SELECTIVITY OF CALIX [6]ARENE-COATED PIEZOELECTRIC QUARTZ CRYSTAL SENSOR FOR THE DETECTION OF SOME ORGANIC AMINE IN GAS FLOW

Iosif GERGEN[1], Despina Maria BORDEAN[1], Monica HARMANESCU[3], Florina RADU[1], Marilena MICLAU[2]

[1]. USAMVB-Faculty of Food Technology, Timisoara, Calea Ardului 119, RO 300645, igergen@yahoo.com
[2]. INCEMC (Institutul National de C-D pentru Electrochimie si Materiale Condensate), Timisoara
3. USAMVB-Agriculture Faculty, Timisoara

Abstract: *In this study, we developed calixarene-coated PQC sensors for the determination of organic amines in gas faze and study the selectivity of this coated sensor for normal and iso- form of propyl and butyl amines. p-tert-Butylcalix[6]arene compound was applied as piezoelectric quartz crystal (PQC) sensory coatings for the selective detection of volatile organic in gas phase. The AT-cut quartz crystals used in this study (Stanford Research Systems) having a diameter of 25.4 mm and a thickness of 0.33 mm. An oscillator circuit providing an alternating voltage will produce a fundamental frequency of 5 MHz for this particular crystal diameter and thickness. About 10.0 µl of analyte was injected into the mixing chamber with an approximately volume of 250 ml. The measuring chamber with coated PQC has a volume of approximately 5 mL. The concentration of amine sample in mixing chamber and respectively in gas flow was around 40 ppm. Al experiments were conducted at 30^oC. The complexation based on the host–guest interaction between the calixarene coating and the analyte makes the coated PQC sensors sensitive to organic amines and results in quasi-irreversible frequency changes. A PQC sensor coated with a p-tert-Butylcalix[6]arene exhibits different selectivity for amines in gas phase, in the order: iso-propylamine< iso-butylamine<<n-butylamine. The relative selectivity of the analytes is explained by the cavity inclusion of analyte molecule, complete or partial, or by steric hindrance interaction. The application of PQC sensors to gas faze has provided new analytical possibilities for the food control, environmental science, biotechnology and medicine.*

Keywords: *food quality, volatile amines, calixarene, sensitive membranes*

Introduction

The detection of food quality and freshness is of increasing interest both for the consumer and food industry. Amines, especially volatile amines, are the principal compounds formed by the activity of bacterial amino acid decarboxylase during the degradation processes of proteins, which have a carcinogenic effect on human body and can be used to indicate bacterial contamination, respectively food quality and freshness. Gas chromatography methods are the best for control and monitoring the quality and freshness of food. But these methods usually require long time and pre-treatment processes which are not suitable to perform an in situ analysis and field application [1].

Developments in quartz crystal microbalance (QCM) sensor technology has progressed in the area of gas phase analysis since the first report in **1964,** where King [2] used a QCM as a gas chromatograph absorption detector. Since then, a series of reports of other detection schemes for different gas phase analytes have appeared in the literature. The change of resonance frequency (ΔF in Hz) related to the mass (Δm in g) deposited on the crystal surface of area (A in cm2) and the fundamental frequency (F_0 in MHz) of the PQC can be calculated from Sauerbrey's equation [3]:

$$\Delta F = -2.26\times10^{-6}\times F_0{}^{2}\times(\Delta m/A) \quad \textbf{(1)}$$

The theoretical detection limit of an oscillating quartz crystal is reported to be as low as 10^{-12} g (if F_0 = 10 MHz) for coating materials according to Sauerbrey's equation. Piezoelectric quartz crystal (PQCs) with appropriate coating materials can interact effectively with specific analytes. To improve the sensitivity and selectivity of PQC sensors, lately macrocyclics, *e.g.*, crown ethers, cryptands, cavitants, cyclodextrins and calixarenes, have been used as coatings for gas detection. Simple dispersion forces and dipole–dipole interactions lead to sensor signals with poor selectivity but good reversibility. Hydrogen bonding (biochemistry) and steric interactions (key– lock principle) between the sensor coating and the analyte result in an increased signal intensity but it is quasi-irreversible. The application of PQC sensors to gas faze has provided new analytical possibilities for the food control, environmental science, biotechnology and medicine [4].

In this study, we developed calixarene-coated PQC sensors for the determination of organic amines in gas faze and studied the selectivity of this coated sensor for normal and iso- form of propyl and butyl amines.

