Calixarene-based QCM sensors array
and its response to volatile organic vapours

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This work reports on the results of investigation of quartz crystal microbalance (QCM) sensors array response to wide range of volatile organic molecules. Three different gas-supplying systems (regimes) have been involved in our experiments. Shape and magnitude of kinetic sensor response turned out to depend on chosen measuring regime and gas cell size. Several calixarene derivatives of different types were used as sensitive layers. Various techniques of deposition have been studied with the aim to obtain good-quality films.

Key words: *QCM sensor; gas sensing system; artificial receptor centres; calixarene*

1. Introduction

Nowadays a great attention is paid to creation and development of miniaturized, low-cost, smart chemical sensing systems based on various physical and chemical principles, which provide accurate and reliable real-time control of ambient medium. Among a large amount of aspects regarding this branch of sensor application and technology, we may emphasize such main direction as:
- introducing new types of transducers and developing those existing,
- synthesizing new organic materials to be used as artificial receptor centres to increase sensitivity and improve selectivity of sensor and sensor array,
- optimizing gas cell parameters and choosing appropriate gas supplying regime for better functionality of sensing system as a whole,
- involving various statistical approaches (PCA, Neural Network, etc.) for pattern recognition of gas components.

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In this paper, we present the results of our studies on the influence of the capacity of the gas cell and of the gas supplying regime on the response of gas sensors. Several calixarene derivatives were used as artificial receptor centres sensing volatile organic molecules.

2. Experimental

2.1. Experimental set-up

From overall gas sensing systems (called *Electronic nose*) presented in the literature [1–7], we may mark out three main classes (regimes) shown in Fig. 1.
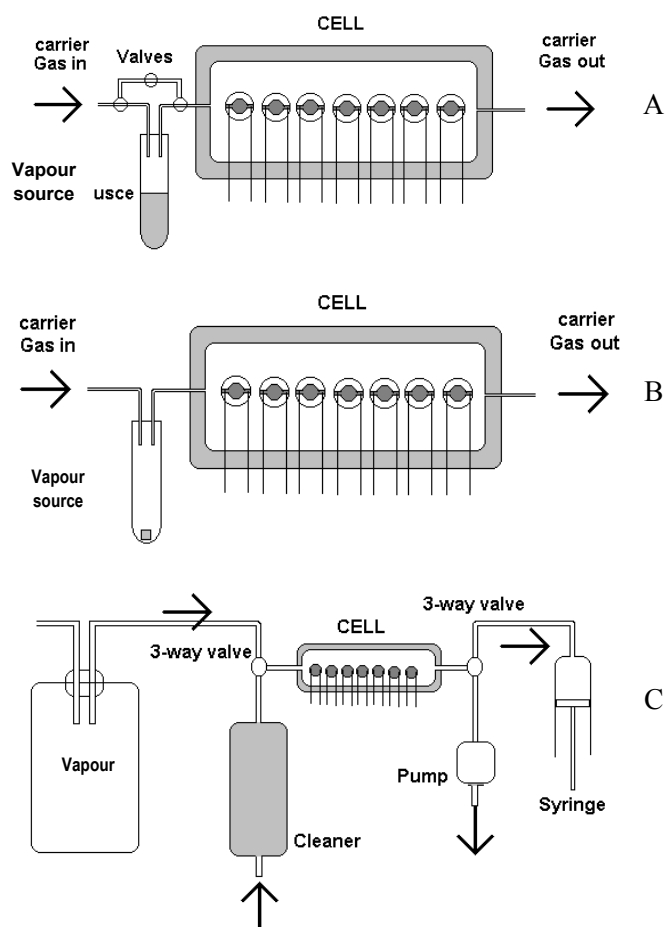

Fig. 1. Three different gas-supplying systems (three regimes) for EN device

A. Generation of volatile molecules is done by means of bubbling carrier gas through a vessel (evaporator) containing liquid phase of the matter analyzed. There is a sufficient amount of matter in the evaporator to provide flat boundary between gaseous and liquid phases. In other words, the area of the liquid phase is constant during all the time of sampling. An air pump provides a constant velocity of the carrier gas flow [1, 2].

B. There is a limited amount of matter analyzed (drop) in the evaporator. The drop area diminishes on evaporating the matter. Again, a constant velocity of a carrier gas flow is provided with an air pump [3, 4]. This regime of gas supplying is characterized by the typical peak in the sensor response curve.

C. Vapour analyzed is in the headspace of a vessel. Some amount of vapour is injected (rapidly) into gas cell by means of a syringe or sampler, the cell is then cut off from the headspace (three-way valves). No carrier gas is applied during measuring [5–7]. The capacity of the vessel is much bigger than the capacity of the gas cell, hence the dilution of vapour in the headspace is negligibly small. Between sampling, sensors and cell are purified with clean air. One of the main advantages in comparison with the two former regimes is the absence of the precision air pump and rotameter for providing stable gas flow velocity.

Two gas cells: big (350 ml) and small (9 ml) made of duralumin were used in our experiments. The sensors array consisted of 16 quartz crystals (AT-cut, $\varnothing$ 8 mm, silver metallisation, fundamental frequency 10 MHz, Philips) situated in two rows for the big cell and 8 single-planed quartz crystals for the small one. The electronics consisted of oscillator circuits and a frequency counter. The oscillator circuit was built on "OR-NOT" logical microchips and allowed one to obtain stable meander oscillation with frequency of about 10 MHz. Frequency counter was based on AT89C2051PI microcontroller. Period of measuring frequency from a single quartz was about 1 sec with resolution of 1 Hz. Experiment controlling and data acquisition were implemented via RS-232 interface by means of a laboratory-built software.

