Bulgarian Chemical Communications, Special Issue F, (pp. 69 – 73) 2016

Study on gas recognition and determination based on gas sensors

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Received February 12, 2016; Revised December 26, 2016

Study on odor sources with help of gas sensors is of important theoretical value and practical significance. Study of electronical nose is greatly helpful to gas recognition and determination. Study of gas sensor arrays has become more and more popular. We can identify phytochemical volatiles with gas sensors. We can do explore analysis to the data with cluster analysis method without using training samples. Thus, it is widely applied in gas sensor array mode recognizing. In this article, we used the comprehensive grey cluster algorithm with certain choosing principle to recognize gas sensors array models and did description and data analysis and sorting. The result shows that we can use the improved method to recognize different volatile chemical constituents more effectively.

Keywords: Odor Recognition System, Cluster Analysis, Choosing Principle, Factor Analysis

INTRODUCTION

Odor is a sort of phytochemical floating in the air that can generally be sensed by living organisms. However, there are some locations not suitable for living organisms to detect. Study how to imitate the olfactory behavior of living organisms and integrate the olfactory technology with electronic products has great theoretical value and practical significance in identifying the odor sources. This study result could be used in environmental disaster prevention like explosive substance searching, post- disaster-searching and rescuing, detecting and identifying poisonous gas, etc. Results of some scientific studies showed that the faster the odor appearances or the faster it gets stronger the serious the accident is. In current time, scientist from many countries sees Rn, He, H_2, Hg, CO_2etc as the signs for earthquakes. So these types of gas have become study target for gas recognition and determination.

The odor source recognition methods are methods in which we can use sensors to detect the material construction and the concentration distribution of the odor and use some certain method to determine the odor's type and its location. There are two types of methods to determine the odor sources. One is static detecting method; the other is the active searching method work with mobile robots. Studying of electronic nose is of great help to odor sources recognition. More and more study related to gas sensor has been published in chemistry literatures [1,2,3,4]. The main purpose of studying the gas sensor array is to find a system that can imitate the breathing system to effectively recognize the gas chemistry types and to determine their concentration [5,6,7]. The sensor array can supply multi-aspect information and its changeable response models can generate large amount of data. Model recognizing method is the main tool to process the gas sensor data and recognizing different phytochemical volatiles has always been a hot study topic in gas sensor array.

Many model recognizing methods like cluster analysis method, discriminatory analysis method, artificial neutral network method, support vector machine have been applied in gas sensor study [8]. In these methods, we do not require training sample to do the exploratory classifying to the data in cluster analysis method. It is widely applied in recognizing the gas sensor array models. Correlation analysis, factor analysis and some other statistical methods have been applied in chemistry study. Through factor analysis, we can reduce the high dimension data's dimension to make the data easy to study. In this way, we can also find the latent variables thus to find the data structure to get the useful chemistry information. We have improved the cluster analysis method and make it comprehensive cluster algorithm by applying certain choosing principles. We use the comprehensive cluster algorithm in gas sensor array recognizing. The gas sensor data were sorted and the result shows that the improved algorithm can help us to recognize different phytochemical volatile component effectively.

MATERIAL AND METHODS

Gas Sensor

According to the sensor mechanism, gas sensor methods could be sorted into chemical sensor method, gas chromatographic method and absorption spectrum analysis method. Materials used in chemistry study are usually electrolyte, metallic ox-

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ide (ceramics or semiconductor) and macromolecular polymeric film.

Following are the sensors usually used to make chemical gas sensor array: metal oxide semiconductor sensor (MOS), metal oxide field effect transistor sensor (MOSFETS), Quartz Crystal piezo transistor sensor (QCM), surface acoustic wave sensor (SAW), Chemresistor, and optical sensor, etc [9]. Seiyama was the first person that used semiconductor effect of $SnO_2$to determine the air composition in 1964. Later in 1968, a company in Japan has started to make SnO_2 sensors for business reason. Currently, SnO_2 is used as the main material for most metallic oxide gas sensors. People make each type of gas sensors by mixing SnO_2 with other components to determine the composition and concentration of the tested gases. SnO_2 gas sensors are widely used in our daily life and in industrial production activities for their high sensitivity, short response and recovery time, their good performances and low cost. SnO_2 gas sensors' structure is described in figure below (Figure 1). Usually a gas sensor is formed by a foundation, the electrode leads and its sensitive materials and the heating units.

