

Surface-engineered Sensors: Polymer-based Sensors for the Capacitive Detection of Organic Pollutants in Water

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Abstract:

The matured technology of electronic noses and tongues makes it promising to utilize the technique of combining chemically diverse sensor multi-arrays with multi-component analysis tools and pattern recognition techniques for a wider range of medical and environmental applications. With a self-designed sensor system and flow cell setup-up we studied the capacitive response of a polydimethyl siloxane (PDMS) covered interdigitated electrode (IDE) sensor upon exposure to methyl *tert*-butyl ether (MtBE) contaminated MilliQ water and plain mineral water. The sensor responded to MtBE concentrations as low as 2 ppm for both aqueous solutions with full reversibility. Signal drifts due to temperature effects can be remedied by sensor calibration. State-of-the-art sensor interfaces, system minimization and integration, and smart sensing layer design promise further significant optimization possibilities for system sensitivity, stability and response time.

Key words: electronic nose and tongue, interdigitated electrodes, polydimethyl siloxane, methyl-*tert*-butyl ether, drinking water standards

Introduction

Water quality remains an issue as the presence of diverse pollutants poses risks to the health of humans, flora, and fauna. Much effort is done to avoid exposure to pollution though its prevention stays priority without doubts. To minimize the uptake of water pollutants, technologies are developed to treat drinking water sources and to monitor its quality. A well-known problem is the pollution of ground water by methyl *tert*-butyl ether (MtBE) nearby gas stations. MtBE is used as an anti-knock agent in gasoline and is introduced into the environment by spilling of gasoline and its leakage from underground tanks. Due to its polar ether group MtBE has a lower octanol-water partition coefficient than other organic constituents of gasoline such as toluene and benzene and therefore it migrates easily with the ground water and may eventually end up in drinking water to which it gives an objectionable taste and odor. Therefore, the drinking water standard for MtBE is set low as 20-40 ppb by the World Health Organization (WHO) [1]. Several sensor systems can already detect and distinguish between different volatile organic

pollutants. Some make use of polymer-based resistors, cantilevers and silicon disks as transducer elements [2-4] or even use the advantages of different transducers (interdigitated electrodes, cantilevers, and thermoelectric calorimeters) in a single chip design [5]. Detection of methyl *tert*-butyl ether (MtBE) in water at concentrations as low as in drinking water standards was realized by using commercial metal oxide sensors [6]. Others imply analytical lab techniques combined with micro-extraction technology [7]. However, these systems rely on an *indirect* detection method by measuring in the gas phase that is in equilibrium with the aqueous pollutant solution.

Our research goal is to study the feasibility of polymer-based interdigitated electrode (IDE) sensors for the detection of both volatiles as MtBE and non-volatile water pollutants at standard drinking water concentration *directly* in the water phase. This study focuses on the application of polydimethyl siloxane (PDMS) as an affinity layer for the detection of MtBE.

Theoretical Background

Polymer-based IDE chips (Fig. 1, left) as capacitive sensor platforms for the detection of organic volatiles in the gaseous phase have already been studied intensively by Igreja and Dias. [8-10]. They discussed how the different processes of pollutant adsorption, absorption and consequent swelling of the polymer layer contribute to the overall sensor response as well as the effects of different sensor designs. For thick polymer layers – (thicknesses larger than at least one-half spatial wavelength (λ)) and fixed electrode geometries (unchanged electrode width (W) and area (A) and electrode gap (G) or distance (d)) (Fig. 1, left) the changes in capacitance (ΔC) can be attributed to the change in the permittivity ($\Delta\epsilon$) of the sensing layer upon pollutant absorption [9] as according to the simplified eq. (1):

$$\Delta C = \Delta\epsilon \frac{A}{d} \quad (1)$$

Direct capacitive measurements in the aqueous phase are much more complex as compared to gas-phase analysis due to the presence of ions. Ions may distort the electric bending field established between the electrode fingers and with increasing ionic strength the conductivity of water increases. Adverse electrical effects on capacitance measurements have been reported [11-12]. Depending on the environmental conditions, the pH and redox-potential will vary and so the pollutants' speciation. But also, the polymer layer itself may retain chemical groups –such as silanol ($-\text{SiOH}$) in the case of PDMS– on its surface and in the bulk that may ionize when exposed to liquid water. For a given polymer layer its affinity for a pollutant is predominantly determined by the relative polarity of the pollutant. A measure of polarity is the octanol-water partition coefficient, $\log K_{\text{ow}}$, which is ~ 1.24 for MtBE (Fig. 1, right) [1].