The gas system was put into an isothermal box, which provided stable temperature conditions in the range of 30–50 °C with the accuracy of ±0.5 °C. All measurements were carried out with the evaporator kept at room temperature except measurements of concentration dependences, when the evaporator was situated in a special thermostat allowing heating and cooling.

2.2. Sensing materials and coating deposition

Calixarenes are cyclic supramolecules, which form cavities of various diameters (depending on the number of phenol rings) and are able to capture metal ions and organic molecules into these cavities ("host-guest" complexation) [8]. A great number of calixarenes varying in shape and diameter of the nano-cavity (cylinder, truncated cone) as well as in the type of peripheral functional groups have been recently developed [9]. Such features reveal wide possibilities of using calixarene films as sensitive layers for various kinds of sensors, particularly QCM-based [10–12].

Tert-butyl-calix[4, 6, 8]arenes (Fig. 2a), resorcinol calix[4]arene (Fig. 2b) and ca-lix[4]arenes with different number of propyl and phenyl functional groups (Figs. 2c–e) have been synthesized in the Institute of Organic Chemistry (Kiev, Ukraine). They were used as sensitive layers for coating quartz sensors.
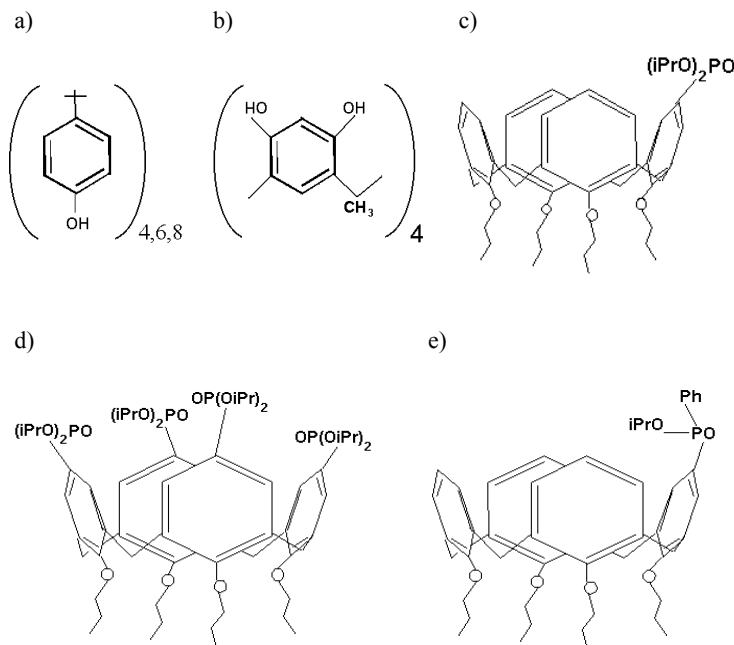

Fig. 2. Chemical structure of calixarenes used as sensitive layer:
a) tert-butyl-calix[4, 6, 8]arenes, b) resorcinol calix[4]arene, c) calix[4]arene
with one isopropyl functional group, d) calix[4]arene with four isopropyl func-
tional groups, e) calix[4]arene with single isopropyl and phenyl aggregates

Several methods of deposition were tested in our experiments:

• "Thin and thick drop" – an amount of calixarene dissolved in an appropriate sol-vent (usually chloroform, acetone, toluene) was dropped from pipette onto the quartz surface. After drying, the sensor chip was ready to utilize. Terms "thin" and "thick" refer to the quantity of dissolved calixarene, i.e. to the concentration level.

• Langmuir–Blodgett (LB) technique – many calixarenes are soluble in non-aqueous solvents, thus it is possible to use the LB technique for deposition. Up to 10–15 layers of calixarene could be transferred onto the quartz surface. The advantage of this method is a controlled thickness (each step of transfer – one monolayer) and good quality of the film obtained. Disadvantages are arduousness of the method and that only few monolayers may be transferred (very thin films are obtained) resulting in a weak response of the sensor.

• Thermal evaporation in vacuum – one of the most common and well-developed techniques of deposition used for sensor preparation. Unfortunately, not all classes of

materials applied could be deposited by this method because of their thermal instability. For example, calixarenes containing propyl groups (Figs. 2c–e) cannot be deposited by such a method.

• "Air-brush" – a solution of sensing material is sprayed through a tube with a very narrow tip (capillary). The procedure allows for obtaining a film of a uniform thickness through the whole sensor surface.

The film thickness was estimated by measuring the frequency shift before and shortly after deposition and measured by ellipsometry for selected samples (for thermally evaporated films only).

3. Results and discussion

3.1. Sensor response of various types of gas systems

The backbone of quartz crystal microbalance (QCM) measurement technique is the relation between mass loaded onto the quartz surface Δm and frequency shift Δf. In a simple case it can be expressed by the Sauerbrey equation [13]:

$$\Delta f \approx -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m \qquad (1)$$

where f_0 is the fundamental frequency, A – effective quartz area, μ_q – "piezoelectric stiffness" and ρ_q – quartz density. One can easily observe adsorption-desorption processes following the change of quartz vibration frequency with a high resolution (approx. 10–20 ng·Hz^{-1}·cm^{-2}). Equation (1) is valid if the frequency shift Δf is less than 2% of f_0.

