2022
9(2), 120-124

Journal of MATERIALS NANOSCIENCE

Detection of Geraniol in Palmarosa Essential oil using Silicone Sealant as molecularly imprinted polymer in a QCM sensor

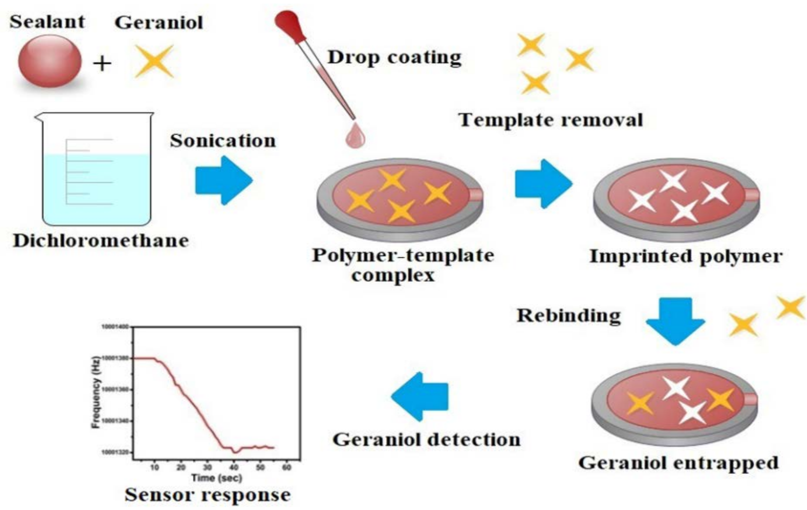
Swatilekha Roy[1], Shreya Nag[1], Mahuya Bhattacharyya Banerjee[1], Samhita Dasgupta[1], Panchanan Pramanik[2], Rajib Bandyopadhyay[1*]

[1]Department of Instrumentation and Electronics Engineering, Jadavpur University, Salt Lake Campus, Plot No.8, LB Block, Sector III, Salt Lake, Kolkata, 700106 India. [2]Department of Chemistry and Nanoscience, GLA University, Mathura, 281406 India.

Submitted on: 17-Nov-2021, Accepted and Published on: 15-Feb-2022 Article

ABSTRACT

Geraniol is a commercially significant terpene alcohol found in the essential oils of a variety of aromatic plants. It is one of the most important molecules in the flavor and fragrance industries, and a common ingredient in consumer products. In order to detect geraniol in real samples, silicone sealant, a readily available commercial product, was used as the polymer to prepare a molecularly imprinted polymer (MIP) based quartz crystal microbalance (QCM) sensor and is presented in this paper. Optimum ratio of sealant was dissolved in dichloromethane and then geraniol was added as the template molecule to synthesize the coating material of the sensor. The surface of the QCM with silver electrode was modified using the synthesized MIP solution by the drop coating method. The developed sensor showed reasonably good sensitivity and selectivity to geraniol and was employed to detect the concentration of geraniol at ppm level in different palmarosa essential oil samples. Good correlation was obtained with the responses from gas chromatography.



Keywords: Geraniol, Molecular imprinting, Quartz crystal microbalance (QCM), Sealant Polymer, Portable QCM Device

INTRODUCTION

Palmarosa oil is extensively used for its preventing and inhibiting properties of both bacterial and viral infections,[1,2] aiding in digestion, fighting depression[3] and anxiety, boosting respiratory system, and reducing fever. Geraniol is a key component of palmarosa essential oil. It is extensively used in the flavor and fragrance industries and is a common ingredient in consumer products produced by these industries.[4] In addition to its pleasant odor, geraniol is known to exhibit insecticidal and repellent properties[5] and used as a natural pest control agent exhibiting low toxicity. Geraniol has been suggested to represent a new class of chemoprevention agents for cancer.[6] Other biological activities such as antimicrobial, anti-oxidant, anti-inflammatory and some vascular effects have also been reported in different literatures. So, it is very important to detect geraniol using an accurate and cost-effective method.

