QCM-based Sensor for the Determination of Mango Ripeness

Fathi Nashrullah

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by

Fathi Nashrullah
(0830210301)

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Author's full name	:	FATHI NASHRULLAH
Date of birth	:	30 JANUARY 1985
Title	:	QCM-BASED SENSOR FOR THE DETERMINATION OF MANGO RIPENESS
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Sensor berasaskan QCM untuk penentuan masaknya buah

ABSTRAK

Tesis ini membentangkan kaedah baru dalam menentukan peringkat kematangan buah menggunakan hidung elektronik yang berasaskan hablur kuarza mikroneraca (QCM). Untuk QCM mengesan wap organik secara terpilih, lapisan nipis penderiaan perlu disalutkan di permukaannya. Sensor QCM yang digunakan dalam penyelidikan ini disalut dengan beberapa jenis polimer menggunakan teknik salutan spin. Polimer-polimer ini memiliki gerak balas bertindih apabila berinteraksi dengan analit (sampel). Dengan menggabungkan beberapa jenis lapisan penderiaan dalam satu tatasusunan, satu profil dari isyarat setiap QCM dapat diperoleh dari sampel. Sifat daripada QCM yang digunakan adalah tidak mengesan secara selektif setiap komponen, tetapi dapat dimanfaatkan dalam penentuan tahap kematangan buah. Buah klimakterik membebaskan amaun zat meruap yang tinggi semasa proses masak. Zat meruap dikumpulkan di dalam bekas sebelum didedah kepada QCM dan akan berinteraksi dengan lapisan penderian di permukaan QCM. Lapisan penderian ini akan menjerap zat meruap dan akan menghasilkan perubahan sedikit pada jisim QCM, seterusnya persamaaan akan membuat anjakan di titik resonan. Dengan mengetahui anjakan frekuensi alunan daripada QCM, jisim bahan terjerap boleh ditentukan. Jumlah zat meruap yang terjerap bergantung kepada interaksi molekul dengan lapisan penderiaan. Jumlah zat meruap sendiri berhubung kait secara langsung kepada tahap kematangan buah-buahan. Dengan mengukur anjakan dari frekuensi QCM itu, tahap kematangan boleh ditentukan. Kerja-kerja penyelidikan telah dibahagikan kepada tiga bahagian. Pertama adalah pembangunan peranti pengesan QCM. Pembangunan ini meliputi penyediaan pengesan QCM, iaitu bahan penderiaan, dan reka bentuk dan pembangunan litar elektronik. Bahagian kedua ialah eksperimen. Kerana QCM adalah pengesan wap, maka buah-buahan klimakterik iaitu mangga dari kultivar Raja dan Namdokmai dipilih sebagai sampel untuk memperoleh aroma mereka. Buah-buahan ini dipantau selama 7 hari. Bahagian ketiga ialah analisis data. Dalam bahagian ini, data dari pemerhatian dianalisis dengan menggunakan plot sederhana dan analisis multivariat. Plot sederhana tidak dapat membezakan dataset secara sepenuhnya. Dengan menggunakan analisis multivariat, iaitu PCA dan LDA, dataset dari hari yang berbeza dapat didiskriminasi dengan betul. Untuk meningkatkan pengkelasan data, pencantuman dari pengesan QCM dan pengesan kepadatan berasaskan akustik telah dilakukan. Dengan cara ini, kualiti pengesan QCM dapat ditingkatkan.