When a sensor (or an array of several sensors) is situated in a gas cell and the medium is changing, the kinetic response of the sensor can be described in the frame of the principle of causality [14]:

$$U(t) = \int_{-\infty}^{t} N(t') \cdot h(t-t') \cdot dt' \qquad (2)$$

where $h(t - t')$ is the sensor response to a unit pulse and $N(t')$ – concentration of analyte. $h(t-t')$ is usually defined by an either exponential function or sum of several exponential functions, whose time constants depend on the properties of the sensitive layer of the sensor and may vary widely. $N(t')$ is defined by the parameters of a gas system: rate of changes of the surroundings and volume of the gas cell. Thus, sensor response will strongly depend on the correlation of these two functions. To investigate adsorption features of sensitive layers it is necessary to reduce the time constant of $N(t')$.
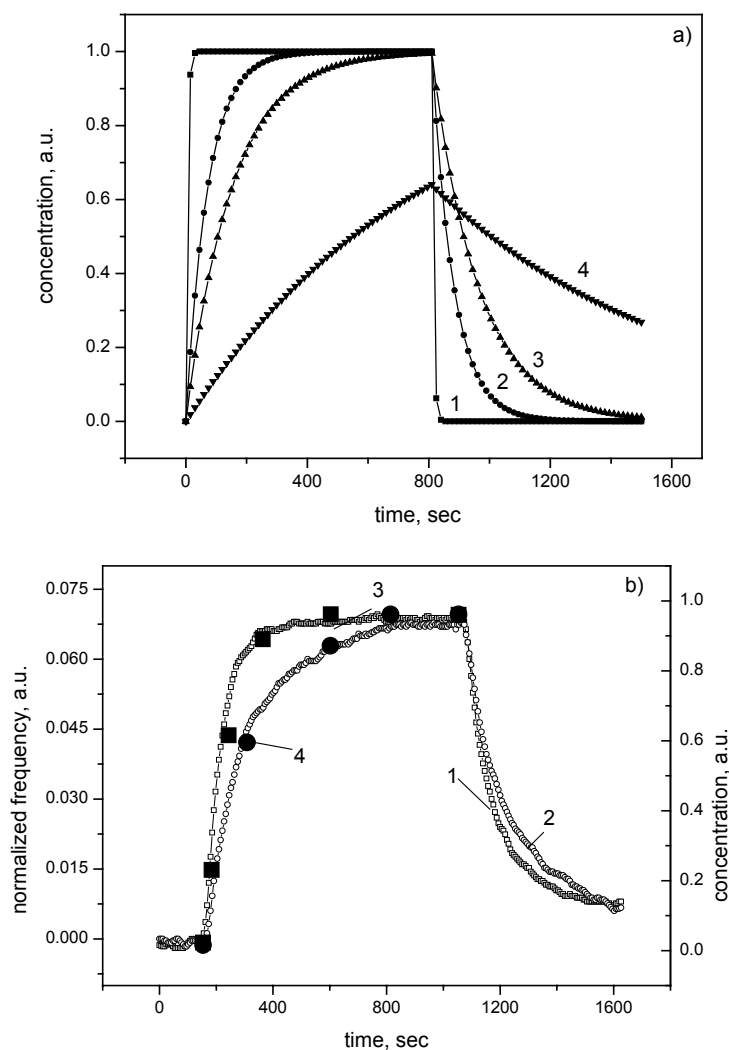
Fig. 3. Measuring regime A: a) simulation of analyte concentration in a gas cell
under varying flow rate ($P1 > P2 > P3 > P4$), b) sensor response (1, 2, left axis)
to ethanol vapour injection and concentration dependence measured
with a gas chromatograph after the gas cell (3, 4, right axis) under varying flow
rate: 1, 3 – 100 ml/min; 2, 4 – 50 ml/min. Capacity of gas cell is 350 ml

Figure 3 presents the results of numerical calculation of analyte concentration in
gas cell (a) and experimental data (b). They were obtained for the "big" gas cell when
the measurement run according to the regime A. Hereafter "normalized frequency"
means the frequency shift due to adsorption of analyte molecules (sensor response)
divided by the frequency shift due to sensitive layer deposition (film "thickness"). In
this case kinetic response is driven rather by $N(t')$ than by $h(t-t')$ and the sensor fol-

lows analyte concentration. This is seen when comparing simulations and experimental results. The flat part of each curve corresponds to the equilibrium value of the concentration in a gas cell. Note that the higher flow rate, the steeper is the slope of the curve with the same value of equilibrium concentration (except for curve 4 in Fig. 3a, where the flow rate is very slow).
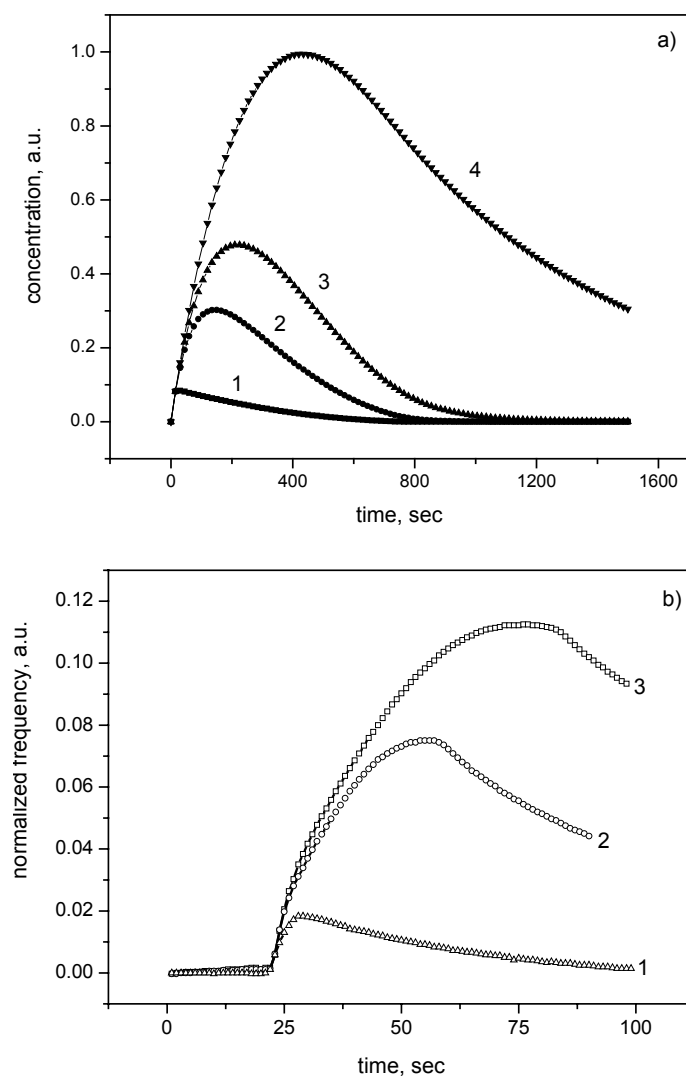