The conventional assay technologies for the analysis of volatile organic compounds using high end analytical instruments i.e., Gas Chromatography Mass spectrometry (GC-MS) have high sensitivity and selectivity, but they are costly and cannot be tailored for real time analysis. Hence, there is a practical demand for low-cost, low-power and portable device for VOC detection.[7–9] Apart from GC-MS, other promising sensor technologies are metal oxide semiconductor (MOS) sensors,[10] optical waveguides, acoustic oscillator device, chemically sensitive field effect transistor (FET) and different metal nanoparticle interfaces.[11–17] Recently polymer materials are surging as effective coating materials on quartz crystal microbalance (QCM) sensors, where QCMs are modified to detect volatile organic compounds,[18] heavy metal ions,[19] water vapor,[20] and other organic compounds.[21] Different polymers in

*Corresponding Author: Prof. Rajib Bandyopadhyay
Department of Instrumentation and Electronics Engineering, Jadavpur University, Salt Lake Campus, Plot No.8, LB Block, Sector III, Salt Lake, Kolkata, India, PIN - 700106.
Tel: 9331038954
Email: bandyopadhyay.rajib@gmail.com

URN:NBN:sciencein.jmns.2022.v9 305

ISSN:2394-0867
http://pubs.thesciencein.org/jmns

the polymethylemethacrylic group, chloromethane siloxane group and poly-aniline composites are, in general, used for the QCM based sensors. Molecularly Imprinted Polymer (MIP) is a designed material that can be explained in analogy with the "lock and key model".[22] The MIPs have many cavities that are complementary to their template molecules in shape, size, and chemical functionality, giving them a distinct and predetermined selectivity toward those target molecules.[22] MIP research has received a lot of attention due to their advantages such as simple and convenient preparation, predetermined selectivity, robustness in organic solvents, acidic or basic reagents, and high temperature durability.[23]

There are many earlier work reports related to detection of geraniol in different commercially available products. Detection of geraniol was carried out previously by patch test or β-cyclodextrin as the sensing material on Quartz Crystal Microbalance (QCM) platform.[7]

We have developed MIP coated QCM sensor using commercially available Silicone sealant as the polymer and geraniol as template. The presence of geraniol has been detected using a low cost portable QCM sensor device.[24] For the measurement, initially we have calibrated the sensor with standard geraniol and then applied it on the real samples. The integration of a MIP-based QCM sensor in a portable gas sensing device that can be modified to get a dedicated system for quick measurement of the target analyte in real samples is a novel feature of our work.

Experimental Details

A. Materials and Standards

Silicone sealant was purchased from Dow Corning and geraniol [$C_{10}H_{18}O$], dichloromethane [CH_2Cl_2], chloroform [$CHCl_3$] and ethanol [C_2H_5OH] were purchased from Merck.

B. Polymer Optimization

A set of ten sensors have been prepared with different ratios of sealant as polymer with four solvents viz. acetone, chloroform, ethanol and dichloromethane. The response of these sensors has been observed for a fixed concentration of geraniol vapor to choose the most suitable polymer-solvent combination.

C. MIP Synthesis and Sensor fabrication

The optimum ratio of sealant was dissolved in dichloromethane for the synthesis of MIP solution. The template molecule, geraniol, was added to the solution after the sealant was completely dissolved in dichloromethane. The solution is then sonicated for half an hour to prepare the final solution with which the surface of the QCM has been coated.

We have used mass-sensitive quartz crystal microbalance (QCM) with the fundamental resonance frequency of 10 MHz as the transducer. QCM surfaces were cleaned with pure ethanol solution before the experiment. The coating on the surface of the QCM was carried out by drop casting method. The polymerization conditions were optimized to obtain a stable and highly selective polymer network. The MIP coated QCM was then dipped into the ethanol solution for 15-20 minutes to remove the template. The non-imprinted polymer (NIP) film was prepared in the same manner as that of the MIP film except the addition of the template.

D. Instrumentation

In this experiment, we have used the low cost portable QCM sensor device developed in our lab.[24] Figure 1 shows the block diagram of the sensing interface. The target molecule vapor at different concentrations was injected in the sensor chamber using a syringe pump so that maximum impact in a short period of time could be achieved. The frequencies were recorded before and after the injection once the sensor reached to equilibrium.

After use, the QCM sensors were dipped into ethanol for 15-20 minutes for purging, so that they can be reused.

