DOI 10.5162/IMCS2012/P2.0.10

SnO_2 based tea aroma sensors for Electronic Nose

N. Bhattacharyya[1], D. Dutta[1], S. Ghosh[2], S. Mandal[2], M. Narjinary[2], A. Sen[2], R. Bandyopadhyay[3]
[1] C-DAC, E-2/1, Block-GP, Sector-V, Kolkata -700091, India,
, nabarun.bhattacharya@cdac.in, debashis_dutta76@hotmail.com
[2] CSIR-Central Glass and Ceramic Research Institute, Kolkata -700032, India
saptarshi@cgcri.res.in, m_saikat6@yahoo.com, mnarjinary@cgcri.res.in, asen@cgcri.res.in
[3]Jadavpur University, Kolkata -700098, India
rb@iee.jusl.ac.in

Abstract :
A sensor array composed of SnO_2 based thick film metal oxide sensors for quality evaluation of black tea is described in this paper. Simple sonochemical technique has been used to synthesize the composition. Different elements such as Ag, Au, Pd, Pt, Fe are doped in SnO_2 and their responses (change in resistance) are observed towards the volatile components present in dry black tea leaves. After repeated trials, some of these sensors are selected to form the sensor array on the basis of their discriminating ability. Responses from multidimensional array are visualized using principal component analysis.

Key words: electronic nose, tea aroma, SnO_2 based gas sensor, principal component analysis.

Introduction

Among all the non-alcoholic beverages, tea is the most widely consumed one. China, Sri Lanka, Japan, Kenya and India are the main tea producing countries in the world. This agricultural product has enormous impact on the economy of these countries and it provides livelihood to a large population. Even then, the quality evaluation of tea is still age-old and traditional and experienced tea tasters are employed by the industries for this purpose. These human tasters assign scores on the different quality attributes of tea like aroma, size of tealeaves, infusion, colour and taste and their verdict is final for the price of tea. But this subjective nature of assessment is no longer liked by the tea industry and they are in the lookout of a non-invasive, repeatable instrument that can aid or replace a human taster.

Out of the different attributes of tea, aroma is one of the most decisive attribute behind tea quality. For measurement of aroma of tea, metal oxide sensor based electronic nose has been successfully applied for classification using customized electronic nose [1], where an array of Figaro MOS (Taguchi type) sensors were used. The target molecules of these MOS sensors are methane, ethyl alcohol etc., and not the chemicals present in tea. In fact, no sensors are available now which are specific to the tea volatile compounds and hence, an attempt has been made in this work to develop such sensors.

The aroma in tea largely depends on geographical locations, clonal variety of tea plant, weather condition throughout the period of production and processing techniques [2]. Several volatile compounds are formed during processing sequences i.e. withering, rolling, fermentation and drying of tea. The GC-MS profile of tea clones produced at different agro climatic conditions shows varying compositions of volatile components [4].

More than 200 volatile organic compounds (VOCs) are present in minute quantities in tea and they contribute to the aroma or flavor of tea [2]. Composition and concentration of these VOCs differ from one tea sample to another, which plays an important role in the valuation of tea. It is reported that among many volatile flavor compounds, Linalool, Geraniol, Methyl Salicilate and Trans-2-Hexenal are the principle constituents for tea flavors like Sweet, Floral, Fruity and Fresh flavor respectively [2]. In the pursuit of developing sensors sensitive to tea aroma compounds, these four volatile organic compounds have been targeted and the sensors have been selected based on their sensitivity to these chemicals.

Experimental

Ammonia solution is added drop-wise slowly into an aqueous solution of 0.2 M tin chloride ($SnCl_2$, $2H_2O$) under continuous sonication [Ultrasonic processor model – VPL P_2, VIBRONICS, 25KHz, 250 watt.] for 30 min. During sonication, ammonium hydroxide solution is added drop wise into the stannous chloride solution (maintaining a pH of 9) under stirring, so that all the hydroxides are precipitated simultaneously. The sonication is continued for 1 hr and the warm solution is allowed to cool. The precipitate is then centrifuged, washed with distilled water and acetone in sequence followed by heating in oven. The dried powder obtained is calcined at a temp (up to 600 ^{0}C) for two hours in air to get the desired phase. In order to enhance response in targeted volatile organic compounds the chlorides/nitrates of different metals (Ag, Pt, Cu, Ca, Fe, Pd, Au) are added in appropriate ratio with the stannous chloride solution before sonication assisted simultaneous precipitation method.