Fig. 4. Measuring regime B: a) simulation of analyte concentration into
gas cell for different volumes of analyte drop (V drop$_1$ < V drop$_2$
< V drop$_3$ < V drop$_4$), b) sensor response obtained with the "big" gas cell
for volume of analyte drop (toluene): 3 – 180 ml, 2 – 125 ml, 1– 12.5 ml
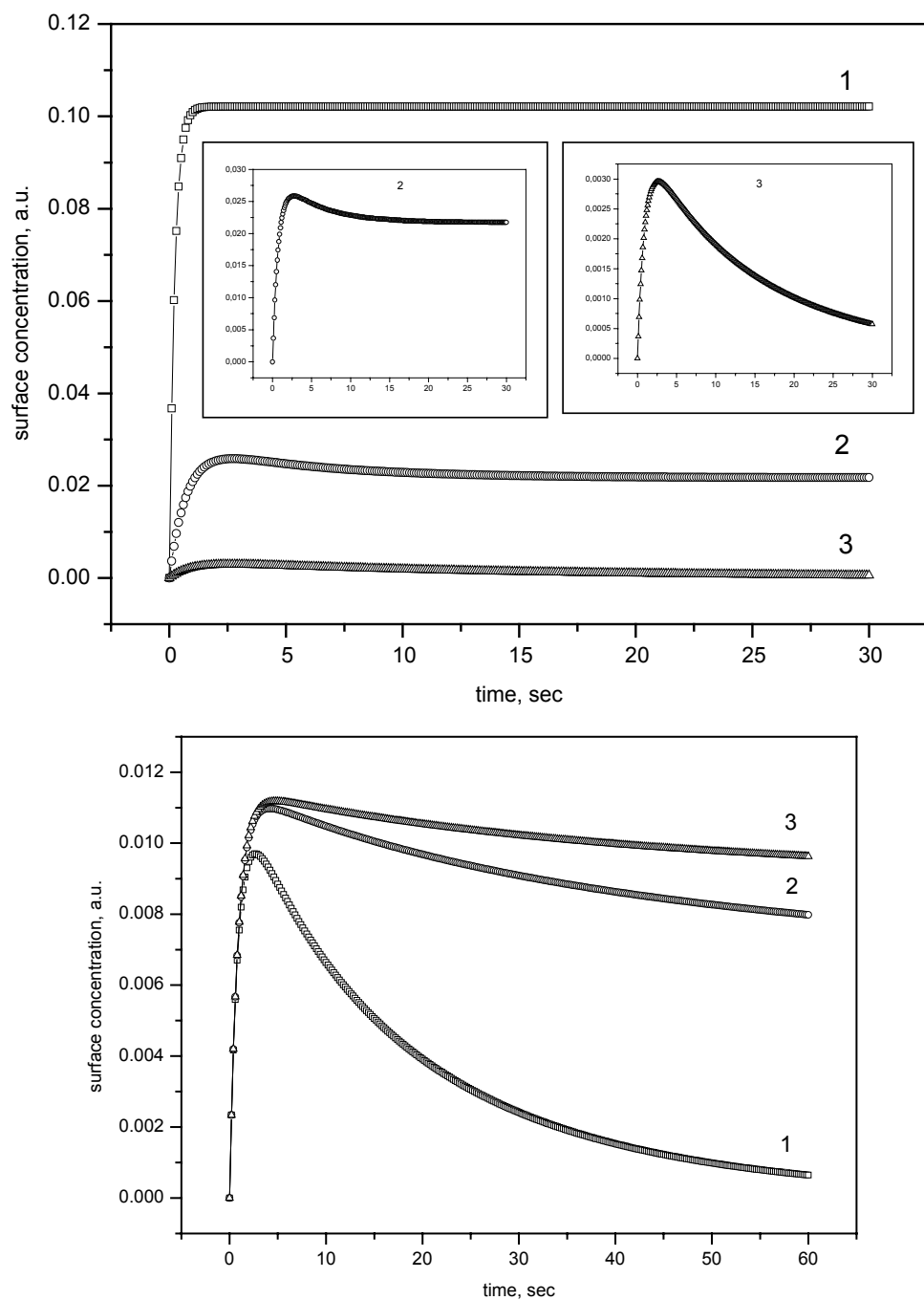
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Fig. 5. Numerical calculation of the kinetics of volatile molecules adsorbed on the sensor surface:
a) the parameter is initial number of molecules injected into gas cell ($N_1 > N_2 > N_3$),
b) the parameter is the number of adsorption centres (sites) on the cell surface ($N\text{cell}_1 > N\text{cell}_2 > N\text{cell}_3$)