Experimental

Quartz Crystal Microbalance

The AT-cut quartz crystals used in this study were purchased from ***Stanford Research Systems*** (Sunnyvale, California) [5] having a diameter of 25.4 mm and a thickness of 0.33 mm. They were patterned with two concentric gold-on-chrome electrodes having a wrap around geometry that allows both ground and radio frequency Q connections to be made to one side.

Application of a voltage to the two electrodes produces a strain in the surface of the QCM along the cut of the crystal. An oscillator circuit providing an alternating voltage will produce a fundamental frequency of *5* MHz for this particular crystal diameter and thickness. The QCM200 System is a stand-alone instrument with a built-in frequency counter and resistance meter. It includes controller, crystal oscillator electronics, crystal holder, and quartz crystals. Series resonance frequency and resistance are measured and displayed directly on the front panel, and there is an analogue output proportional to the relative frequency to interface directly with potentiostats.

In addition, the QCM200 has an RS-232 interface and comes with both Windows and Mac software providing real-time display, analysis and storage of your QCM data. Figure 1 depicts the experimental set-up of the PQC sensor detection system with the assembled computer interface. The frequency of the vibrating crystal was measured with a QCM 200 (***Stanford Research Systems***) type frequency counter connected to a microcomputer system. About 10.0 μl of analyte was injected into the mixing chamber with an approximately volume of 250 ml. The measuring chamber with coated PQC has a volume of approximately 5 mL.

The concentration of amine sample in mixing chamber and respectively in gas flow was around 40 ppm. All experiments were conducted at 30^{o}C.

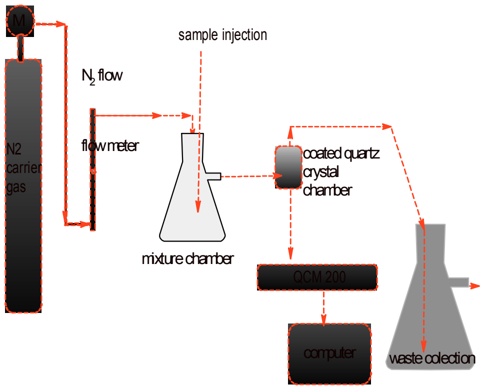

Figure 1. Experimental set-up for the calixarene-coated PQC sensor and amines.

Coatings

The coating solutions were prepared by dissolving 20 mg of the calixarene in 5 mL of chloroform. The concentrations of the resulting solutions were about 4 mg/ mL. Superior sides of the crystals were coated with the calixarene solution *via* the dropping method with a micro-syringe. An aliquot of 3.0 µL of calixarene was dropped on to superior side of the quartz crystals. A thin membrane was obtained after solvent evaporation and dried with a hot air blower for approximately 30 s.

Reagents

The analytes *iso*-propylamine (98%), *n*-butylamine (99%), *iso*-butylamine (98.5%), and pure solvents were all of analytical-reagent or chemically pure grade (Sigma Aldrich). The boiling point and molecular mass is presented in Table 1. Pure N_2 was used as carrier gas.

Table 1.

Boiling point and molecular mass of amines

Nr.	Compound	Bp (^{0}C)	MW
1	*Iso*-propylamine	33	59.11
2	*Iso*-butylamine	68-69	73.14
3	*N*-butylamine	78	73.14

Sensing material, calixarenes (CA) are cyclic oligomers containing large-scaled molecular cavities, dimensions of which depend on the number of aryl fragments (usually 4, 6, 8) in macro-cycle (Figure 2). Various functional groups can be bound to upper and lower rim. It is known that calixarenes can form “host–guest” complexes. Calixarene molecule is as a “host”, while metal ions and different organic compounds are as “guests”. Varying the number of aryl fragments and functional groups one can easily manage with sensitivity and selectivity of calixarene films [6]. Especially the cavity of calix[6]arene (2.1-2.8 Å cavity diameter) is sufficiently large to accommodate organic amine guests, whereas that of calix-[4]arene is too small [7]. It is probable that the close correspondence between the relative magnitudes of the organic amine (ionic diameter of ammonium ion = 2.96 Å) and the calixarene cavity diameters is an important factor in determining the complexation interactions between the calixarene and the amine guests [8].

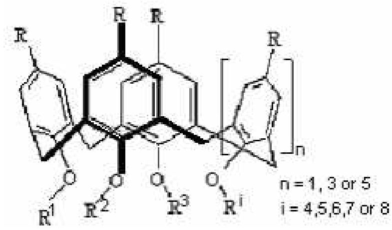

Figure 2. General structures of the p-R-calix[n] arene [7]; R=*tert*-butyl, R^i= OH and n=3 for *p-tert*-butylcalix[6]arene.

