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Development of a quartz crystal microbalance sensor array for discrimination of black tea

Prolay Sharma[1], Arunangshu Ghosh[1], Bipan Tudu[1], Rajib Bandyopadhyay [1], Nabarun Bhattacharyya[2], Anutosh Chatterjee[1]
[1]Dept. of Instrumentation and Electronics Engineering, Jadavpur University, Kolkata- 700098, India,
[2]Centre for Development of Advanced Computing, Kolkata-700 091, India.

Abstract:

Evaluation of aroma quality of tea and its classification is extremely critical from the commercial point of view. The most widely practised method for evaluating the quality of tea is by human sensory panel, called "Tea Tasters". But this method is very subjective and its accuracy is also uncertain. For this reason various instrumental setups have been investigated in recent times. Electronic Nose is one such device which has been implemented for tea quality evaluation. An electronic nose with an array of quartz crystal microbalance (QCM) sensors has been developed to differentiate among different tea samples. The important volatile organic components (VOC) responsible for aroma of tea have been considered and the corresponding sensing materials have been identified. Five AT-cut 10 MHz Quartz crystal blanks coated with different sensing materials have been used to differentiate the aroma of orthodox and CTC (cut-tear-curl) tea samples. The developed sensors can distinguish not only between the orthodox and CTC tea but distinct clusters are also obtained for the four different tea-samples, as visualized through principal component analysis (PCA) and by ICA in conjunction with LDA. Comparison of these two techniques is presented by Dunn's indices. Back-propagation multilayer perceptron (BPMLP) classifier has also been used along with 10-fold cross validation technique for classification of data.

Key words: QCM, Orthodox, CTC, PCA, BPMLP.

Introduction

The aroma of food like fruits, vegeTable-s and tea is an important indicator about their quality. Aroma of food is determined by contribution of many organic compounds. It is therefore a complicated task to develop sensors for each of the contributing VOCs. In an array based approach, the sensors are exposed to the aroma headspace and their overlapping and composite response pattern generates a fingerprint. This fingerprint can be analyzed using multivariate data processing methods to obtain qualitative information about the aroma. Such a device in addition with soft-computing modules is commercially known as an "electronic nose". Most of the literature reported the use of an array of broadly selective metal oxide semiconductor (MOS) sensors in electronic nose for quality assessment of agro products including tea. Commercially available MOS sensors are needed to be operated at elevated temperatures and their performances are limited by the presence of moisture that affects the baseline values of the sensors. Most importantly they exhibit low selectivity towards aroma producing compounds in tea. To overcome these problems, QCM based electronic nose has been explored. QCM sensors are made of a thin plate of quartz crystal blanks with metal electrodes on each side. When an alternating electrical excitation is applied to the electrodes, the deformation and relaxation of crystal faces occurs at natural resonant frequency depends on the crystal dimensions, physical parameters and type of crystal cut. QCM sensors are frequently used as they can be easily fabricated, have fast response and recovery characteristics and can be coated with a variety of materials to obtain different sensitivities and selectivities. For sensing applications, QCM sensors are coated with appropriate analyte-sensitive coating. The target analyte is adsorbed on coating surface increasing the mass of QCM sensors, results in a change in its resonance frequency. According to Sauerbrey equation [1] the QCM resonance frequency decreases linearly on the adsorbed mass. The target gases with different molecular weights can be detected in terms of different frequency deviations. In other words, for different VOCs, the differences in values of deviations in resonance frequency can indicate the selectivity of sensors and the magnitude of deviations will indicate the sensitivity. Array of QCM sensors have been successfully utilized in a range of electronic nose systems for agro products such as orange [2], melon [3], apple [3-4] and banana [5] etc. In this paper, we investigate the development of an array of QCM sensors to differentiate the odour of black tea.

Experimental

Major chemical compounds responsible for flavour in tea are reported in [6] and are listed in Table-1.

Tab. 1: Major tea chemicals responsible for flavour in black tea.