QCM-based sensor for determination of fruit ripeness

ABSTRACT

This thesis presents a new method for fruit maturity stage determination using electronic nose based on Quartz Crystal Microbalance (QCM) which is well known for gas sensing. To allow the QCM selectively detect volatiles, a thin sensing layer has to be coated on its surface with several polymers using spin coating technique. These polymers have overlapping selectivity that interacts with analytes (samples). By combining different kinds of sensing layers for array QCM, each QCM has some response to the samples to give samples profile instead of selectively detect each component from the samples. This QCM characteristic is used to determine fruit maturity level. A climacteric fruit release an elevated amount of volatiles during ripening. These volatiles are contained and accumulated in a container before being exposed to the array of QCMs. The volatiles will be adsorbed at the sensing layer of the QCMs causing a slight mass change and thus a shift in its resonant frequency. From the value of this shift, the mass of the adsorbed materials could be determined. The amount of adsorbed volatiles depend on its molecular interaction with the sensing layer and are directly correlated to the fruit maturity level. The study is divided into three parts. The first one is the development of the QCM sensor device. This development covers the QCM sensor preparation; that is selecting suitable sensing materials, and design and development of electronic circuitry. Secondly is the data collection. Raja and the Namdokmai cultivars of mango were chosen. The fruits ripening process are observed for 6 days. Finally is the data analysis. In this part, the data from the observation are analyzed by using simple plot and multivariate method. However, simple plot cannot distinguish daily basis datasets completely. By applying multivariate analyses namely PCA and LDA, the datasets from different day of monitoring are discriminated properly. However, the QCM sensor alone is somewhat inadequate for a proper discrimination of the maturity levels. By implementing data fusion with acoustic firmness sensor, better results have been obtained.

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LIST OF ABBREVIATION

AFM	Atomic Force Microscopy
AFS	Acoustic Firmness Sensor
ANOVA	Analysis of Variance
API	Application Programming Interface
BAW	Bulk Acoustic Wave
EC	Ethyl Cellulose
CTAB	N-Cetyl-N,N,N-trimethyl-ammoniumbromide
DOP	Dioctyl Phosphate
FPGA	Field-Programmable Gate Array
GC	Gas Chromatography
IC	Integrated Circuit
LDA	Linear Discriminant Analysis
LW	Lamb Wave
OA	Oleylamine
PC	Personal Computer
PCA	Principal Component Analysis
PDIP	Plastic Dual In-line Package
PEG	Polyethylene Glycol
PQC	Piezoelectric Quartz Crystal
PTFE	Polytetrafluoroethylene
QCM	Quartz Crystal Microbalance
QMB	Quartz Microbalance
SAW	Surface Acoustic Wave
SOP	Standard Operating Procedure
SPSS	Statistical Package for the Social Sciences
STM	Scanning Tunneling Microscopy
THF	Tetrahydrofuran

USB	Universal Serial Bus
VOC	Volatile Organic Compound

CHAPTER 1

INTRODUCTION

1.1 Piezoelectricity Sensors

Piezoelectricity is the charge which accumulates in response to applied mechanical strain in certain solid materials, notably crystals and certain ceramics. The word *piezoelectricity* means electricity as a result of mechanical pressure. It is derived from the Greek *piezo* or *piezein,* which means to squeeze or press, and *electric* or *electron*, which stands for amber, an ancient source of electric charge.

The piezoelectric effect is understood as the linear electromechanical interaction between the mechanical and the electrical state in crystalline materials with no inversion symmetry. The piezoelectric effect is a reversible process. The materials that exhibit direct piezoelectric effect (which is the internal electrical charge generation as a result of a mechanical force) also exhibit the reverse effect. It could generate mechanical force resulting from an applied electrical field. Microphone and speaker is a good example. Both have the exact basic design with differentiation only to optimize its function. Microphone transforms mechanical wave (sound) to electrical field as a result of piezoelectric effect exhibited by the piezoelectric material part of the microphone. The speaker is the opposite of that. The speaker transforms electrical charge to mechanical wave produced by mechanical transformation of the piezoelectric material within the speaker that oscillates in sonic area (audible by human ear).

Piezoelectricity is useful for applications such as the production and detection of sound, generation of high voltages, electronic frequency generation, microbalances and ultrafine focusing of optical assemblies. It is also the basis of numerous scientific instrumental techniques with atomic resolution, the scanning probe microscopies namely Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), etc.

