Available on-line at www.japt.tpa.usab-tm.ro

Journal of Agroalimentary Processes and Technologies 2009, *15*(2), 310-315

Journal of Agroalimentary Processes and Technologies

Application of piezoelectric sensors in detection of biogenic ammines and meet alteration

Valentin Stremtan, Lavinia Sarbu, Alina Matyas, Iosif Gergen*

Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine Timisoara (BUASVMT), Romania

Abstract

Piezoelectric sensor is a very sensible device to mass variation detection of gaseous or fluidic substances. Because in the process of meet alteration usually gaseous substances as NH3, CO2, H2S, volatile ammines, volatile esters, volatile thiols or thioeters, volatile organic acids are formed, an device with can detect these substances is also capable to detect alteration of primary meet products. In present work a piezoelectric device on the basis of α-quart crystal is tested in detection of volatile substances produced in the process of meet alteration. The sensibility of piezoelectric device to different alteration level of meet and the factor with can influence this sensibility was investigated

Keywords: piezoelectric sensor, quartz crystal microbalance, biogenic amines, QCM200, n-hexan isopropylamine, isobutylamine,

1. Introduction

The rapid expansion of the field of piezoelectric sensing devices, within the larger area of chemical sensors and biosensors, requires improved classification and characterization of relevant concepts and principles [4].

A piezoelectric sensor is a device that responds to changes occurring in its environment with changes of the resonant (fundamental or harmonic) frequency, or wave (phase) speed.

The piezoelectric effect arises when pressure applied to a dielectric material deforms its crystal lattice which causes separation of centers of opposite charges giving rise to dipole moments of molecules [6,15].

Piezoelectricity occurs in crystals with no symmetry centers. If electrical contacts (electrodes, electronconducting metal films) are applied to the sides of a thin slab or rod of a piezoelectric material, current will flow through an external circuit when stress is applied to the crystal. When the stress is released, then the current flows in the opposite direction. The converse piezoelectric effect is experienced when alternating voltage is applied to the attached electrodes. Then, mechanical oscillations occur within the crystal lattice.

These oscillations are stable only at the natural resonant frequency of the crystal. At that frequency, impedance of the crystal to the exciting voltage is low. If the crystal is incorporated into the feedback loop of an oscillator circuit, it becomes the frequency-determining element of the circuit, as its quality factor, *Q*, is very high. The quality factor is inversely proportional to the resonance bandwidth, which makes the precise determination of the resonance frequency possible [14,5].

The resonant frequency primarily depends on thickness of the piezoelectric crystal and the attached layer, on the viscoelastic properties of the crystal and that of the adjacent phase, as determined by the coupling boundary conditions. Mass loading, ambient viscosity, and electric permittivity, compression or extension

---

* Corresponding author: *e-mail address*: igergen@yahoo.com

stresses, local electric fields, charge, film conductivity, and surface tension affect the coupling conditions [3].

The crystal cut determines the mode of oscillations. For instance, the AT-cut quartz crystals, vibrating in a thickness shear mode, are used for the majority of piezoelectric work in analytical chemistry in liquids and gas phase. The oscillation frequency decreases when the crystal is loaded with mass.

Selective surface films can deliberately be applied over the oscillator, such as the quartz crystal, in order to enhance selectivity, i.e., the specific mass response caused by adsorption or absorption of an analyte [6].

A piezoelectric chemical sensor is a piezoelectric oscillator that responds to changes in the chemical composition of its environment with changes of the resonant frequency, or wave speed. Piezoelectric chemical sensors are generally selective surface filmcoated piezoelectric crystal oscillators. The surface film coating boosts selectivity through selective adsorption or absorption.

AT-cut quartz crystals are most commonly used as QCM sensors because of their superior mechanical and piezoelectric properties*1*, and because they can be cut to give nearly zero temperature coefficients at room temperature [5].

Quartz crystal microbalance (QCM) is a thickness-shear-mode acoustic wave mass-sensitive detector based on the effect of an attached foreign mass on the resonant frequency of an oscillating quartz crystal [17,7].

The QCM responds to any interfacial mass change. Initially, QCM has been used as a mass sensor in the vacuum and gas-phase experiments. However, the response of QCM is also extremely sensitive to mass and viscoelastic changes at the solid-solution interface. In order to boost selectivity, selective surface films are applied. In contrast to the inherent oscillator material, such as quartz, these films may suffer, however, changes in their elastic constants by virtue of absorption of ambient substances (e.g., parameters of a deposited palladium surface film change after absorption of hydrogen).

The quartz crystal microbalance is an extremely sensitive sensor capable of measuring mass changes in the nanogram/cm2 range with a wide dynamic range extending into the 100 μg/cm^2 range [19].