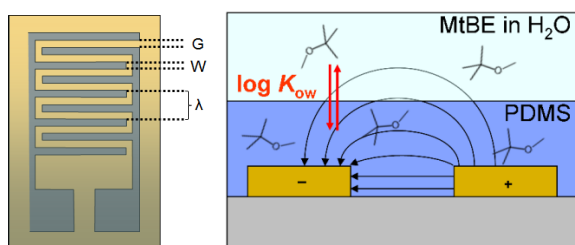


Fig. 1. Schematic representations (not to scale) of (left) a polymer-based interdigitated electrode (IDE) sensor (top view) with indication of electrode width (W), electrode gap (G), and spatial wavelength (λ) and (right) the distribution of MtBE over the water phase and the PDMS layer and of (undistorted) field lines (black arrows) between the electrodes. The red arrows refer to the partition of MtBE, while $\log K_{\text{ow}}$ stands for the logarithm of the partition coefficient.

Experimental Section

IDE Sensor Platform: The sensor chip consists of a transducer element of 221 gold IDE finger electrodes of 40 nm thickness on 10 nm thick chromium adhesion layer deposited onto borosilicate glass wafer chips of $1 \text{ cm} \times 1 \text{ cm}$. The electrode finger width and gap are 6 μm and 3 μm , respectively. The electrode finger length is 2 mm (custom-made by LioniX BV). As a sensing layer served a spin-coated PDMS layer (Sylgard®184) of $\sim 35 \mu\text{m}$ thickness, which is about twice the electrode wavelength of 18 μm to ensure that swelling and adsorption effects on the overall capacitance could be excluded. The sensor chip is wire-bonded to a printed circuit board (PCB) to make easy contacts to the electronics. For electronic readout served a LabView supported Universal Transducer Interface (UTI) that supplies a 5 V signal at 30 kHz frequency [13].

Drop Evaporation Experiment: Drops (4 μl) of different volatile organic compounds (VOCs) are deposited onto the polymer based IDE sensor. The VOCs chosen for this experiment were chloroform, MtBE, m-xylene, toluene, benzene, and n-hexane to cover a wide range of dielectric values. The change in capacitance was recorded from the moment of deposition until complete evaporation of the compounds.

Flow Cell Experiments: A sensor and flow cell setup was designed to allow measurements in water under continuous flow conditions while controlling the water flow rate and composition at any time. The sensor setup consists of a Teflon flow cell that is mounted onto the polymer-coated sensor chip and placed in a grounded flow cell holder from which electrical connection is made to the UTI. Solutions were delivered to the flow cell by a Harvard Syringe Pump 33 that is equipped with two individual syringe drives. One syringe was filled with MilliQ water or plain mineral water and the other one with a 10 mM MtBE solution of the same water source. The water composition was controlled via flow rate setting. Three measurements series were performed, in which the MtBE concentration was decreased from 1 mM to 0.1 mM. The total flow rate was kept at 600 $\mu\text{l}/\text{min}$.

Results and Discussion

The drop test results are shown in Fig. 2 and Tab. 1 summarizes common values of related properties of the compounds deposited including their relative dielectric constants (ϵ_r), octanol-water partition coefficients ($\log K_{\text{ow}}$) and vapor pressure as a measure for volatility. All observed changes in capacitance are in accordance with expectation from their physical properties. Capacity increases for the more

hydrophilic (polar) compounds chloroform and MtBE, and decreases for the more hydrophobic compounds.

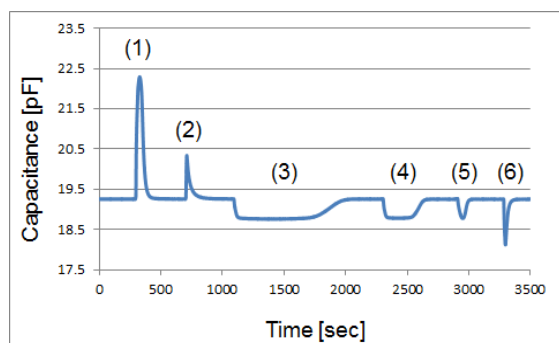


Fig. 2. Capacitive sensor response to the deposition and subsequent evaporation of the organic liquids chloroform (1), MtBE (2), m-xylene (3), toluene (4), benzene (5), and n-hexane (6).

Tab. 1: Relative dielectric constant (ϵ_r), octanol-water partition coefficient ($\log K_{OW}$), and vapor pressure of the organic compounds used in this study.

Chemical compound	Relative dielectric constant (ϵ_r)	Partition coefficient ($\log K_{OW}$)	Vapor pressure [mmHg]
(1) Chloroform	4.81	1.97	197
(2) MtBE	2.60	1.24	249
(3) m-Xylene	2.36	3.20	8
(4) Toluene	2.38	2.73	18
(5) Benzene	2.28	2.13	95
(6) n-Hexane	1.89	4.00	153

Though the dielectric constant of Sylgard®184 is reported to be 2.68 (at 100 kHz) [14], our results indicate that for thin layers, the dielectric constant is slightly lower, between 2.60 (MtBE) and 2.36 (m-xylene), since in that range the capacity response passes zero. This deviation could be related to the difference between electronic properties of thin layer PDMS and bulk PDMS as observed by others [15]. From the results it is also obvious that higher vapour pressures result in shorter retention times. With these results we have demonstrated the sensor platforms suitability for studying various physical processes.

