square' denote carbon monoxide, benzene, toluene and ammonia, respectively.

and therefore 60 min are enough. However, more alcohol transfer samples would be better for the calibration accuracy of ANN training. Compared with UDS, PLS and neural methods, the RAPT model would consume less time in standardization. It is worth noting that only five target gas samples were needed in GAT-RWLS method, however, the RAPT method is based on nontoxic alcohol.

3.4. Discussion

In this paper, five instrument related signal shift standardization methods are presented. Among the five methods, the RAPT model using alcohol as reference gas is competitive relatively from the experiments and simulations. In implementations, UDS was

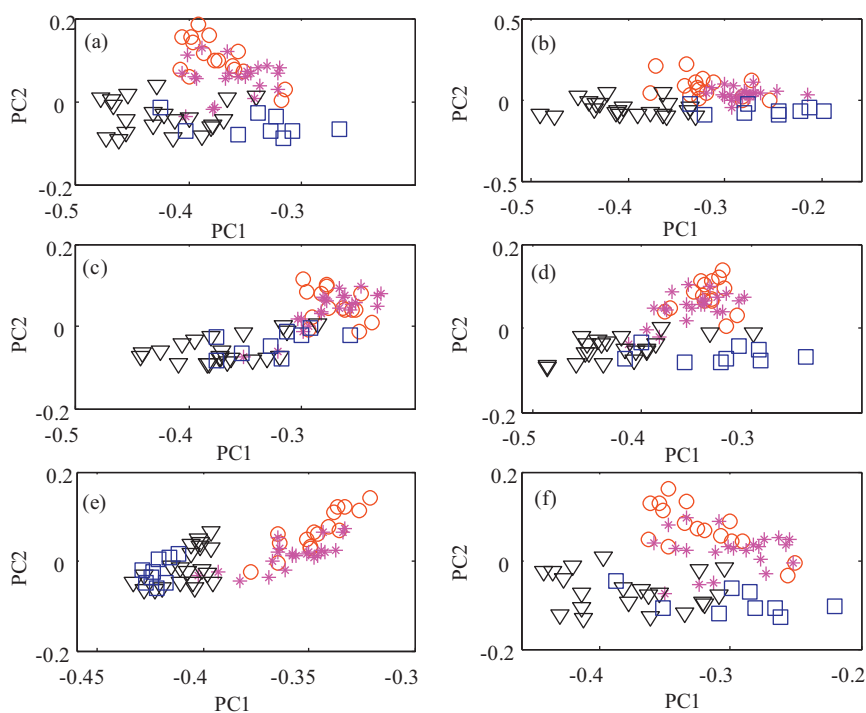


Fig. 6. First two principal components of the data set on the slave 2 instrument with raw data (a), RAPT (b), Neural (c), UDS (d), PLS (e) and GAT-RWLS (f), respectively. 'circle', 'star', 'triangle' and 'square' denote carbon monoxide, benzene, toluene and ammonia, respectively.