Another shape of sensor response is observed under the regime B. As was said above, the surface of the analyzed liquid matter decreases upon evaporating the drop, resulting in a decrease of the number of volatile molecules, which come into the gas cell from the evaporator. Because of this feature, a characteristic peak can be seen on the kinetic response. Results of numerical calculation and experimental sensor response are presented in Figs. 4a and b, respectively. It should be noted that the evaporation rates are different for the two liquids used in the experiments. Thus analyzing the kinetic response, we should take this difference into account.
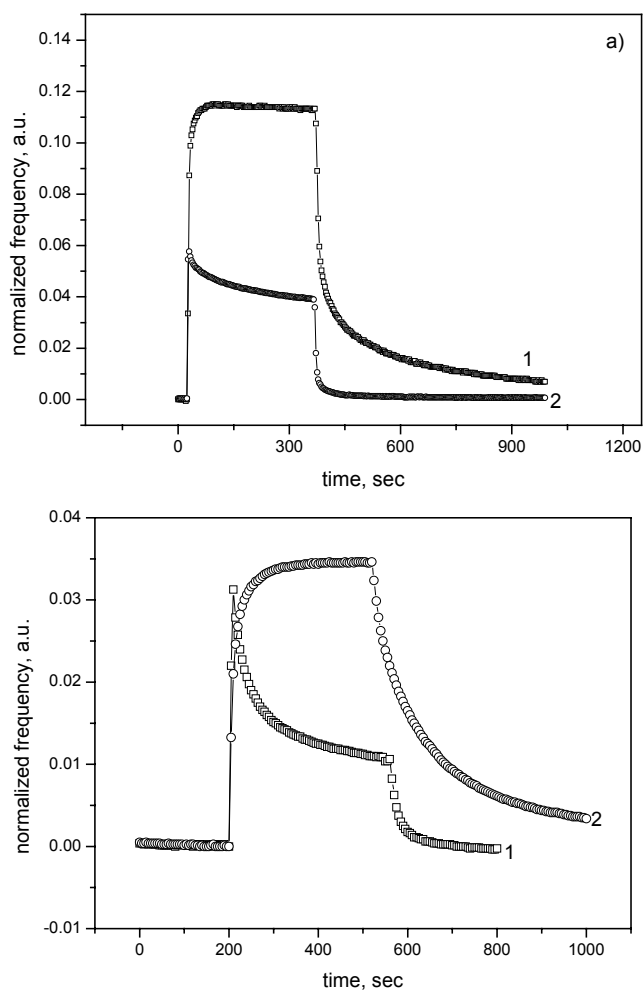

Fig. 6. Experimental kinetic sensor response to: a) injection of acetone vapour; sensitive layers are: 1 – calix[4]arene (Fig. 2b), 2 – calix[4]arene containing single O=P(OPr$_i$)Ph functional group (Fig. 2e), b) injection of toluene (1) and acetone (2) vapour; sensitive layers are the same – four O=P(OPr$_i$)Ph functional groups (Fig. 2d)

The measuring regime C was tested on the "small" gas cell. The main feature of this regime is the absence of gas flow through the gas cell. Thus adsorption of molecules onto sensors and cell surfaces leads to a decrease in the number of molecules initially injected into the cell. It may cause the lack of analyte molecules in the cell space to fill up all sites of both sensors and cell. Depending on the correlation of such factors as cell capacity, initial number of volatile molecules injected, numbers of sensors and cell sites, and their time constants ("slow" or "fast") various shapes of sensor response may be observed.

We have simulated the kinetics of the adsorption analyte molecules on sensors and cell surfaces based on the Langmuir adsorption theory [15]. Some results of the simulation are presented in Figs. 5a, b. As we can see, the shape of the curve may vary from a flat-type (curve 1, Fig. 5a) to the shape with a pronounced peak (curve 3, Fig. 5a and curve 1, Fig. 5b). Experimental kinetic response of sensors coated with different type of films sensitive to volatile organic molecules is presented in Fig. 6a. The first sensor shows a "slow" kinetic response with a flat part of the curve, while the other ones show a "fast" response with the maximum followed by a dip of the curve. Moreover, sensors coated with the same sensitive layers may show different shapes of responses to different volatile molecules (Fig. 6b). Lastly, we should note that under conditions of the regime C (capacity of gas cell many times lower than capacity of headspace, and the injection occurs during a very short time) just after the injection into the gas cell there is almost the same concentration of analyte as in the headspace.

3.2. Sensitive film deposition technique. Temperature dependence of sensor response

The four methods of deposition of sensitive films onto quartz surface mentioned above have been studied in our experiments (regime A, "big" cell). Tert-butyl-calix [4, 6, 8] arenes (Fig. 2a) were used. The results obtained for tert-butyl-calix[8]arene are shown in Fig. 7. As we can see, the maximal response was obtained from sensors with the film deposited by means of the "thick drop" technique. Unfortunately, the quality of such films was poor because of a non-uniform spreading of calixarene solution on quartz surface which led to unequal thickness of the film. As a result, the drift of the signal increased. Another problem we faced utilizing this technique, is the solubility limit of a given calixarene in a given solvent. We had to use wide range of solvents to reach desirable concentration (and hence the film thickness) for all calixarenes studied.

The LB-technique provided quite good quality of deposited films, but the thickness was very small and absolute values of sensor response were insufficient.