Results and Discussion

The response curves for calixarene coated PQC sensor detection systems for 40 ppm of 3 organic amines at 30 °C in the measuring chamber are shown in Figure 3 and absolute area values of measurement in Table 2.

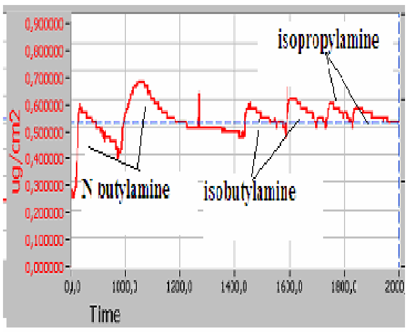

Figure 3. The response characteristics of PQC sensors coated with calyx[6]arene to 40 ppm of 3 organic amines.

Table 2.
Absolute response for three amines detected in N_2 flow with the PQC sensor

Amines (Number of determina tion)	Iso-propyl amine (4)	Iso-butyl amine (4)	N-Butyl amine (2)
	Area, sqμm		
Average values	118	222	1090

The response characteristics of PQC sensors coated with p-tert-butylcalyx[6]arene to 40 ppm of organic amines decrease in the order *n*-butylamine>>*iso*-butylamine>*iso*-propylamine. This is attributed to the extra lypophilic stabilized interaction between the host (calixarene) and guest (amines) molecules. Organic amines are incorporated in the cavity of calixarene (CA) to form *endo*-CA complex and the complex involves hydrogen bonding with inclusion of the non-polar moiety of the organic amines in the CA cavity. On the basis of the data in Figure 3, it can be seen that *n*-butylamine have remarkable higher responses and *iso*-butylamine and *iso*-propylamine have relative lower responses. This is due to the bulkiness of their non-polar moieties that cannot be incorporated into the cavity of CA, while *n* butylamine, can be incorporated into the cavity of CA to form hydrogen bonding [4]. In similar experiment but with acetate derivatized calixarene (R^i = acetate), Wang et al [4] obtain similar results for linear long chain amines (*n*-butylamine, *n*-hexylamine, *n*-octylamine and dodecylamine). It is concluded that a long alkyl group is another important factor controlling the response of organic amines.

Conclusion

In this study, we investigated *p-tert*-butylcalix[6]arene-coated PQC sensors for the detection of organic amines in gas flow. The relative sensitivity of amines is based on host–guest complexation between the organic amine and the calixarene. Stronger responses were observed for *n*-butylamine molecules which are easy included in the calyx[6]arene cavity. The response of the amines with a bulky group (*iso*-forms) is weak, since the bulky group hinders the amine from being included in the cavity.

Acknowledgement
The authors are grateful to the CNCSIS Romania for financial support (GRANT PNCD II Prog. 4 – Nr. 102/01.10.2007, New α-quartz structure compounds-performat piezoelectric sensor for food quality and safety, SENZALI).

References

1. GUANG L., JUNBAO Z., XINGFA M., YU S., JUN F., GANG W.; Development of QCM Trimethylamine Sensor Based on Water Soluble Polyaniline, *Sensors, 2007*, 2378-2388.
2. KING, W.H. Piezoelectric Sorption Detector, *Anal. Chem.,1964,* 36, 1735-39
3. SAUERBREY, G. Verwendung von Schwingquarzen zur Wagung diinner Schichten und zur Mikrowiigung, *Z. Phys., 1959, 155,206.*
4. CHUN W., XI-WEN H., CHEN L.X. : A piezoelectric quartz crystal sensor array self assembled calixarene bilayers for detection of volatile organic amine in gas*, Talanta, 2002,57, 1181–1188.*
5. Stanford Research System, QCM200,Quartz Crystal Microbalance, Digital Controller QCM25, 5 MHz Crystal Oscillator, Operation and Service Manual, , Revision 2.1(6/2005)
6. KOSHETS I.A., Z.I. KAZANTSEVA, YU.M. SHIRSHOV, S.A. CHERENOK, V.I. KALCHENKO, Calixarene films as sensitive coatings for QCM-based gas sensors, *Sensors and Actuators B 106, 2005, 177–181.*
7. URSALE T.N., I. SILAGHI-DUMITRESCU, E.-J. POPOVICI, A. URSALE, N. POPOVICI; New materials based on phosphorilated calix[n]arene, *Journal of Optoelectronics and Advanced Materials Vol. 6, No. 1, March 2004, p. 307 – 313.*
8. CHEN L.X. , XI-WEN HE, XU-BO HU, HUA XU; Calixarene-coated piezoelectric quartz crystal sensor for the detection of organic amine in liquids, *Analyst*, 1999, 124, 1787–1790.