We usually have to test the gas of very low concentration when we do gas determination. We could improve the catalytic activity on surface of the SnO_2semiconductorsby mixing$SnO_2$with some kinds of metals or metallic oxide sand then improve the sensors' sensitivity and selectivity thus to extend the fields the sensors can be applied in. Maekawa and Suzuki and some others has make serial gas sensors by coating different metallic oxides catalyst on SnO_2film mixed with PbOx.

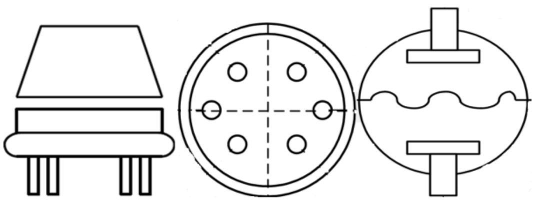

Fig. 1. SnO_2 Gas sensor architecture.

They made the SnO_2sensors with and without catalyst coating into a MOS gas sensors array of high selectivity. This gas sensors array were used and have helped us determined 40 phytochemical volatiles. The sensors data in this article was quoted from reference articles [10,11]. There were sensitivities data from SnO_2film with 7metallic coating and an original SnO_2film with no coating. Here below we call it M-S data. Since we cannot cite all the data, we listed part of the data in chart below (Table 1).

Method

We mark the original data matrix of the gas sensors sensitivity $S = (S_{ij})$. In the matrix, $S_{ij}, i = 1, \cdots, 8, j = 1, \cdots, 40$,stands for the sensitivity of the gas sample ranked *I* that is acquired by the gas sensor ranked *j*. Sensitivity is the ratio of the resistant value in the oxygen environment (or we say in the air) and the resistant value in the chemical atmosphere. To make it easy to record, we use abbreviations for the variables' names. For example, we use W for W/Al_2O_3, and we make an analogy in the same pattern for the other names.

Descriptive data analysis is a method we present the data in a form easy for people to understand. It might be a chart, a figure or an index. For example, from the mean value and variance of the data we can see the data's characteristics with descriptive data analysis method in chart (Table 2). Deductive data analysis is a method using a statistical model to predict and test the data's regularity. We want to find the specialty of each method, so we used box plots, see figure (Figure 2), in this article.

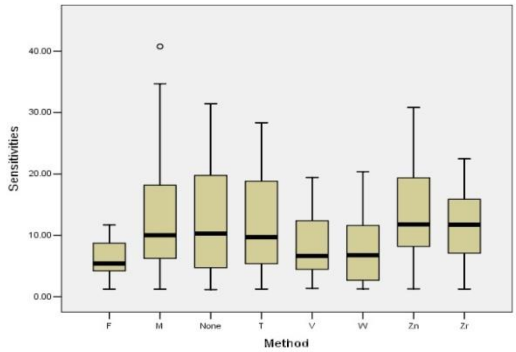

Fig. 2. Box Plots.

Compare the original data and the mean value, we can see that ZnO method and Mo/SiO_2methodhave highier sesitiviry in their mean value. We see that thegas sensitivity has been improved 75% from the orignal data. The Fe-Mo-O_x method is more stable. Its variance is smaller and we can see that none of the skewness or kurtosis of the data is in normal distribution. We can intuitively see the mean value and the variance of the date in figure 2 and at the same time there are some exceptional values in the Mo/SiO_2 method.

We can make the scatter diagram from the connection between different methods, see figure (Figure 3). We can intuitively see the positive linear relationship between the original film method and the ZnO, V/SiO_2, TiO_2, Mo/SiO_2methods. In fact, we can calculate and get the Pearson correlation coefficient of None & TiO2, None &Mo/SiO_2, None&Fe-Mo-O_x.

Table 1. Sensitivities to odor gases for sensors with various catalytic layers.