Thick homogeneous paste obtained by mixing the above-synthesized powder in isopropyl alcohol (IPA) is uniformly coated over alumina substrate (length 4 mm, outer diameter 2 mm and thickness 0.5 mm). Gold electrodes and platinum lead wires are attached at the ends of the tubes (by curing at high temperature) before applying the paste. The consistency of the paste and the processing variables are optimized to get final coating of around 100µm thickness. After painting, the coated alumina tubes are cured at 650 ^{0}C for 1 hr. Nichrome-heating coil (having twenty four turns) is inserted inside the tube. A supply of +5 V is applied at the heating terminal to obtain a temperature of 350^{0}C (optimum working temperature) for seventy-two hours to achieve the stability.

The sensors developed along with their codes are given in Tab. 1.

Tab. 1: Sensors developed

Sensor code	Sensors developed
S1	SnO_2-Ag (1 wt. %)
S2	SnO_2-Pt (1 wt. %)
S3	SnO_2-CuO (1 wt. %)
S4	SnO_2-CaO (5 wt. %)
S5	SnO_2-PdO (1 wt. %)
S6	SnO_2-Au (1 wt. %)
S7	SnO_2-Fe_2O_3 (1wt. %)
S8	Pure SnO_2

Tea Sample Collection

Most of the tea industries in north and north-east India have multiple tea gardens and tea samples produced in their gardens are sent everyday to the tea tasting centers for quality assessment. A few such samples have been collected from different geographical locations for testing purposes. The sample codes and the respective locations are presented in Tab. 2.

The sensors are arranged in the form of an array and are placed in the customized electronic nose set up with an optimized experimental condition, the details of which are available in [1]. Each tea sample has been exposed to the sensor array twenty times.

Tab. 2: Tea samples used

Sample code	Location of tea garden
T1	Assam
T2, T4, T5	Darjeeling
T3	Nepal
T6, T7, T8	Dooars

Results and discussion

The electrical properties of sensors are measured using digital multimeter Agilent 34401A. The responses of the sensors are measured at a temperature of 350^{0}C by comparing the resistance of sensor in air (R_a) with that in target gas (R_g). Hence, the response in presence of VOC molecules is expressed as the fractional change in resistance due to the application of target gas [(R_a- R_g)/ R_a x 100 (%)] [5]. Each of the sensors is tested at 20 ppm of targeted VOC and the sensitivities with each of four VOCs are shown in Table 3.

Tab. 3: Response by each sensor (%)

Sensor code	Response in VOC (%)			
	Linalool	Geraniol	Methyl salicylate	Trans-2-hexenal
S1	87	52	68	86
S2	87	63	70	84
S3	79	59	59	75
S4	71	70	32	47
S5	62	58	50	67

S6	81	58	42	82
S7	84	65	63	77
S8	69	59	61	67

The response pattern shows, most of the sensors show high sensitivity to linalool and trans-2-hexenal compared with geraniol and methyl salicylate.

In practice, gas sensors are not completely orthogonal i.e. their partial specificity to all components makes a complex response pattern for the gas mixtures, which is the case for tea aroma.

MOS sensors suffer a drawback of repeatability i.e. slight difference in output voltage is obtained in repeated trials for a tea sample even at controlled experimental environment. This error is due to many factors such as drift, change in environmental condition like little temperature change, variation of concentration of components in the sample or natural variation in the sample itself.

