Development of QCM Gas Sensors for the Detection of Important Volatile Organic Compounds from Indian Cardamoms

Thesis Submitted By

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2022

Abstract

Cardamom is a well-known spice worldwide due to its flavour, aroma, various health benefits and culinary uses. Both large and small cardamom is considered costly spices and thus provide significant economic benefits in global trading. India is the leading producer of large cardamom and small cardamom globally and is the largest producer and exporter of small cardamom, significantly impacting the Indian spice industry. Because of the high demand for cardamom in the international market, the quality of the spice must be as high as possible, and proper analytical gradation of spices can result in improved export chances, consumer appeal, and financial benefit to the producers. However, there is a severe deficiency of appropriate post-harvest practices and quality evaluation of cardamom in India, where post-harvest production primarily relies on ancient procedures with little contemporary technological input. Since cardamom is highly aromatic, the volatile organic compound (VOCs) and semi-VOCs profile of spices are essential aspects of consumer's perception and can be considered an appropriate benchmark to assess quality. Quartz crystal microbalance (QCM) is a valuable gas sensor detecting VOCs in multiple aromatic products. QCM sensors offer reliable, accurate time detection of VOCs because of their specificity, sensitivity, high accuracy, stability, and repeatability. This thesis reported VOCs of 24 (21 large; 3 small) cardamoms samples using Solid Phase Micro Extraction guided Gas Chromatography-Mass Spectrometry (GC-MS) based analysis. Following this, four QCM sensors were prepared to detect the significant volatiles influencing the aroma of large and small cardamom, **i.e., α-pinene, β-pinene, 1,8-cineole and α-terpinyl acetate**. A portable instrument has been developed to identify the VOCs using QCM sensors. The system is comprised of an 8284A oscillation circuit, a Teensy 3.2-based counter module, and a Raspberry Pi 4 with a 7-inch touch display for data monitoring and control. A customized Python-based graphical user interface was designed to facilitate the recording and storing of sensor data. For the detection of **β-pinene a QCM sensor was with the olive (OLV-QCM) oil to detect this marker VOC β-pinene**, in Indian cardamom. The developed sensor shows high sensitivity towards β-pinene with a sensitivity of 0.3105 Hz/ ppm with R^2 = 0.9979 for volatile concentration ranging between 10-1000 ppm. Furthermore, the sensor is adequately selective towards β-pinene in the presence of other dominant VOCs present in the cardamoms. The average reproducibility and repeatability of the OLV-QCM sensor have

been calculated to be 93% and 95.14% within a 95% confidence interval. Similarly, **QCM sensor coated with rice bran oil was developed for the detection of α-pinene.** The sensor showed sensitivity measuring 0.367 Hz/ppm and having an R^2 of 0.9976. Furthermore, even in the presence of other main VOCs present in cardamom, the sensor is adequately selective for α-pinene. Again, at 67.7 %RH, the developed sensor exhibits quick recovery, long-term stability, short-term stability, little humidity impact, and 95.91% average repeatability. Following that, **a modified castor oil-coated QCM (phenolated phenyl ricinoleate by derivatization) sensor was developed to identify 1,8-cineole in cardamom.** The designed sensor showed high sensitivity to 1,8-cineole, as indicated by its sensitivity of 0.262 Hz/ppm and its R^2 value of 0.9964. In addition, the sensor has acceptable selectivity for 1,8-cineole. The GC-MS was used for validation for twenty-one large cardamom samples, and the findings indicated a correlation of 0.98 with the 1,8-cineole peak areas of the chromatogram. Moreover, a mathematical model has been formulated to predict the 1,8-cineole content from the samples using the developed sensor responses. The results showed an accuracy of 89.09% in predicting the 1,8-cineole content from the samples. Finally, **molecularly imprinted polymer (MIP) based QCM gas sensor was fabricated to detect α-terpinyl acetate in cardamom.** The sensor shows high responsive towards aTA with sensitivity of 0.3876 Hz/ppm. The average repeatability and reproducibility of the sensor are obtained as 94.72% and 93.76%, respectively. In all cases, structure and surface morphology of the sensor responses were analyzed by Fourier Transform Infra-Red (FTIR) spectroscope, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) and in each cases the sensor responses were tested with GCMS estimate of natural cardamom samples. Therefore, it is concluded that these developed QCM sensors which are user-friendly, portable and cost-effective can be used by gradual modification for quality assurance of large and small cardamom of our country in near future.