Compounds	Flavour
Linalool, Linalool oxide	Sweet
Geraniol, Phenylacetaldehyde	Floral
Nerolidol, Benzaldehyde, Methyl salicylate, Phenyl ethanol	Fruity
Trans-2-Hexenal, n-Hexanal, Cis-3-Hexenol	Grassy
Beta-ionone	Fresh flavour

The sensor array is consists of five sensors. These sensors were coated with D-Glucose (Glu), Adenine (Ad), Polyethylene glycol (PEG), D-Phenylalanine (D-Phy) and Ethyl cellulose (EC) targeting three significant volatiles of black tea [6] aroma i.e. Linalool, Geraniol and Trans-2-Hexenal. Adenine and D-Phenylalanine are amino acids, Polyethylene glycol is a gas chromatography-stationary phase material and Ethyl cellulose is a polymer. These materials are selected as they are extensively used for study of odour components founds in different fruits, that containing significant amount of Linalool, Geraniol and Trans-2-Hexenal [2-4][7]. Solutions of these materials with appropriate solvents (Table-2) have been prepared and deposited on the silver electrodes of QCM (10 MHz, AT-Cut) using Electrostatic spraying methods [8]. In electrostatic spray method, a solution of sensor-active material is loaded into a glass syringe. A high DC voltage of about 18kV is applied between the needle and the electrode of the QCM. The high electric field at the tip of needle spreads out the droplets in a form of finely divided spray, yielding a uniform coating. All five QCM sensors are prepared with the average loadings of 3 kHz.

The array of QCM sensors are placed in a small sensor chamber (490 ml) as shown in Fig. 1. A suction pump attached to sensor chamber sucks the tea aroma for sampling and fresh air (selected by the selector switch) for purging. The oscillation frequencies of the crystals has been generated by IC 8284 and the sensor responses have been monitored online through PCI-6602; NI DAQ card.

The conditions under which experimentation has been done are listed below:

- Volume of sensor chamber: 490 ml.
- Air flow rate: 4L/min.
- Amount of dry tea sample: 15 gm.
- Sampling duration: 30 sec.
- Purging time : 3 min.

Samples

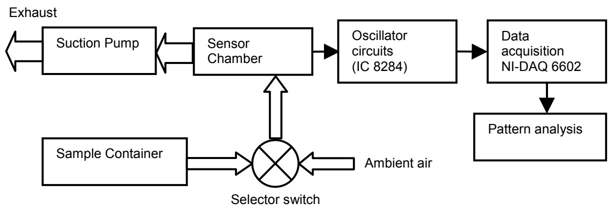
Orthodox is mainly known for its aroma and CTC for its liquor quality. Samples of two types of tea have been collected from market as listed below:

1) CTC of market price INR 300 (denoted as CTC 300).
2) CTC of market price INR 500 (denoted as CTC 500).
3) Orthodox of market price INR 500 (denoted as Orthodox 500).
4) Orthodox of market price INR 1000 (denoted as Orthodox 1000).

Each type has been subjected to experimentation and 20 experimental values for every type have been recorded.

Tab. 2: List of coating materials their solvents and concentrations used for the preparation of five sensors.

Coating materials	Solvent	Concentration
D-Glucose	Millipore water	0.5% w/v
Adenine	DMSO	0.5% w/v
Polyethylene glycol	Chloroform	0.17% w/v
D-Phenylalanine	Millipore water	0.5% w/v
Ethyl cellulose	Tetrahydrofuran	1% w/v



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Results and Discussions

Data has been collected over four different tea samples. Each tea sample has been presented for five times and exposed for four repeated sniffs to all five sensors. Thus a data set of size 80 (4 tea samples x 5 replenishments x 4 repeated sampling) x 5(sensors) is obtained. Fig. 2 depicts the time series response of each of five sensors. The adsorption of target gases is manifested in terms of reduction in resonant frequency due to mass loadings on analyte coatings. The purging duration of 3 minutes ensures recovery of sensor baselines on application of clean air. The characteristics of sensor coated with polar chemicals e.g D-glucose and polyethylene glycol are most sensitive. This behavior can be explained by the fact that these polar coatings shall have an affinity for alcohols like linalool, geraniol etc that make a significant portion of aroma [6]. The weakly-polar coatings of ethyl cellulose and D-

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phenylalanine is expected to have good affinity for weakly-polar VOCs like trans-2-hexenal, beta-ionone and methyl-salicylate. The composite response of all the sensors will depend on the mixture of different VOCs in the aroma headspace that differs on tea varieties taken.