Since the concept of piezoelectricity was discovered, there have been a series of reports concerning the application of piezoelectric sensors, as well as their oscillator circuits. Theoretically, if an appropriate coating material could be found, which is selective to a volatile organic, one could prepare a piezoelectric sensor detecting this particular volatile organic in air (Rong Ni, 2003). Unfortunately, it is almost unrealizable to construct such an entirely selective chemical sensor, for the co-existing compounds would always show some interfering effects. Besides searching for selective coating materials, designing piezoelectric sensor arrays is another important approach to improve the selectivity of gas sensing. The sensor array approach has the same advantage over individual sensors as the multiplexing advantage of measuring a series of sensor responses over the individual sensor measurement. It is possible to accomplish the qualitative and quantitative analysis for multiple components simultaneously. Therefore, a lot of papers about the application of piezoelectric sensor arrays were published (Mecea, 1994). Unfortunately, papers addressed the circuit design for quartz crystal microbalance (QCM) sensor arrays device were very few. The simultaneous involvement of many sensors in the measurement process might cause some special problems associated with the circuit design. For example, it is rather difficult to eliminate the mutual interference among individual oscillators caused by their high working frequencies.

The detection of volatile compounds in atmosphere harmful to human health is an important routine analytical task in environmental monitoring. Besides gas chromatography, optical sensors, metal-oxide semiconductor gas sensors, etc., piezoelectric sensor arrays provide a useful alternative for volatile organic detection which are especially valuable in terms of the possibility to design subminiature, portable and inexpensive devices. In this research, a device with five oscillators and five frequency counters were designed for piezoelectric sensor arrays. Problem of interference is considered none since the circuit oscillators and frequency counters are designed and run independently. In order to work in a stable manner, the QCM sensor device utilizes 2 channel of power source. The first one is 5 V for powering the circuit board and the second on is 12 V for powering a pump. It is possible to make it more lightweight and portable by optimizing the circuit layout and chamber design.

1.2 Quartz Crystal Microbalance

The quartz crystal used in the making of QCM sensor is shown in the Figure 1.1. It is the typical AT-cut crystal used in many digital devices as clock generator. The difference is that the crystal in this experiment utilized gold coated electrodes.

Figure 1.1: A typical QCM crystal.

A quartz crystal sensor typically consists of a thin AT-cut quartz disc with circular electrodes on both sides of the quartz disc. Due to the piezoelectric properties of quartz crystal, a voltage between these electrodes leads to a shear deformation of the quartz crystal. Sauerbrey (1959) introduced a relation between the mass deposition on the quartz surface and the resulting shift in the fundamental oscillation frequency of the quartz crystal. Since then this relation had been widely used for monitoring film thickness and gas concentrations.

By introducing this relation, Sauerbrey developed a new technique of mass measurements. Instead of measuring the tipping angle of a beam balance, or the displacement in case of a spring balance (two techniques used by every existing balance), he used the change in the frequency of a quartz resonator to measure the mass of a film deposited on the quartz resonator surface. Thus, it was possible to detect even 10^{-16} kg, while the commercial analytical microbalances can detect about 10^{-10} kg.

Since Sauerbrey demonstrated that mass can be measured using vibrations and frequency change is related to the mass change, several vibrating systems were developed to measure the mass. The mass measuring principle introduced by Sauerbrey was named Quartz Crystal Microbalance (QCM). It became a largely used instrument for small mass measurements in vacuum, gas and liquid phase.

QCM was used also with one face of the quartz resonator in contact with a liquid. Kanazawa and Gordon (1985) calculated the frequency change when one face of a quartz resonator is in contact with a liquid. The equation derived by Kanazawa and Gordon, supported by dozens of experimental results, revealed that the frequency response of the QCM in contact with a liquid does not only depend on the liquid density, but also on its viscosity. Thus, more and more QCM users came to the idea that QCM is not a real mass sensor and, therefore, it is more appropriate to use the name thickness shear mode (TSM) sensor instead of QCM. By then many terms are used regarding this QCM principle. PQC, QMB, QCM, just to name a few. But Mecea (2006) described thoroughly by comparing Classical Mechanic proposed by Newton and complimentary theory proposed by Einstein and conclude that the QCM is actually a (micro) balance.