Sauerbrey was the first to recognize the potential usefulness of the technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of the QCM electrodes. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

$$\Delta f = -C_f \cdot \Delta m$$

where:
Δf = the observed frequency change in Hz,
Δm = the change in mass per unit area, in g/cm2,
Cf = the sensitivity factor for the crystal (56.6 Hz μg^{-1}cm2 for a 5 MHz crystal at room temperature).

The minimum detectable mass change is typically a few ng/cm2 and limited by the noise specifications of the crystal oscillator and the resolution of the frequency counter used to measure frequency shifts. The Sauerbrey equation relies on a sensitivity factor, Cf, which is a fundamental property of the QCM crystal. Thus, *in theory*, the QCM mass sensor does not require calibration [1].

Biogenic amines represent a group of low-molecular-mass organic bases occu-rring in all organisms. Amines are formed and degraded during normal metabolic processes in living cells and therefore they are ubiquitous in animals, plants, and microorganisms [16].

In foodstuffs, biogenic amines are usually generated by microbial decarboxylation of amino acids.

Thus, from histidine, tyrosine, tryptophane and phenylalanine, monoamines histamine, tyramine, tryptamine and 2-phenylethylamine, respectively, are formed and, similary, diamines putrescine and cadaverine are formed from ornithine and lysine, respectively. Putrescine is a precursor for the formation of polyamines spermidine and spermine [20].

The concentration of produced ammonia was found to be proportional to the concentration of biogenic amine and could hence be used to determination of biogenic amines in food matrixes [21].

2. Materials and Method

2.1. Equipment

The QCM200 system is a stand-alone instrument with a built-in frequency counter and resistance meter. Series resonance frequency and resistance are measured and displayed directly on the front panel without the need for an external frequency counter or precision voltmeter.[16]

The dependence of the frequency change on the mass coverage per unit area, emphasizes the fact that, within certain limits, the sensitivity factor is independent of the electrode geometry. Thus, in theory, the QCM mass sensor does not require calibration for this application. This ability to calculate mass loading from first principles is obviously a very attractive feature of these devices [14].

The apparatus consisted of an AT-cut piezoelectric quartz crystal with a fundamental frequency of 5 MHz, 25,4 mm in diameter and with gold-plated electrodes on both sides.

Crystal thickness is 331 μm as required for fundamental oscillation at 5 MHz, the unperturbed crystals will normally be within ±1,000 ppm of their nominal frequency.

The frequency change was monitored by an QCM200 system attached to a computer system [9,10].

The Quartz Crystal Microbalance consists of two circuits - the QCM25 Crystal Oscillator located in a small enclosure that attaches directly to the crystal holder, and the QCM200 Controller. The QCM25 attaches to the QCM200 via a Cat-5 cable

The QCM25 consists of transformer isolated and gain controlled RF amplifiers which maintain the 5 MHz oscillation of the crystal in the holder. The QCM25 is powered from the QCM200, which also provides the varactor bias to the QCM25 to null the effect of the crystal's static and holder capacitance, allowing the crystal to run at the series resonance frequency.

The 5 MHz signal from the QCM25 is sent differentially to the QCM200 via one twisted pair in the Cat-5 cable, allowing measurement of the crystal's series resonant frequency. An analog voltage, which is proportional to the RF gain in dB required to sustain the crystal's oscillation, is also passed to the QCM200, allowing measurement of t he crystal's motional resistance [18,3].

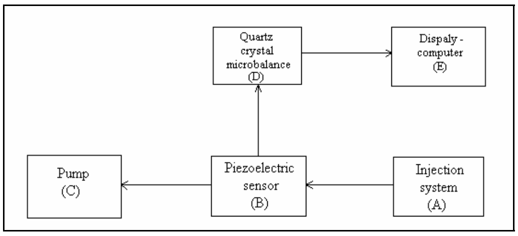

Figure 1. Schematic presentation of the work device

2.2 Work procedure

We have injected 0,05 ml n-Hexan, Isopropylamine and Isobutylamine into the cell injection (A), present in following scheme, below a air supply of 35 ml/min at 5 rotation per minute.

Response of piezoelectric sensor (B) measured of the quartz crystal microbalance (C) and plotted in Figure 1 in μg/cm^2, it is displayed whit a support soft on the computer display (E).

3. Results and discussion

Response of sensor at different tested substances (n-Hexan, Isopropylamine, Isobutiylamine) is presented in table 1 and more suggestive in figure 1-3. In table 1 are present the response of the sensors als peak area. We can observe that for hexan and isopropylamine the response of sensor is quit similar but very different for isobutylamine.