As a measure of repeatability of sensor responses, the ratio of standard deviation and mean is calculated over 18 observations for each sensor. Fig. 3 presents the frequency deviations obtained for PEG sensor. A visual inspection will reveal that, the variations among sensor responses are not very significant. Table-3 presents the relative percentage standard deviations with respect to mean, which is below 10% for all the sensors. The repeatability of D-Phy and EC sensors are not very good due to lower value of mean response obtained, however the absolute standard deviation for these sensors are below 1.0.

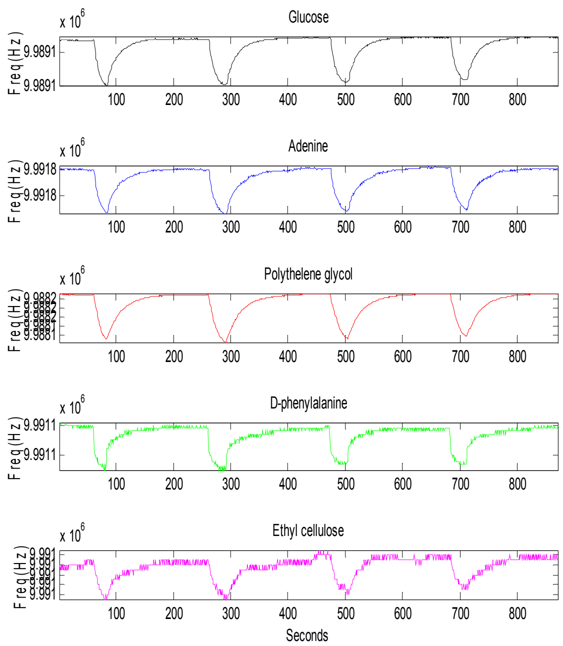

Figure- 2. Sensor response of five sensors for four repeated sniffs.

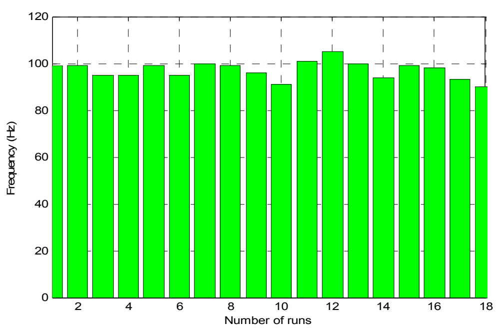

Figure- 3. Response of polyethylene glycol coated QCM sensor for a given tea sample.

Tab. 3: Percentage ratio of standard deviation and mean response of each sensor.

D-Glu	Ad	PEG	D-Phy	EC
3.69 %	5.35 %	3.88 %	7.74 %	9.43 %

The composite responses of all five sensors are presented in Figure-4. It can be seen that distinct response patterns are obtained for each type of tea samples. The composite responses can be subjected to multivariate analysis for extraction of qualitative information about tea aroma. Principal component analysis (PCA) plot of response space is present in Figure- 5. Most of the information is contained in PC1, PC2 and PC3 axes with variances of 95.3%, 2.6% and 1.4% respectively. The round (o) and asterisk (*) markers indicating orthodox tea are separated from the CTC tea responses.

