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# Liquid-Phase Chemical Sensing Using Lateral Mode Resonant Cantilevers

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Liquid-phase operation of resonant cantilevers vibrating in an out-of-plane flexural mode has to date been limited by the considerable fluid damping and the resulting low quality factors (*Q* factors). To reduce fluid damping in liquids and to improve the detection limit for liquid-phase sensing applications, resonant cantilever transducers vibrating in their in-plane rather than their out-of-plane flexural resonant mode have been fabricated and shown to have *Q* factors up to 67 in water (up to 4300 in air). In the present work, resonant cantilevers, thermally excited in an in-plane flexural mode, are investigated and applied as sensors for volatile organic compounds in water. The cantilevers are fabricated using a complementary metal oxide semiconductor (CMOS) compatible fabrication process based on bulk micromachining. The devices were coated with chemically sensitive polymers allowing for analyte sorption into the polymer. Poly(isobutylene) (PIB) and poly(ethylene-co-propylene) (EPCO) were investigated as sensitive layers with seven different analytes screened with PIB and 12 analytes tested with EPCO. Analyte concentrations in the range of 1–100 ppm have been measured in the present experiments, and detection limits in the parts per billion concentration range have been estimated for the polymer-coated cantilevers exposed to volatile organics in water. These results demonstrate significantly improved sensing properties in liquids and indicate the potential of cantilever-type mass-sensitive chemical sensors operating in their in-plane rather than out-of-plane flexural modes.

Toxic or carcinogenic water contaminants pose a major threat to human health;<sup>1–4</sup> monitoring wastewater and groundwater for harmful chemicals currently requires large and expensive laboratory equipment.<sup>2,4</sup> Consequently, a key demand in environmental

monitoring is creating analytical tools that are portable or hand-held and allow for on-site measurements.<sup>5</sup> State-of-the-art laboratory techniques such as conventional gas or liquid chromatography, mass spectrometry, and optical spectroscopic techniques are of limited applicability for in-field deployment or use by first responders. Two notable exceptions are microgas chromatography systems ( $\mu$ -GC)<sup>6,7</sup> and fiber-based infrared (IR) sensors,<sup>8</sup> which are continuously evolving technologies. While both of these systems have the potential of being integrated into hand-held platforms, their potential cost and complexity may still limit widespread routine use. Thus, for targeted analyte detection, chemically sensitized microsensors are a viable alternative. For environmental monitoring applications, microsensors may potentially streamline testing procedures and reduce sensor cost, as they are easily batch manufactured in large quantities, and seamlessly integrate with a wide variety of microfluidics.<sup>9–11</sup> In order to facilitate the introduction of microsensor technology into environmental monitoring scenarios, low-cost microsensors with integrated electronics for reliable operation in aqueous environments and with detection limits at the low parts per billion concentration range need to be developed.

In the area of microscale sensor research, there has been substantial interest in cantilever-based devices.<sup>9,12</sup> For chemical sensing applications, cantilevers are operated either in a static bending mode, which is sensitive to changes in the surface stress, or in a dynamic resonance mode, which is sensitive to mass changes of the cantilever. While molecular constituents may not provide attributes that easily lend themselves to detection with sensing schemes requiring, e.g., electrochemical or optical activity, all molecules have an associated mass. For this reason, mass-sensitive sensors have attracted considerable research interest. In addition, if cantilever-based sensors are operated in the dynamic regime (i.e., their resonance frequency shifts in response to analyte binding), simple electronic circuitry permits tracking these frequency shifts using, e.g., a digital counter. As a result, a number of studies have been dedicated to cantilever-based chemical

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<sup>§</sup> University of Ulm.

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sensors for gas-phase sensing applications.<sup>13–17</sup> In contrast, significantly fewer attempts have been made to utilize mass-sensitive cantilever sensors in the liquid phase<sup>18</sup> due to substantial fluid damping and a relatively large effective fluid mass affecting conventional out-of-plane (or transverse) flexural modes. An elegant strategy minimizing effects of fluid damping has been presented by Burg et al.<sup>19</sup> by routing the liquid sample through fluidic microchannels embedded within the resonator, while operating the resonator itself in air or even vacuum. However, the resulting system is fairly complex, and the currently implemented resonant sensors require external excitation and detection mechanisms.

In contrast to previous work, this study utilizes the cantilever's in-plane flexural or lateral mode, the motivation being to reduce the resistance of the surrounding fluid primarily to that associated with shear stresses at the cantilever-fluid interface along the direction of motion.<sup>20</sup> While the fluid resistance on the smaller faces (those perpendicular to the direction of motion) is nonzero, theoretical considerations indicate that its effect will be relatively small, especially concerning the quality factor and, thus, the limit of detection for the range of cross-sectional dimensions considered herein.<sup>21,22</sup> Advantageously, the drop in resonant frequency upon immersion into liquid and, thus, the drop in device sensitivity due to the surrounding fluid are greatly reduced when the in-plane flexural mode is used, as the effective mass of the accelerated fluid is much smaller during in-plane flexural vibrations. It was shown that immersion of such devices into liquid typically yields only a 5–10% shift in resonant frequency,<sup>20</sup> while for cantilevers operated in out-of-plane flexural modes, 50% frequency shifts are typically observed.<sup>18</sup> In addition, the decreased damping associated with the in-plane flexural modes results in quality factors that are up to 5 times larger than those reported for devices operated in out-of-plane modes in liquid. In fact, for in-plane mode cantilevers, quality factors as high as 67 have been measured in liquid.<sup>20</sup> As will be shown in the present study, lower damping directly relates to an improved limit of detection for cantilever-based chemical sensors.