This signify that sensibility of the sensor is equal for hexan and isopropylamine and more high for the isobutylamine

Tabel 1. Area response of piezoelectric cristal to differrent substance

Nr.	Substance	Volume [ml]	Mass [g]	Peak area [sqmm]			Average [sqmm]
1	n-Hexan	0,05	0,033	0,0071	0,0046	0,0055	0,0057
2	Isopropylamine	0,05	0,034	0,0080	0,0050	0,0067	0,0065
3	Isobutiylamine	0,05	0,036	0,0231	0,0205	0,0302	0,0246

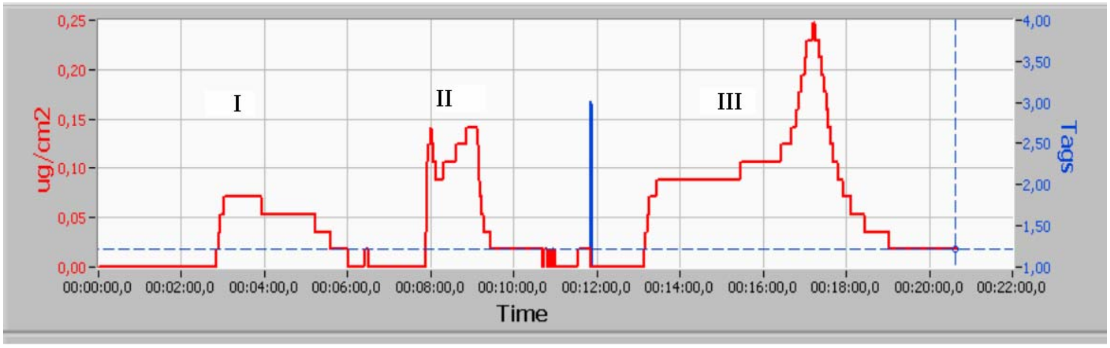

Figure 2. I – n-Hexan , II – Isopropylamine, III – Isobutiylamine

In figures 3-4 are presented the sensor responses for the two meat samples stored in two different conditions. In figure 3 is presented the sensor response for the meat sample stored for one day at room temperature (24 ^{0} C) and in figure 4 for the meat sample stored four day to room temperature. We can observe the big difference between the sensor responses for the two samples. Decomposition processes from sample two (stored for 4 day at room temperature) generate more gaseous substances that in case of sample one (stored for 1 day at room temperature). These results suggests the possibility use of this sensors in presented device to monitoring the alteration of meat samples in the time.