The airbrush technique seems to be promising for quartz sensor coating allowing obtaining uniform films of required thicknesses. Only a few samples prepared by this technique have been tested. The results obtained are not satisfactory in terms of thickness and film dispersion, hence further investigation must be carried out.
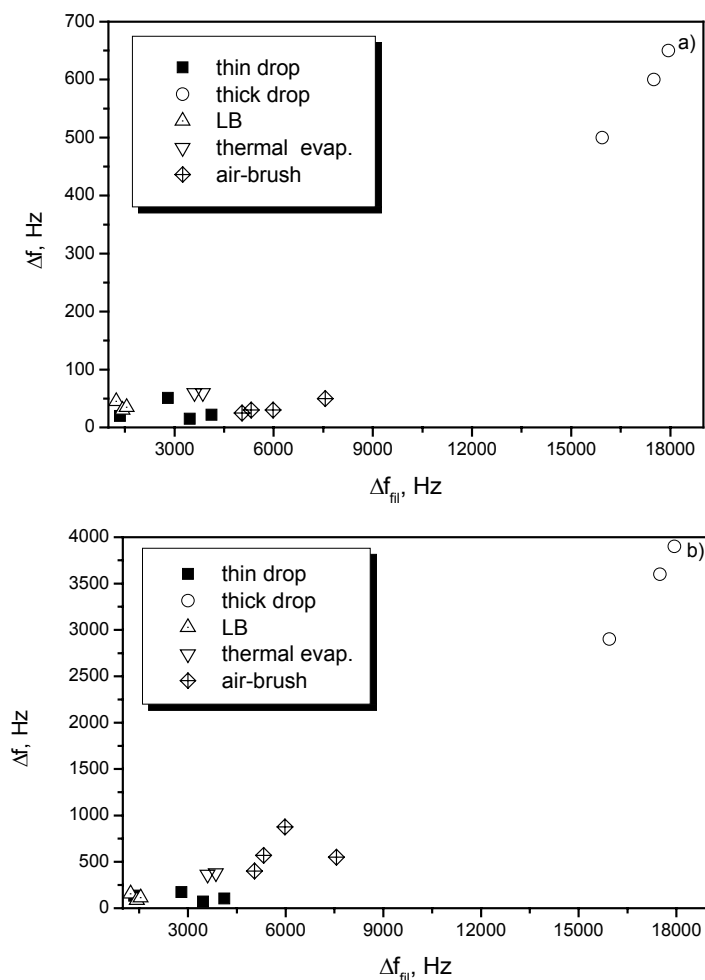
Fig. 7. Dependence of sensor response to ethanol (a) and toluene (b)
vs. frequency shift Δf_{fil} due to deposited film (in other words, film "thickness"
expressed in Hz). Different symbols correspond to various deposition methods

Sensors coated by the thermal evaporation showed the most stable and repeatable results but, as mentioned above, not all types of calixarenes may be deposited by this method.

The influence of ambient temperature on the sensor response has been studied using quartz sensors coated with thermally evaporated tert-butyl-calix[6]arene (Fig. 8). Almost constant slope is observed with increasing temperature. It might be expedient to keep the gas cell under low temperature but the period of purifying sensors between sampling increases with lowering the temperature. Moreover, maintaining the temperature of the gas cell below the ambient temperature requires special cooling system, resulting in an increase of dimensions (and price) of the device. We found that 30–35 °C was the most appropriate temperature for our aims.
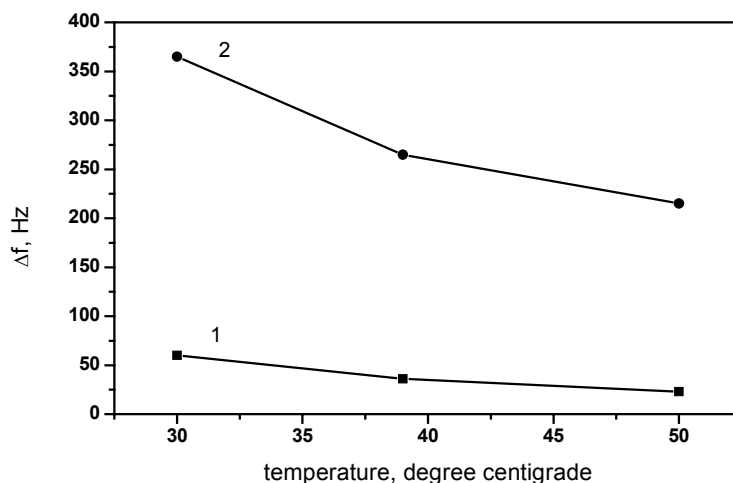
Fig. 8. Response of a quartz sensor coated with thermally evaporated C[6]A
to ethanol (1) and toluene (2) at different temperatures

3.3. Sensitivity of calixarene films towards various organic molecules

Tests of sensing capabilities of all available calixarenes (Fig. 2) towards wide range of organic molecules have been carried out applying the "small" gas cell, measuring the regime C.
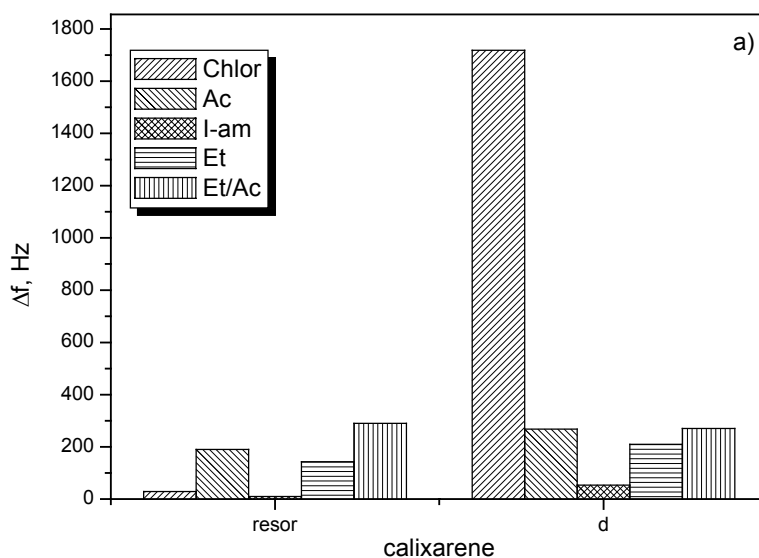