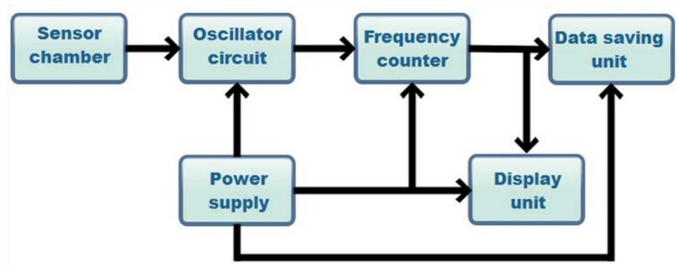


Figure 1. Block Diagram of portable gas sensing device

E. Geraniol Vapor Generation

Geraniol vapor was generated by keeping the chemical in liquid form in a 10L desiccator. Different amounts of the analytes were kept in order to generate various concentrations of geraniol vapor. Each sample was incubated in the desiccator for almost 24 hours, so that the chemical was completely evaporated to generate the aroma headspace. 1mL to 50mL glass syringes were used to draw the vapor of the aroma from the desiccator and injected into the sensor chamber. The concentration has been calculated using equation (1) where V_{SC} and V_{Syr} imply volume of the sensor chamber and syringe respectively, whereas, S_{SC} and S_{Syr} are the gas concentration of sensor chamber and syringe respectively.

$$V_{SC} \times S_{SC} = V_{Syr} \times S_{Syr} \qquad (1)$$

F. MIP Coating Thickness

The MIP coating thickness is optimized in terms of initial frequency shift of the QCM and after template removal from the MIP.[25] To standardize the thickness, at least six QCM sensors were fabricated in different batches by varying the mass deposition and consecutive frequency deviation of the sensor is noted.

Results and Discussions

Table 1 demonstrates different compositions of solvents and sealant. Ten sensors were prepared by varying the ratios of acetone, ethanol, chloroform and dichloromethane with fixed amount of sealant labeled as S1 to S10. These sensors were exposed to 100 ppm of geraniol vapor.

A. MIP Optimization

Table 1: Different compositions of sealant and solvents

Sample Id	Solvent	Amount of solvent (in mL) used to dissolve 0.1 gm Sealant
S1	Acetone	25
S2	Acetone	15
S3	Ethanol	25
S4	Dichloromethane	25
S5	Dichloromethane	10
S6	Dichloromethane	15
S7	Dichloromethane	20
S8	Dichloromethane	25
S9	Chloroform	15
S10	Chloroform	25

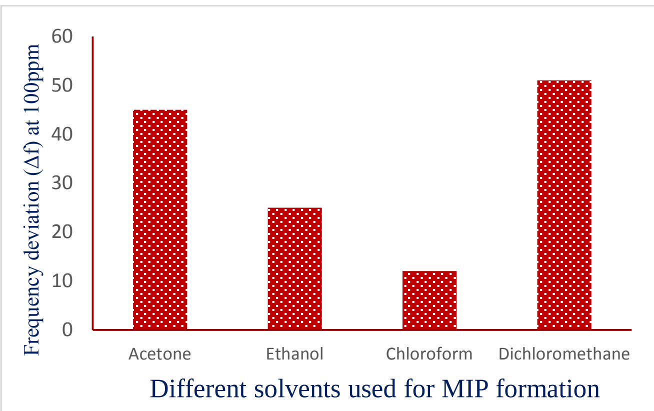


Figure 2. MIP optimization plot at 100ppm

B. Coating Thickness optimization

The optimization of the coating thickness is shown in Figure.3. Here, the coating thickness is measured in terms of frequency deviation caused by different mass deposition on the QCM surface. In Figure 3, molecularly imprinted polymers from 2 to 5 kHz have been shown. The frequency shift has been measured for a fixed concentration of geraniol vapor with increasing coating thickness. The maximum frequency deviation has been obtained for the coating thickness of 3500Hz.

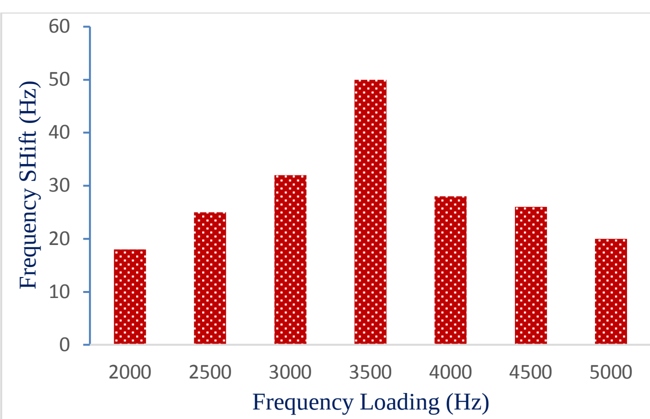


Figure 3. Coating Thickness Optimization

C. Sensitivity Analysis

The study of the sensitivity of the developed sensors under optimum condition was experimented by injecting saturated geraniol vapor into the sensor chamber. The difference between the initial frequency and the stabilized frequency after adsorption was noted to obtain the frequency deviation profile of the sensor. The real time frequency deviation profile of the sensor sample S6 with dichloromethane as solvent and geraniol as template for the concentration of 100 ppm vapor is presented in the Figure.4.