Let, the sensitivity of a sensor due to odor sample A at n repeated trials be a_1, a_2, a_3, … a_n. These response points occupy a region in n-dimensional sensor space (mapped from odor space). Similarly, a different volumetric region is obtained from response points due to odor sample B. Two odor samples are mapped into two separate regions in n-dimensional space. Ability of the sensor to distinguish these odor samples is expressed using a factor, called resolving power [3] which takes into account both the distance of the response vectors *A* and *B* and the errors encountered. Mathematically, it is expressed in eq. (1).

$$R = \frac{|S_{AB}|}{\sqrt{\sigma_A^2 + \sigma_B^2}} \qquad (1)$$

$$\sigma^2 = \frac{\sum_{i=1}^{N} (r_i - r_{avg})^2}{N-1}$$

where, N = the dimension of the vector, r_i = Sensitivity at *i*th instant and $r_{avg} = \frac{\sum r_i}{N}$

Here, $|S_{AB}|$ is the Euclidean distance between the response vectors *A* and *B*. σ_A and σ_B are the errors calculated along the direction of the distance metric. Larger this factor, higher is the discriminating ability of the sensor.

Prior to computation of the resolving factors, data are preprocessed using the autoscale method so that the vector elements are mean centered with a standard deviation of one. From the data acquired, the resolving powers of the sensors are calculated using eq. (1) and the results are displayed in Tab 4. From this table, five sensors - S1, S2, S3, S5, and S8 show significantly high values and these five sensors are selected for further analysis.

Principal component analysis (PCA) is commonly used for dimensionality reduction and visualization of datasets. In the response matrix of multi-dimensional array, each column is associated to a sensor, while each row is associated to a different trial. The standardized data matrix is visualized using principal component analysis by taking the first two or three principal components.

Discrimination ability among samples is found with a quantitative measure called Separability Index (SI). Separability Index (SI) is a measure that captures the class separability well. This method quantifies how the classes are distributed with respect to each other. Separability Index of two arrays (Tab. 5) suggest that improved result is obtained by reducing number of sensors from eight to five.

Conclusion

An array is made of SnO_2 based metal oxide semiconductor sensors for tea flavor assessment. Different dopants are doped with SnO_2 to obtain different response patterns. On the basis of the resolving powers, five sensors are selected to design a sensor array. It has also been validated using the separability index. The result suggests that tea classification is possible using electronic nose, where the selected five sensors, adequaqtely sensitive to tea aroma compounds, are used in the sensor array.

Tab. 4: Sensors with their resolving power

	S1	S2	S3	S4	S5	S6	S7	S8
T1-T2	3.1988	1.5673	3.4613	4.4687	6.0932	2.5820	1.9669	6.4031
T1-T3	7.8345	21.6425	2.8298	2.7735	6.5376	2.3458	1.8946	9.6372
T1-T4	11.9307	33.1956	3.9054	2.9259	12.5	2.9881	2.8743	20.3578