Fig. 9. Response of QCM sensors coated with resorcinol
and calixarene "d" (Fig. 2d) to organic molecules; Et – ethanol, Tol – toluene, Chlor
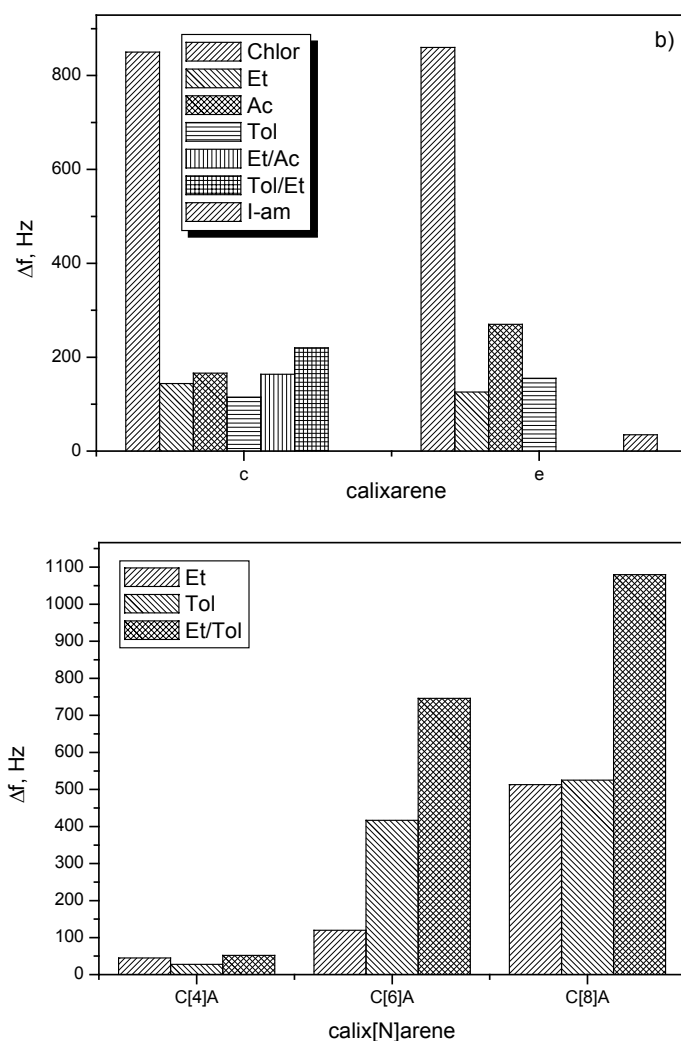– chloroform, I-am – isoamyl alcohol, Ac – acetone as well as their mixtures

Fig. 10. Response of QCM sensors coated with" a) calixarenes "c"
and "e" (Fig. 2c and e, respectively), b) tert-butyl-calix[4, 6, 8]arenes
to organic molecules; Et – ethanol, Tol – toluene, Chlor – chloroform,
I-am – isoamyl alcohol, Ac – acetone as well as their mixtures

Tert-butyl-calix[4, 6, 8]arenes were deposited onto a quartz surface by thermal evaporation, other types of calixarenes – by means of the dropping technique. Thickness of tert-butyl-calixarene layer was 150 nm (corresponding to 3800 –4000 Hz frequency shift); other sensors have been chosen with the film "thickness" of about 3500–4500 Hz. The results of these experiments are presented in Figs. 9, 10. The largest response was observed under injection of chloroform vapour for sensors coated with propyl-containing calixarenes (Figs. 2c–e) and of toluene for sensors with

tert-butyl-calix[6, 8]arene films. Chloroform is one of the best solvents for most calix-
arenes and such huge signals are not surprising. "Host-guest" complexation of tert-
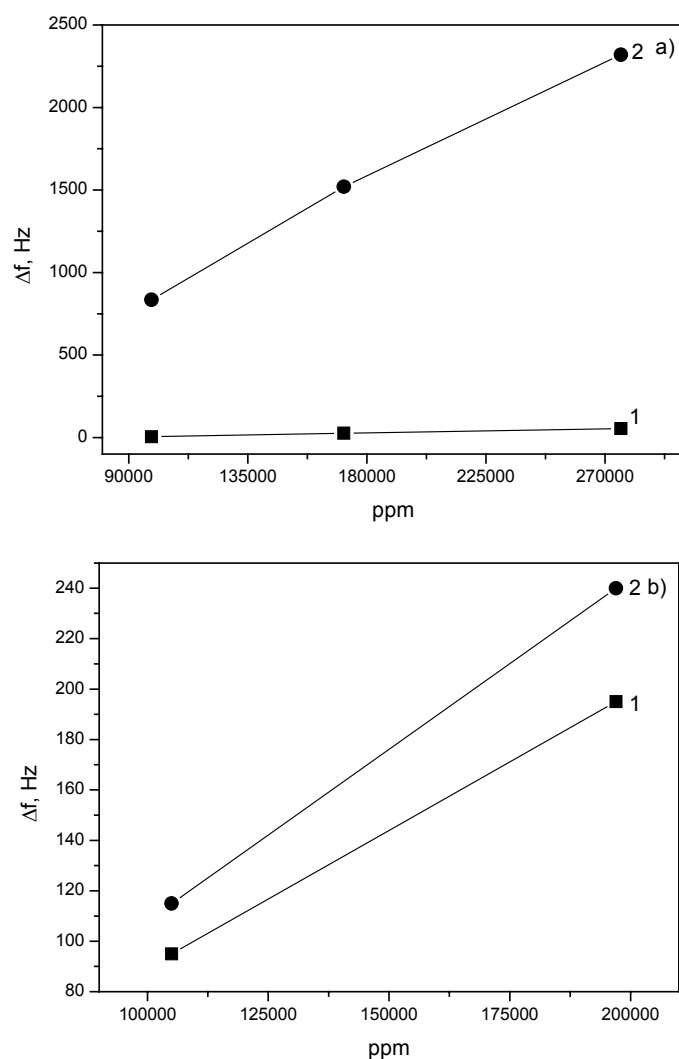butyl-calixarenes with toluene has been studied and reported [8].