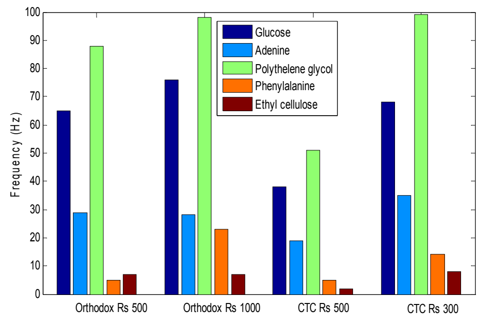

Figure- 4. Response pattern of developed sensors for different tea samples.

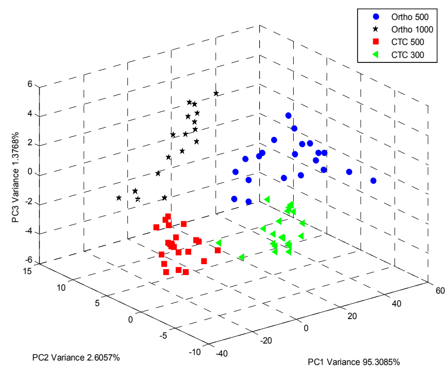

Figure- 5. The PCA plots of sensor responses show distinct clusters for orthodox and CTC tea samples.

The composite sensor responses are again subject to ICA in conjunction with LDA. The response plot is presented in Figure- 6. It can be seen that distinct response patterns are obtained for each type of tea samples. Triangle (Δ) and asterisk (*) markers indicating orthodox tea are separated from the CTC tea responses.The efficacy of cluster formation of the combination of ICA and LDA over PCA has been presented by Dunn’s indices in Table-4. It was observed that indices were subsequently improved for the combination plot of ICA and LDA over PCA.

Tab.4 Value of Dunn's Index for PCA and combination plot of ICA and LDA

Data set	Dunn's Index
PCA	0.2037
ICA in conjunction with LDA	0.5338

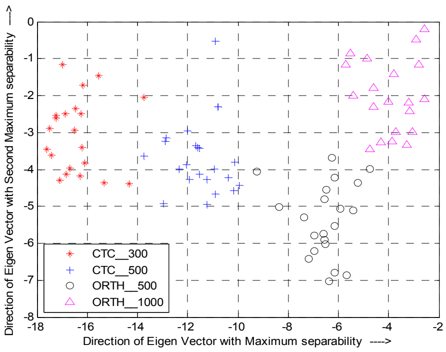

Figure- 7. Result as obtained after transformation of the raw data by ICA in conjunction with LDA.

A BPMLP network is used for classification of the sensor response. The network consists of three sensory units - one input layer with five neurons, two hidden layers with five neurons in each layer and one output layer with a single neuron. The neurons of the hidden layer use transfer function 'Tan-Sigmoid' and the network has been trained with the Levenberg-Marquardt back propagation model. A 10-fold cross-validation method has been used for the purpose of training and testing of network. Results obtained are shown in Table-5. The cross validation method gives an average classification of 92.5% over the entire data set, but the standard deviation of 12.07% is due to small size of data set.

Tab. 5: Results for 10 fold validation test for data patterned from E-nose system

Fold	Number of Data: Training/Test	Data Misclassified	Classification rate (%)
1	72/8	2	75
2	72/8	2	75
3	72/8	2	75
4	72/8	0	100
5	72/8	0	100
6	72/8	0	100
7	72/8	0	100
8	72/8	0	100
9	72/8	0	100
10	72/8	0	100
Total number of data misclassified		6	
Average Classification Rate			92.50 %
Standard deviation			12.07 %

Conclusion

The development of an array of QCM sensors for discrimination of two major types of tea aroma (orthodox and CTC) has been explored. The results indicate that the developed sensors have significant sensitivity to tea aroma and reproducibility is good enough. The sensors can not only distinguish between the orthodox and CTC tea samples but also among all the presented tea samples, as indicated by formation of distinct clusters. The composite response of the sensors coupled with suiTable-data analysis techniques can be used for rapid quality analysis of tea aroma. However further research is required to improve the sensitivity, selectivity and life of sensors.

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