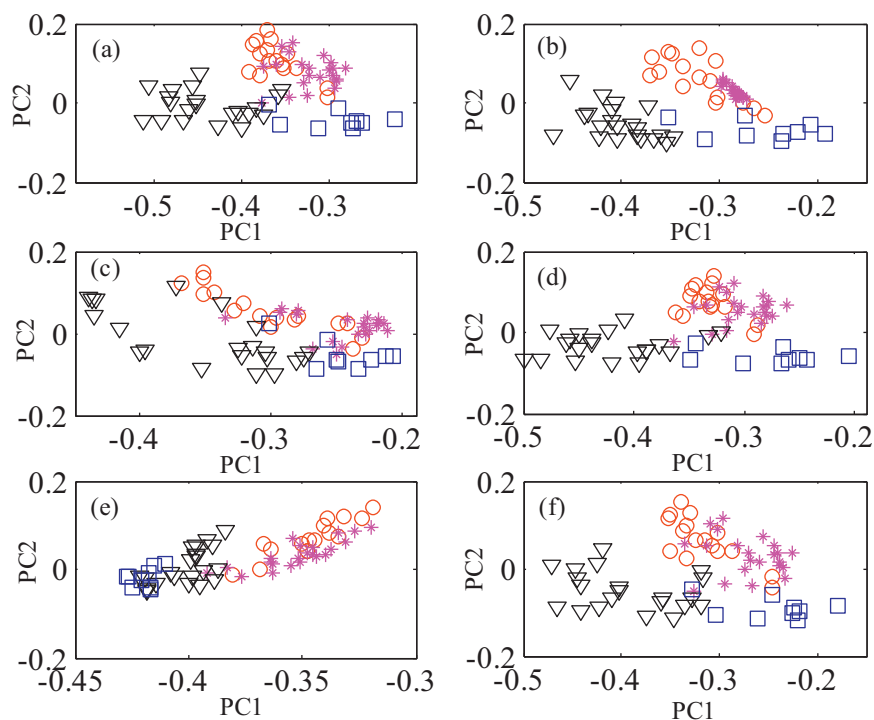


Fig. 7. First two principal components of the data set on the slave 3 instrument with raw data (a), RAPT (b), Neural (c), UDS (d), PLS (e) and GAT-RWLS (f), respectively. 'circle', 'star', 'triangle' and 'square' denote carbon monoxide, benzene, toluene and ammonia, respectively.

simple and easier to be used based on linear least square regression. Though it can reduce some instrument related variations, this method may not be applicable to the new instruments or new measurements. The reason is that the metal oxide semi-conductor gas sensors are sensitivity to temperature, relative humidity, environmental background noise and sensor drift (e.g. time drift and sensitivity drift). Then the UDS based model will fail to fit with the noise disturbed sensor signal. PCA based PLS was also employed as a standardization model which is more complex than UDS. Besides, a number of training samples should also be necessary to calculate the PCA coefficients and promise the calibration accuracy. Another problem is the determination of the principal components which influences the robustness due to the overfitting [18]. GAT-RWLS method was developed as a linear method for consideration of the experimental complexity of electronic nose instrument calibration. It has been proved to be feasible in on-line calibration and overcome the flaw of complex experiments of UDS and PLS in standardization.

Neural method is a nonlinear calibration technique which is different from UDS and PLS. The nonlinear characteristic, such as ANN, may make the standardization of the new measurements for the same instrument applicable, only if we have enough measurements to train the nonlinear model. However, the standardization for new instruments can still not be solved by a direct neural method, because of the difficulties in repeated employment of a large number of hazardous gas measurements on one new instrument for a new standardization. It certainly becomes more difficult to achieve standardization of mass production of instruments, and even become impossible. Choice of the number of training samples, which is similar with the choice of the number of hidden neurons, is difficult to make decision in theory. Indeed, the complexity of the model grows with the number of hidden neurons and so also the number of samples needed to train the ANN without overfitting. Thus, we attempt to find another functional way to reduce the possible number of hazardous gas measurements for new standardizations through reference alcohol gas. We introduce

ANN to solve the problem of the instrument signal shift based on the strong nonlinear regression ability and generality.

Alcohol is chosen as reference gas (to be equivalent to transfer set) to project it onto the measured hazardous gases. We select alcohol for three reasons: first, alcohol is nontoxic compared with the target gases; second, metal oxide sensors have fast response to alcohol; another reason may be conservative for that the relation between alcohol and the target gases appears to be approximately linear under the same temperature and humidity. However, alcohol is not a unique reference gas and other reference gases such as clean air may also be used. This will be included in our future research. One of the attractive features of the model is its simplicity which promotes its functional use in actual E-nose applications. Though more alcohol transfer samples would be beneficial for high calibration accuracy, six alcohol transfer samples with humidity of 60%RH are enough in mass production and reduce the complexity of repeated experimental measurements to a large extent. The presented model can be used not only on sensor array, but also on a single sensor if other sensors show no signal shifts.

4. Conclusions

Sensor arrays play an important role in electronic nose (E-nose) systems. Generally, due to the temporal and spatial variability in the responses of chemical sensors, E-nose instruments with the same sensor array may provide significantly different smell prints. Therefore, this paper aims to find out the solution of the sensor signal shift problem. For reducing the number of transfer samples, time complexity, experimental complexity and harmfulness of chemical gases in mass calibrations, this paper addresses the critical issue of instrument related signal shift and a simple RAPT standardization model based on ANN is proposed and compared with previous UDS, PLS, Neural and GAT-RWLS methods. The most important advantage of RAPT is that only nontoxic alcohol is considered in mass standardizations, and a large number of harmful gases experiments

can also be avoided due to the design of ANN “bridge”. Four instruments based on identical metal oxide semi-conductor sensor array, one master instrument and three slave instruments were used to evaluate the performance of the presented standardization methods. Standardization results on the measured data sets demonstrate RAPT method is more competitive. Standardization models on complex mixtures (e.g. mixtures of benzene and toluene or more) will be developed and validated in the future work.

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