Fig. 11. Concentration dependences of QCM sensors with calixarene
sensitive layer deposited: 1 – resorcinol, 2 – C[4]A "e" in Fig. 2, towards:
a) chloroform, b) acetone

    Interesting results were obtained for mixtures of analytes. For some systems (tert-
butyl-C[6,8]A–Et/Tol, resorcinol–Et/Ac, etc.) an additional increase of signal relative
to signals obtained from analytes alone was observed. We may suppose that the com-
ponents of the mixtures occupy different sites of calixarene molecules or the number

of sites is high enough to accept all molecules. Another possible mechanism is inducing site for one component by complexing calixarene with another component of gas mixture. For other pairs, there is no additional signal increase or a small one. In this case, each component occupies the same sites.
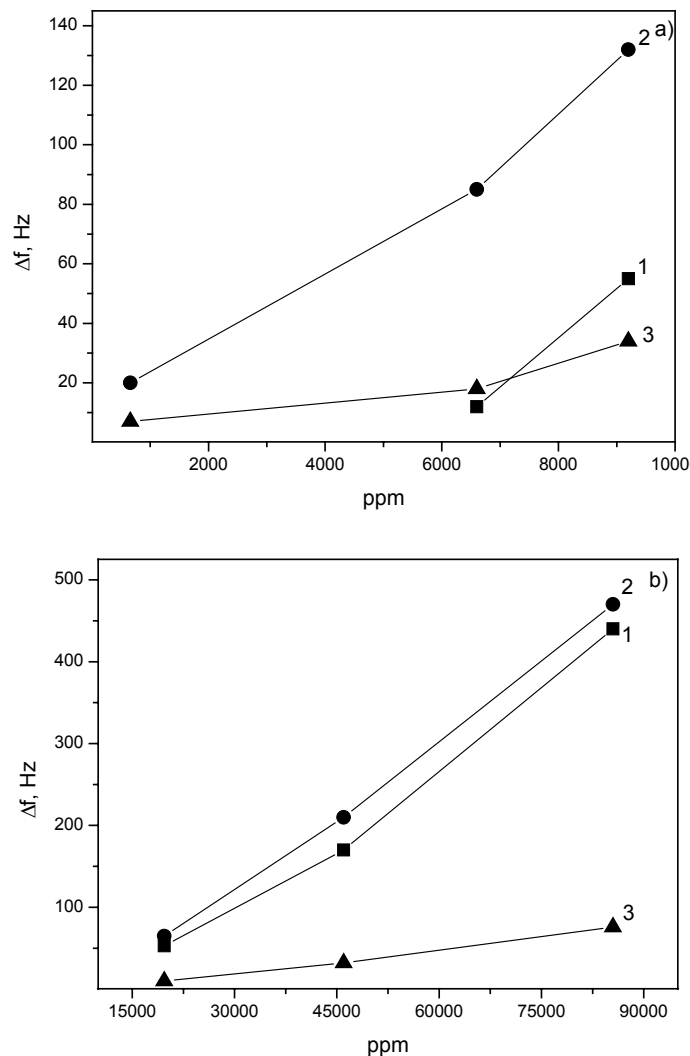

Fig. 12. Concentration dependences of QCM sensors with calixarene sensitive
layer deposited: 1 – resorcinol, 2 – C[4]A "e" in Figs. 2, 3 – C[4]A "c"
in Fig. 2 towards: a) isoamyl alcohol, b) ethanol

Concentration dependence of the response of several calixarenes to selected analytes has been studied as well. These results are presented in Figs. 11, 12. The analyte concentration was varied by keeping the vessel containing a liquid analyte at a defined

temperature in the thermostat. As saturated vapour pressure depends on temperature, we were able to obtain required concentration by setting a preselected temperature. Unfortunately, the thermostat did not allow to attain the temperature below 0 °C, therefore concentration level was very high (especially for chloroform and acetone). Nevertheless, the relations obtained may be useful for creation of vapour pressure transducers towards different organic molecules.

4. Conclusion

QCM-based sensors and sensor arrays are promising devices for the detection of organic volatile molecules in ambient air. Use of different types of calixarenes as sensitive layers reveals wide possibilities in control of sensitivity and selectivity of sensors. Treating of data obtained from sensors with special statistical methods (Neural Network, PCA, etc.) gives reliable and quick recognition of volatile organic molecule.

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