The results of the continuous flow experiment of varying MtBE concentrations in MilliQ and plain mineral water are shown in Fig. 3 and Fig. 4. No significant effect was observed using MilliQ or plain mineral water. The conductivities of MilliQ water and the plain mineral water were measured to be 0.75 $\mu\text{S}/\text{cm}$ and 415 $\mu\text{S}/\text{cm}$, respectively. The effect of (small) temperature changes was much more significant. In a separate experiment it was found that the sensor has a positive temperature coefficient of 13 fF per degree Celsius. Therefore, as done with most sensor systems correction for temperature induced change is necessary.

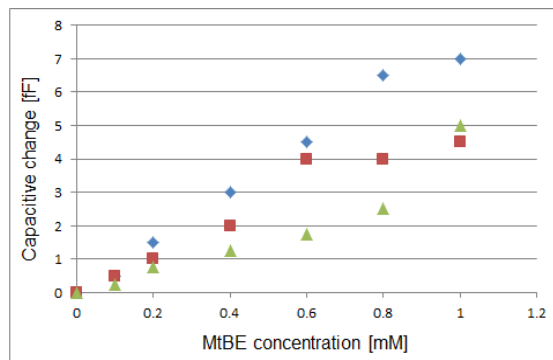


Fig 3. Changes in the average capacitance as function of the MtBE concentrations in MilliQ water. Three measurement series were performed as indicated by the colored symbols.

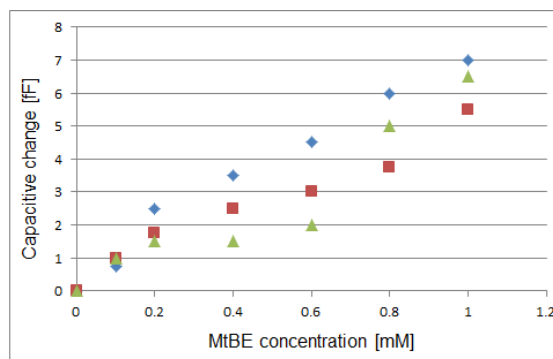


Fig 4. Changes in average capacitance as function of the MtBE concentration in plain mineral water. Three measurement series were performed as indicated by the colored symbols.

Fig. 5 shows an example of the sensor response upon ad-/absorption and desorption of MtBE (0.6 mM in MilliQ water) into the polymer layer showing complete reversibility of the sensor response.

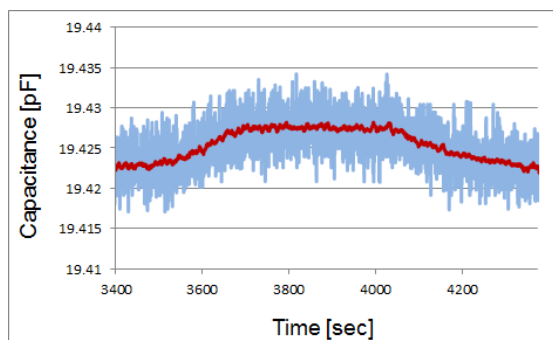


Fig 5. Changes in the capacitance averaged over 100 measurement points (red line) and the real-time value (blue line) upon exposure of a 0.6 mM MtBE solution as function of time.

It is observed in Fig. 5 that for the MtBE/PDMS system the process of ad-/absorption is faster than the desorption process. Further investigations on how other possible physical processes govern the overall sensor response is currently under progress.

Conclusion

The results demonstrate that MtBE concentrations as low as 2 ppm (i.e. 0.1 mM) could be detected successfully in water directly under both lab and environmental conditions by the designed sensor system, which utilizes a polymer-based capacitive IDE sensor platform. The target concentration to be detected lays with 20 ppb still a factor of 100 lower. However, from an electronic point of view new sensor chip technologies that will boost the sensitivity and accuracy of the UTI combined with the optimal design of both the capacitive polymer-based sensor platform including minimization and integration of electronics and sensor elements leave still much promising space for system improvements. From a chemical point of view we believe that the polymer affinity for specific pollutants can be significantly increased by incorporation of an appropriate complexation agent thereby further improving the sensor sensitivity. Also, it is anticipated that the sensor stability can be increased by integration of functional monolayers between the electrode structure and the polymer layer providing both adhesive and insulating properties.

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