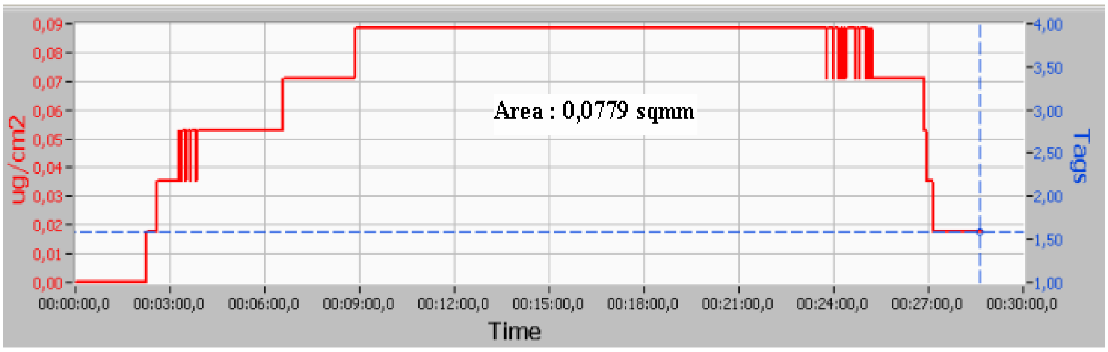

Figure 3. Response area for meat after four day at room temperature

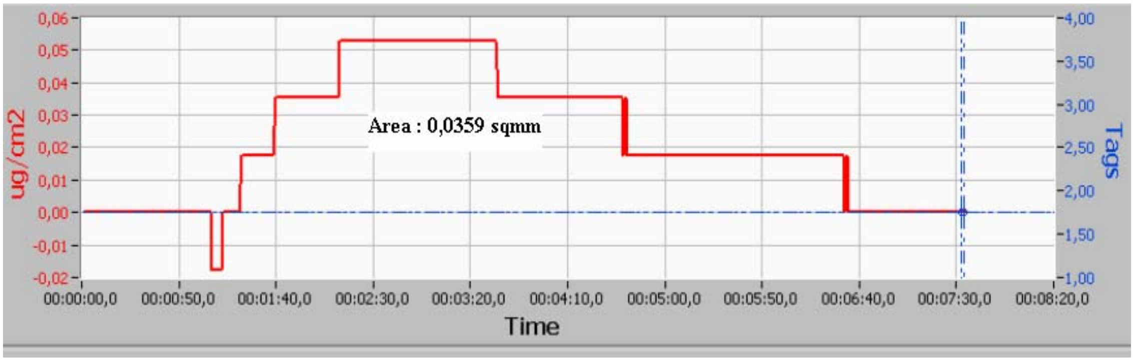

Figure. 4. Response area for meat after a day at room temperature

4.Conclusions

In this study we investigated the sensibility of quartz piezoelectric sensors to n-hexane, isopropylamine, isobutylamine and meat in different alteration stage. For the hexane and isopropylamine the response of the sensor is weakly toward isobutylamine and meat in different stage of alteration when the response of the sensors is highly. The experimental results show that this device is properly to use for investigation the biogenic amines and also the degradation of the meat.

References

1. G. Sauerbrey, Z. Phys. 155 (1959) 206
2. C. Lu and O. Lewis, “Investigation of film-thickness determination by oscillating quartz resonators with large mass load”, J. Appl. Phys. 43 (1972) 4385.
3. D. R. Denison, “Linearity of Heavily Loaded Quartz Crystal Microbalance”, J. Vac. Sci. Technol. 10(1973) 126.
4. C. Lu and A. W. Czanderna. *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, Amsterdam (1984).
5. M. D. Ward and D. A. Buttry. *Science (Washington, D.C.)* **249**, 1000 (1990).
6. P. J. Cumpson and M. P. Seah. *Meas. Sci. Technol.* **1**, 544 (1990).
7. Daniel Buttry, “Applications of the QCM to Electrochemistry”, in A Series of Advances in Electroanalytical Chemistry, edited by Allen Bard, Marcel Dekker, 1991, p. 23-33.
8. C. Gabrielli et. al., “Calibration of the Electrochemical Quartz Crystal Microbalance”, J. Electrochem. Soc. 139(9) (1991) 2657.
9. Michael Ward and Edward J. Delawski, “Radial Mass Sensitivity of the Quartz Crystal Microbalance in Liquid Media”, Anal. Chem. 63(1991) 886.
10. Stephen Martin, Victoria Edwards Granstaff and Gregory C. Frye, “Characterization of a Quartz Crystal Microbalance with Simultaneous Mass and Liquid Loading”, Anal. Chem. 63 (1991) 2272.
11. Celia Henry, “Measuring the masses: Quartz Crystal Microbalances”, Anal. Chem. News and Features, October 1, 1996, p. 626A.
12. R. Lucklum, C. Behling, R. W. Cernosek, S. J. Martin. *J. Phys. D: Appl. Phys.* **30**, 346 (1997)
13. A. D’Amico and E. Verona. *Microfabricated Chem. Sensors Prog. Solid. St. Chem.* **18**, 177 (1998).
14. R.W. Cernosek et. al. “Analysis of the radial dependence of mass sensitivity for modified electrode quartz crystal resonators”, Anal. Chem. 50 (1998) 237.
15. C. K. O’Sullivan and G. G. Guilbault. *Biosens. Bioelectron.* **14**, 663 (1999).
16. Kaniou, I.; Samouris, G.; Mouratidou, T.; Eleftheriadou, A.; Zantopoulos, N. Determination of biogenic amines in fresh unpacked and vacuum-packed beef during storage at 4±°C. *Food Chem.* **2001**, *74*, 515-519.
17. Sasaki, I.; Tshuchiya, H.; Nishioka, M.; Sadakata, M.; Okubo, T. Gas sensing with zeolite-coated quartz crystal microbalances—principal component analysis approach. *Sens. Actutator B: Chem.* **2002**, *86*, 26-33.

18. Scott Grimshaw, “Quartz Crystal Thin-Film Monitoring Forges Ahead”, Photonics Spectra, April 2003,p. 82.
19. Koshets, I.A.; Kazantseva, Z.I.; Shirshov, Y.M.; Cherenok, S.A.; Kalchenko, V.I. Calixarene films as sensitive coating for QCM-based sensors. *Sens. Actutator B: Chem.* **2005**, *106*, 177-181.
20. Chan, S.T.; Yao, M.W.Y.; Wong, Y.C.; Wong, T.; Mok, C.S.; Sin, D.W.M. Evaluation of chemical indicators for monitoring freshness of food and determination of volatile amines in fish by headspace solid-phase microextraction and gas chromatography-mass spectrometry. *Eur. Food Res. Technol.* **2006**, *224*, 67-74.
21. Bota, G. M.; Harrington, P. B. Direct detection of trimethylamine in meat food products using ion mobility spectrometry. *Talanta* **2006**, *68*, 629-635.