1.3 Fruit Ripeness Determination

Fruit maturity or ripeness is a stage of fruit that could be easily determined by a human. By considering the color, firmness, and odor, people usually could distinguish between the mature fruit and the immature one. But these kinds of parameters differ between different kinds of fruit. Even the same fruit from different cultivars have different parameters for its exact maturity. For example, the color of mature Harumanis mango (originated from Indonesia and Malaysia) is different from mature Namdokmai mango (originated from Thailand). A mature Harumanis mango is green while Namdokmai is yellow. In this research work, mango fruit is used as the base sample in studying fruit ripeness, especially Raja and Namdokmai cultivars.

Basically fruit ripeness determination is a simple action for a human. But in term of large scale automation for a large plantation or industry, the determination process will not become simple anymore. An automatic process has to consider several parameters regarding characteristics of mature fruits, its color, firmness, odor, or other related characteristics. These parameters have their unique type of sensors that are able to detect. There are no single sensor, even more no single type of sensor that perfectly able to characterize all kind of fruit maturity level. Therefore scientist and engineers usually develop methods using various sensors in array formation for determining fruit ripeness. The output of sensor array is not a single value, instead the sensor array create profile of the maturity level.

Mango is a climacteric fruit, and important biochemical changes occur during the respiratory climacteric, just before ripening. Most volatile compounds, such as ethylene, terpene alcohols, nor-isoprenoid derivatives, and aromatic alcohols are glycosidically bound, and are liberated during ripening (Sakho et al., 1985). Harvest maturity can affect this process and affect the final flavor/aroma quality of the ripened fruit (Bender et al., 2000). According to Marc Lebrun et al. (2008) a typical mango fruit will emit more than twenty different kinds of volatiles. Some of these volatiles are produced in a significant number and some of them are very small so that unlikely to be detected by common sensors. It is nearly impossible and highly uneconomical to create detectors for each volatile. To overcome this challenge, a sensor device consisted of array QCMs is developed combined with statistical analysis to determine the maturity level of fruits.

1.4 Research Objectives

The objective of this research is to develop electronic nose as a sensor system based on Quartz Crystal Microbalance (QCM) sensor for the detection of the ripeness stage of mango fruit. The sensor system is combined with several statistical analyses to process data acquired by the sensors. In order to achieve the mentioned objective, the following developments or studies had been conducted:

1. To develop QCM sensor device. This includes developing:
    a. Oscillator
    b. Frequency counter
    c. I/O for communication with computer
2. To select suitable sensing materials and study several coating techniques. This includes:

a. Making a solution of sensing materials with suitable concentration.

b. Selecting reproducible coating techniques.

3. To analyze data obtained from the experiments using statistical tools namely Matlab and SPSS.
4. To study and analyze on the performance of the overall sensor system.
5. To study possibilities of complementing The QCM sensing techniques with acoustic sensor and combining the data using low-level data fusion method.

1.5 Thesis Organization

This thesis is consisted of 6 chapters. The first chapter presents general introductory to the overall issue covered by this research. Research objective and thesis organization is presented here as well.

Chapter 2 covers a literature review of this research. The main topics discussed here are the fundamental knowledge of Quartz Crystal Microbalance and its application as a sensor. The fruit ripeness characteristics and the process of how the QCM sensor determines the maturity level is also described in this chapter.

Chapter 3 describes the methodology being used, the overall experiment setup, and the measurement procedure. This includes a brief explanation of the electronic hardware circuitry and the statistical method used to analyze the data. The design and the detail development of the QCM sensor electronic circuitry including the operation of each circuitry such as oscillators, frequency counters, and the controller are also described in this chapter.