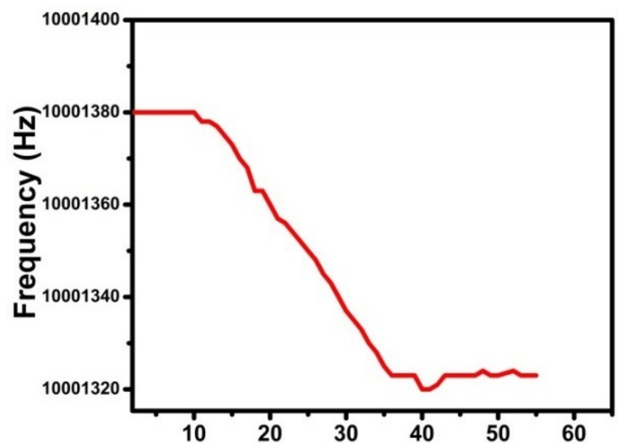


Figure 4. Sensor response (frequency deviation vs time) of S6 when 100 ppm geraniol vapor was introduced

Molar volume and viscosity play important roles here.[26,27] While geraniol molecule can easily penetrate into the film other volatile molecules cannot because of the cavities generated due to molecular imprinting. The calibration curve was acquired for the linear response range from 5 ppm to 200 ppm, by plotting the vapor concentration with the frequency shift. The response curve of S6 sensor with varying concentration of the vapor in the range of 5-200ppm is exhibited in Figure 5. The sensitivity (Hz/ppm) of the sensor towards the target analyte geraniol were calculated from the slope of the calibration graph (Figure.5.).

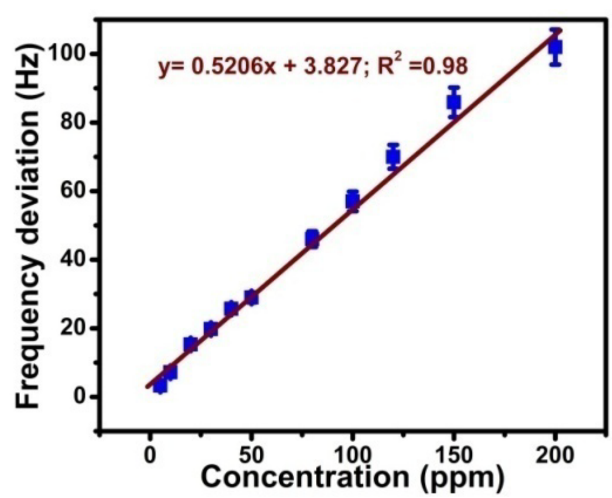


Figure 5. Sensitivity analysis of the QCM sensor

D. Real Sample Analysis

Five different Palmarosa essential oils (PEO-1 to PEO-5)were purchased from local market within one week of experiment; and their GC-MS spectra and consecutive QCM Sensor responses were observed for the samples-MS analysis was carried out using Thermo Fisher Trace 1300 (Thermo scientific, Milan- Italy) connected to a triple quadruple mass spectrometer (Thermo MS-TSQ 9000) with wall coated open tubular column (WCOT), TG-5 MS (30 m × 0.25 mm × 0.25 µm), a 10 m Dura guard capillary column. Table 2 shows percentage peak area of geraniol by GC-MS for five different Palmarosa essential oil samples and their corresponding frequency deviations using the sensor. The geraniol contents in these real samples (PEO-1 to PEO-5) have been measured through GC-MS. The percentage peak areas are different for different samples which infers that the geraniol content of the samples is different. When the sensor responses have been taken for these five samples, the maximum deviation was observed for the PEO-1 sample and the minimum deviation was observed for the PEO-4 sample, which clearly shows that the sensor responses are correlated with the results obtained from GC-MS.

Table 2: Analysis of real samples

Sample Name	GC-MS Spectra %	Deviation in QCM Sensor (Hz)
PEO-1	84%	32
PEO-2	82%	28
PEO-3	72%	20
PEO-4	62%	16
PEO-5	81%	24

E. Comparison of the Proposed Technique with Other Reported Literature

The performance of the proposed technique has been presented in Table 3 by comparing the sensitivity, linear range with the other reported literatures. All the comparisons have been done with different analytical and chromatographic methods.