Sample	Measured object	Catalytic layer None	W/Al_2O_3	ZnO	ZrO_2	Mo/SiO_2	V/SiO_2	TiO_2	Fe-Mo-O_x
1	CH_3OH	5.18	6.04	6.33	4.95	4.92	5.28	5.38	4.24
2	C_2H_5OH	9.38	1.5	10.6	8.84	7.76	6.71	9.65	5.69
3	*n*-C_3H_7OH	16.44	2.81	20.34	16.06	15.89	11.5	17.9	9.18
4	*i*-C_3H_7OH	12.61	2.16	11.62	10.5	8.53	6.63	12.83	6.95
…	…	…	…	…	…	…	…	…	…
39	CH_3SCH_3	1.16	4.9	1.57	1.49	1.33	1.39	1.35	1.47
40	CH_3SSCH_3	2.65	4.91	2.39	2.4	1.71	2	2.32	1.78

Table 2. Statistics

Statistics	None	W	Zn	Zr	M	V	T	F
Mean	12.3273	8.138	14.025	11.657	13.037	8.296	11.959	6.3945
Median	10.275	6.77	11.785	11.725	10.01	6.655	9.695	5.4
Std. Deviation	8.67725	5.65767	8.33631	5.87563	9.83588	5.0191	8.05339	2.99782
Skewness	0.61	0.744	0.646	-0.073	1.142	0.661	0.555	0.185
Kurtosis	-0.828	-0.482	-0.535	-0.787	0.593	-0.693	-0.987	-1.094

Table 3. T Test

		Paired Differences Mean	Std. Deviation	t	df	Sig. (2-tailed)
Pair 1	None - Zn	-1.69775	3.89068	-2.76	39	0.009
Pair 2	None - M	-0.70975	5.94538	-0.755	39	0.455
Pair 3	None - F	5.93275	6.01628	6.237	39	0.000

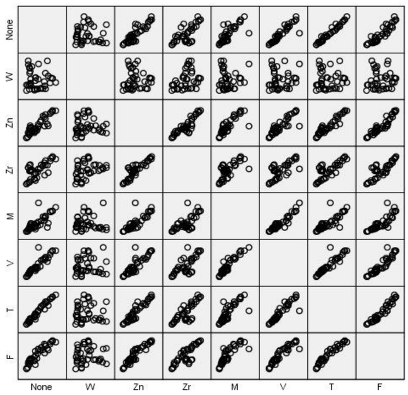

Fig. 3. Scatter Diagam.

We did T test of the data to find the differences between each method. Here we cited results of 3 groupsof compared data in the chart below(Table 3).

From the chart we can see that there are big differences between the mean values of None & TiO_2 and the mean values of None &Fe-Mo-O_x. However, there were no significant differences between the mean values ofNone &Mo/SiO_2.

We proposed the choosing principle based on the above data analysis after consideration ofpractical problems and the numbers of variables.When the number of the variables is bigger than K, the choosing principle is: 1. Choose the variables of higher sensitivity which have variable mean values compared with the oringnal film data. 2. Chooes the variables with sensitivity that are positively correlated to the orignal film data.

This means the variables we analyzed thereafter are marked as X_i, $\{i \mid i \in I_1, i \in I_2, i \geq K\}$. In the data:

$$I_1 = \begin{cases} 1, \mu_i - \mu_1 \geq 0 \\ 0, \mu_i - \mu_1 < 0 \end{cases}, \quad I_2 = \begin{cases} 1, \rho_{i1} \geq 0 \\ 0, \rho_{i1} < 0 \end{cases}. \qquad (1)$$

When the numbers of the variables is smaller than K, we try to use as much variables as we can because the variables here are not easy to obtain. In this condition, the choosing principle is: Chooes the variables with sensitivity that are positively correlated to the orignal film data.

Now the variables are still maerked as X_i, $\{i \mid i \in I_2, i < K\}$, and in the data:

$$I_2 = \begin{cases} 1, \rho_{i1} \geq 0 \\ 0, \rho_{i1} < 0 \end{cases}. \qquad (2)$$

The value of *K*should be supplied by gas sensors specialists. In this article, we value *K* 50 based on the statistical understanding of number magnitude. M-S data is in this condition. We can get the qualified X_i. The coefficient of W/Al_2O_3method is negtive value, so these values will not be used in this article. We get 6 X_i. With the orignal data, we have 7 X_i.