T1-T5	4.1982	2.4980	5.8215	1.6960	2.0107	1.0831	3.2676	13.7140
T1-T6	1.7877	23.2813	2.3065	2.6165	17.3432	2.7433	2.6810	13.5402
T1-T7	3.3286	17.82	3.3325	4.7849	2.1848	2.7751	3.9226	3.8356
T1-T8	14.1428	33.2907	1.9345	1.9356	2.0091	1.5785	3.6046	8.2371
T2-T3	7.4658	12.7967	6.373	4.7101	8.4225	2.1545	1.6149	12.2991
T2-T4	14.588	16.2951	6.3424	2.6611	24.6360	8.0537	2.1352	17.48
T2-T5	5.62	2.5970	5.1401	2.4546	2.0179	2.1386	1.8081	15.3698
T2-T6	2.3255	14.1031	2.1631	3.3847	17.5335	2.0021	2.2169	14.643
T2-T7	3.6521	11.9643	2.6077	0.7517	2.1070	2.2856	2.9064	6.2306
T2-T8	20.9687	16.4121	2.8094	2.6684	1.9847	2.1031	3.0224	11.0208
T3-T4	4.4515	5.2856	2.9002	2.3325	4.7832	2.3168	2.2263	2.1967
T3-T5	8.7425	19.2269	8.2877	2.0148	2.0799	2.2911	1.8259	2.0113
T3-T6	3.8524	2.7343	2.4968	2.0094	6.0857	1.3160	2.3963	2.4626
T3-T7	4.4825	2.7918	4.4755	4.9417	2.3840	2.3141	3.7210	2.6528
T3-T8	5.5782	5.8590	1.9260	2.0678	1.9896	2.2662	3.75	2.5316
T4-T5	11.7757	29.4747	8.2864	1.4241	2.0842	2.2808	2.7164	2.6566
T4-T6	5.1552	2.5373	3.0363	2.0411	4.2008	2.1448	1.3854	2.5910
T4-T7	5.07	4.3911	4.61	2.9582	2.4886	2.1149	4.8933	3.2917
T4-T8	2.4478	2.6379	2.3739	2.4609	2.0524	2.0377	4.0573	1.7145
T5-T6	2.9976	20.9263	2.3250	2.0715	2.1389	2.3096	2.6598	3.7793
T5-T7	2.5153	15.8204	1.909	2.6243	2.3421	2.3953	5.2690	3.8208
T5-T8	12.7142	29.9591	4.4393	1.9515	2.2167	2.0076	4.6763	2.8753
T6-T7	3.0896	3.2509	2.7645	3.7034	2.5811	2.2060	4.5446	2.8860
T6-T8	5.4969	3.0321	2.683	2.5107	2.0921	2.1781	3.7278	1.3003
T7-T8	5.1138	4.2930	3.1079	3.0216	2.3012	2.2064	1.5224	2.8690

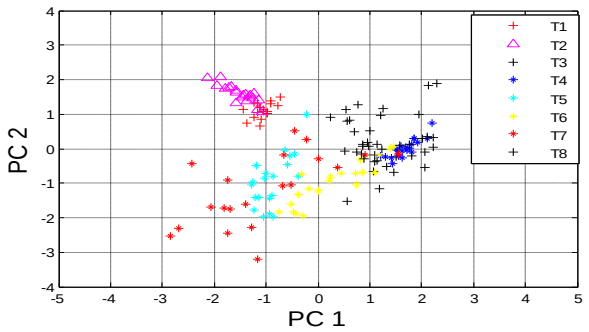

Fig. 1. PCA projection for tea samples

Tab. 5 : Separability index

Sensors in array	Separability index
S1,S2,S3,S4,S5,S6,S7,S8	0.7468
S1,S2,S3,S5,S8	3.4007

Acknowledgements

The work has been funded by Sensor Hub, Kolkata, India, Department of Science and Technology and Council of Scientific and Industrial Research, India.

References

[1] N. Bhattacharyya, R. Bandyopadhyay, M. Bhuyan, B. Tudu, D. Ghosh and A. Jana, Electronic Nose for Black Tea Classification and Correlation of Measurements With 'Tea Taster' Marks. *IEEE trans. Instrum. And Meas.*, vol. 57, no. 7, pp. 1313-1321, (2008); doi: 10.1109/TIM.2008.917189

[2] www. tocklai.net

[3] C. A. Papadopoulos, D. S. Vlachos, J. N. Avaritsiotis, *Sensors and Actuators B* Vol. 42, no. 2, 95-101 (1997); doi : 10.1016/S0925-4005(97)00190-1

[4] Renu Rawat, Ashu Gulati, G.D. Kiran Babu, Ruchi Acharya, Vijay .K. Kaul, Bikram Singh, Characterization of volatile components of Kangra orthodox tea by gas chromatography-mass spectrometry, *Food Chemistry* 105, 229-235 (2007); doi : 10.1016/j.foodchem.2007.03.071

[5] Dae-Sik Lee, Duk-Dong Lee, Sang-Woo Ban, Minho Lee, and Youn Tae Kim. SnO_2 Gas Sensing Array for Combustible and Explosive Gas Leakage Recognition, *IEEE sensors journal*, vol. 2, no. 3, (2002); doi : 10.1109/JSEN.2002.800685.