Table 3: Comparison of proposed work with the previous reports

Material/Method	Linear range (ppm)	Sensitivity (Hz/ppm)	Ref.
QCM-MAL	10-900	0.028	[28]
QCM-D-GLU	10-900	0.16	[28]
QCM-PEG	10-900	0.019	[28]
QCM-PFBBr	10-900	0.002	[29]
β-CD/QCM	10-900	0.48	[7]
Sealant-MIP/QCM	10-200	0.52	This work

Conclusion

Palmarosa oil is extensively used for the preparation of perfumes and the amount of geraniol plays a crucial role in the fragrance. This research work was taken up to develop a low-cost field-deployable sensor for this estimation. Here, molecularly imprinted polymer technology was used on quartz crystal microbalance platform to develop a sensor using a low-cost polymer material – Sealant. The sensitivity of the sensor was obtained as 0.52 Hz/ppm. The correlation with GC-MS results presented in this paper prove the efficacy of the sensor. Thus, this simple, easy to fabricate, reusable sensor integrated with low-cost portable device can be used for field-level quality assessment of commercially available palmarosa essential oil.

Conflict of Interest

Authors declare no conflict of interest.

References and notes

1. K. Lawrence, R. Lawrence, D. Parihar, R. Srivastava, A. Charan. Anioxidant activity of palmarosa essential oil (Cymbopogon martini) grown in north indian plains. *Asian Pacific J. Trop. Dis.* **2012**, 2 (SUPPL2), S888.
2. M.H. Lodhia, K.R. Bhatt, V.S. Thaker. Antibacterial activity of essential oils from palmarosa, evening primrose, lavender and tuberose. *Indian J. Pharm. Sci.* **2009**, 71 (2), 134–136.
3. B.F.M.T. Andrade, C.P. Braga, K.C. dos Santos, et al. Effect of Inhaling Cymbopogon martinii Essential Oil and Geraniol on Serum Biochemistry Parameters and Oxidative Stress in Rats. *Biochem. Res. Int.* **2014**, 2014, 1–7.
4. S.C. Rastogi, S. Heydorn, J.D. Johansen, D.A. Basketter. Fragrance chemicals in domestic and occupational products. *Contact Dermatitis* **2001**, 45 (4), 221–225.
5. D.R. Barnard, R. De Xue. Laboratory evaluation of mosquito repellents against Aedes albopictus, Culex nigripalpus, and Ochlerotatus triseriatus (Diptera: Culicidae). *J. Med. Entomol.* **2004**, 41 (4), 726–730.
6. Y.D. Burke, A.S. Ayoubi, S.R. Werner, et al. Effects of the isoprenoids perillyl alcohol and farnesol on apoptosis biomarkers in pancreatic cancer chemoprevention. *Anticancer Res.* **2002**, 22 (6 A), 3127–3134.
7. P. Sharma, A. Ghosh, B. Tudu, et al. A quartz crystal microbalance sensor for detection of geraniol in black tea. *IEEE Sens. J.* **2015**, 15 (2), 1178–1185.
8. M. Westhoff, P. Litterst, L. Freitag, et al. Ion mobility spectrometry for the detection of volatile organic compounds in exhaled breath of patients with lung cancer: Results of a pilot study. *Thorax* **2009**, 64 (9), 744–748.
9. C.L. Faiola, M.H. Erickson, V.L. Fricaud, B.T. Jobson, T.M. Vanreken. Quantification of biogenic volatile organic compounds with a flame ionization detector using the effective carbon number concept. *Atmos. Meas. Tech.* **2012**, 5 (8), 1911–1923.
10. B.S. Chhikara, R. Kumar, Poonam, P. Bazard, R.S. Varma. Viral infection mitigations using advanced nanomaterials and tools: lessons from SARS-CoV-2 for future prospective interventions. *J. Mater. Nanosci.* **2021**, 8 (2), 64–82.
11. R. Binions, A.J.T. Naik. Metal oxide semiconductor gas sensors in environmental monitoring. *Semicond. Gas Sensors* **2013**, 10 (6), 433–466.
12. C. Zhao, H. Gong, W. Lan, et al. Facile synthesis of SnO2 hierarchical porous nanosheets from graphene oxide sacrificial scaffolds for high-performance gas sensors. *Sensors Actuators, B Chem.* **2018**, 258 (7), 492–500.
13. H. Gong, C. Zhao, F. Wang. On-chip growth of SnO2/ZnO core-shell nanosheet arrays for ethanol detection. *IEEE Electron Device Lett.* **2018**, 39 (7), 1065–1068.
14. K. Inyawilert, A. Wisitsora-At, A. Tuantranont, et al. Ultra-rapid VOCs sensors based on sparked-In2O3 sensing films. *Sensors Actuators, B Chem.* **2014**, 192, 745–754.
15. C. Zhao, W. Lan, H. Gong, et al. Highly sensitive acetone-sensing properties of Pt-decorated CuFe2O4 nanotubes prepared by electrospinning. *Ceram. Int.* **2018**, 44 (3), 2856–2863.
16. A. Mirzaei, S.G. Leonardi, G. Neri. Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceram. Int.* **2016**, 42 (14), 15119–15141.