Factor analysis method in multivariate statistical analysis can help us to reduce the multidimensional variables' dimensions and get the latent variables. We can reduce the variables dimension of X_i and make it anaggregative variable F_i in this way and choose the aggregative variables with variance contribution rates above 90% for the next step cluster analysis. With this method we can find the hidden characterisitics of different gas sensors. The following is the factor analysis model:

$$\begin{cases} X_1 - \mu_1 = a_{11}F_1 + a_{12}F_2 + \cdots + a_{1p}F_p + \varepsilon_1 \\ X_2 - \mu_2 = a_{21}F_1 + a_{22}F_2 + \cdots + a_{2p}F_p + \varepsilon_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ X_m - \mu_m = a_{m1}F_1 + a_{m2}F_2 + \cdots + a_{mp}F_p + \varepsilon_m \end{cases} . \quad (3)$$

We make a line graph based on the orignal data as in figure to intuitively see if there are clusterings(Figure 4). We can find out that the clustering is a big mass when there are relatively morevariables. In this condition we cannot distinguish the clusterings. This is also a factor we need to pay attention. For practicle reason, we need to find a method of highier sensitivity as well. We can find the right method to determine different gases through cluster analysis and find the characterisitics of each method.

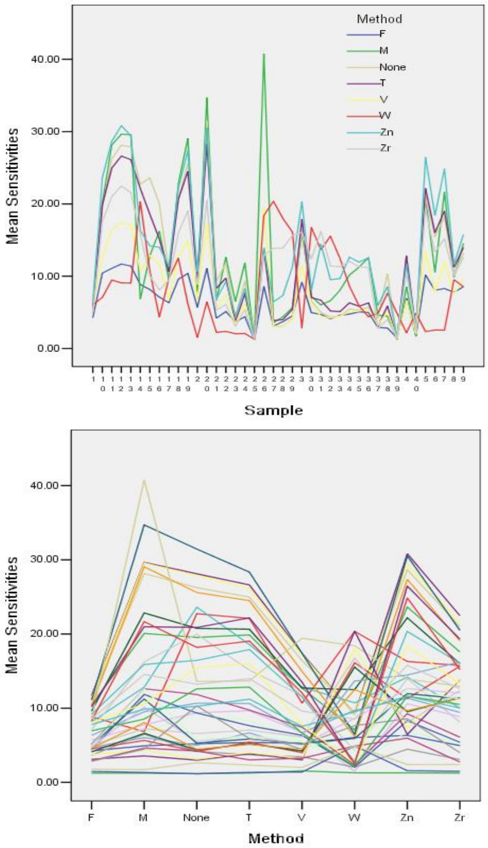

Fig. 4. Line Graph.

RESULTS

We got aggregative variableF_1, F_2 and accelarated variance contribution rate94.42%. F1 indicates the improving capacity of the integrated sensitivity. The high weighted value of F1 in Fe-Mo-O_x, TiO_2,ZnO methods means that these gas sensors have relatively better performances, see in classification map figure (Figure 5). Considering the tree diagram of the system cluster analyzing, we think there are four qualified clusters. These clusters contains 14, 11, 3, 12 variables separately. From the clusters, we can find the proper gas sensors to determine different gases. We think that this integrating variable choosing method is effective from the aspect of accelarated variance contribution ratein factor analysis.

Considering all the above factors, we propose an improved cluster algorithm- comprehensive cluster algorithm. This algorithm is more efficient than the cluster analysis based on the original data because the tested data in this algorithm has been filtrated. At the same time, we find the latent variable to analyze the similarity of different gas sensors.

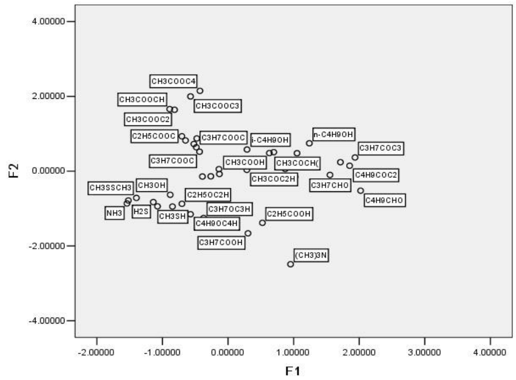

Fig. 5. Classification Map.

DISCUSSION

Gas detection and determinationmethods have deep ifluences in military, industry and our daily life. Recognition of gas sensor array modelshas been widely applied in practices [12, 13]. We have done descriptive analysison the gas sensor data and found that it is more effective if we apply choosing principle. We apply chioosing principle and take comprehensive considerations of the sampled data in the cluster algorithm and apply this method in gas sensors array model recognition. In this way, we sorted the gas sensor data into different types. The result proved that this method has better effect.

Acknowledgements: *This research is supported by National Natural Science Foundation of China under Grant No. 61375066.*

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