17. C. Zhao, F. Wang, S. Liu. Structural Transformation of Mo-Doped In2O3 Nanotubes by Electron-Beam Irradiation. *IEEE Trans. Nanotechnol.* **2018**, 17 (4), 705–708.
18. J. Zheng, G. Li, X. Ma, et al. Polyaniline-TiO2 nano-composite-based trimethylamine QCM sensor and its thermal behavior studies. *Sensors Actuators, B Chem.* **2008**, 133 (2), 374–380.
19. N. Horzum, D. Tascioglu, C. Özbek, S. Okur, M.M. Demir. VOC sensors based on a metal oxide nanofibrous membrane/QCM system prepared by electrospinning. *New J. Chem.* **2014**, 38 (12), 5761–5768.
20. Z. Cao, J. Guo, X. Fan, et al. Detection of heavy metal ions in aqueous solution by P(MBTVBC-co-VIM)- coated QCM sensor. *Sensors Actuators, B Chem.* **2011**, 157 (1), 34–41.
21. H.Y. Yoo, S. Bruckenstein. A novel quartz crystal microbalance gas sensor based on porous film coatings. A high sensitivity porous poly(methylmethacrylate) water vapor sensor. *Anal. Chim. Acta* **2013**, 785 (June), 98–103.
22. V.B. Kandimalla, H. Ju. Molecular imprinting: A dynamic technique for diverse applications in analytical chemistry. *Anal. Bioanal. Chem.* **2004**, 380 (4), 587–605.
23. L.I. Andersson. Molecular imprinting for drug bioanalysis: A review on the application of imprinted polymers to solid-phase extraction and binding assay. *J. Chromatogr. B Biomed. Sci. Appl.* **2000**, 739 (1), 163–173.
24. M.B. Banerjee, S.R. Chowdhury, R.B. Roy, et al. Development of a Low-Cost Portable Gas Sensing System Based on Molecularly Imprinted Quartz Crystal Microbalance Sensor for Detection of Eugenol in Clove Oil. *IEEE Trans. Instrum. Meas.* **2021**, 70, 1–10.
25. M. Bhattacharyya Banerjee, S. Pradhan, R. Banerjee Roy, et al. Detection of Benzene and Volatile Aromatic Compounds by Molecularly Imprinted Polymer-Coated Quartz Crystal Microbalance Sensor. *IEEE Sens. J.* **2019**, 19 (3), 885–892.
26. Y. Acikbas, R. Capan, M. Erdogan, L. Bulut, C. Soykan. Optical characterization and swelling behaviour of Langmuir–Blodgett thin films of a novel poly[(Styrene (ST)-co-Glycidyl Methacrylate (GMA)]. *Sensors Actuators, B Chem.* **2017**, 241, 1111–1120.
27. Y. Acikbas, F. Taktak, R. Capan, et al. An optical vapor sensor based on amphiphilic block copolymer langmuir-blodgett films. *IEEE Sens. J.* **2018**, 18 (13), 5313–5320.
28. P. Sharma, A. Ghosh, B. Tudu, et al. Monitoring the fermentation process of black tea using QCM sensor based electronic nose. *Sensors Actuators, B Chem.* **2015**, 219, 146–157.
29. N. Debabhuti, S.B. Ali, B. Ghatak, et al. Development of a QCM sensor for detection of trans-2-hexenal in tomatoes. *2016 Int. Conf. Intell. Control. Power Instrumentation, ICICPI 2016* **2017**, 93–97.