Disk-type resonant sensors vibrating in a rotational in-plane mode have demonstrated a 2-ppm detection limit for *m*-xylene in water,<sup>13</sup> which is comparable to limits of detection achieved with cantilever sensors vibrating in the first in-plane flexural mode.<sup>18</sup> Generally, for environmental sensors, limits of detection in the

low parts per billion concentration range are dictated by the exposure limits outlined by the EPA.<sup>1</sup> While state-of-the-art acoustic wave devices may achieve limits of detection in the low parts per billion range,<sup>23</sup> their fabrication is more elaborate as they require piezoelectric materials to be incorporated into the fabrication processes.<sup>24</sup> Consequently, the present study takes advantage of cantilever-based resonant sensor platforms fabricated by complementary metal oxide semiconductor (CMOS) compatible processes, yet yielding parts per billion range detection limits for addressing volatile organics in water at environmentally relevant concentration levels.

**Device Design Considerations.** Several parameters must be considered when designing a cantilever-based mass-sensitive chemical sensor. Assuming a silicon cantilever vibrating in one of its in-plane flexural modes in air, the resonance frequency is (to first order) independent of the cantilever thickness and, thus, thinner (and lighter) cantilevers will result in higher mass sensitivities but will suffer from increased noise levels as determined by the short-term frequency stability. Thus, for obtaining the lowest possible limit of detection, the correct balance between frequency stability and mass sensitivity must be achieved.

Conventionally, the limit of detection (in parts per million) is defined as 3 times the noise-equivalent analyte concentration, which itself is given by the ratio of the short-term frequency stability  $\Delta f_{\min}$  (in Hertz) determined via the Allan variance method<sup>25</sup> and the chemical sensor sensitivity  $S$  (in Hertz/parts per million):

$$\text{LOD} = 3 \frac{\Delta f_{\min}}{S} \quad (1)$$

The achievable chemical sensitivity depends on the sorption characteristics of the enrichment membrane coated onto the cantilever surface, which is specific to a particular analyte, and on the sensor sensitivity of the resonant microsensors.<sup>14</sup> As described in ref 14, the chemical sensitivity ( $S$ ) may be written as the product of the gravimetric sensitivity ( $G$ ) of the coated resonant sensor, i.e., the change in frequency  $f$  due to a change in coating density  $\rho_L$ , and the analyte sensitivity ( $S_A$ ), i.e., the change in coating density  $\rho_L$  due to a change in analyte concentration  $c_A$  in the surrounding medium:

$$S = G \cdot S_A = \frac{\partial f}{\partial \rho_L} \frac{\partial \rho_L}{\partial c_A} \quad (2)$$

It should be noted that using the gravimetric sensitivity rather than the mass sensitivity  $\partial f / \partial m$  is appropriate for chemical sensors based on analyte partitioning into a sensitive film. The mass sensitivity of a resonator can be increased by reducing the resonator mass and increasing its frequency,<sup>9</sup> i.e., simply by scaling down the dimensions in the case of a cantilever. In contrast, the gravimetric sensitivity also considers the scaling of the volume of the sensitive layer with changing resonator dimensions. As decreasing the cantilever length and width

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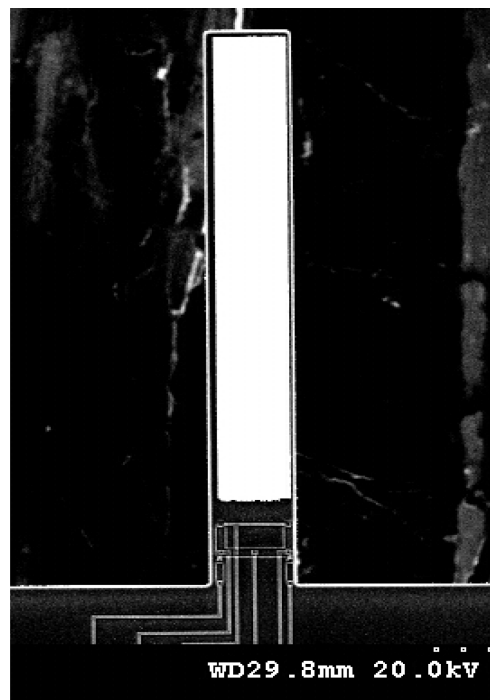
generally reduces the coating volume as well, the gravimetric sensitivity, which is relevant for a chemical sensor based on analyte sorption, does not necessarily improve by simple device scaling. In fact, it can be shown that the relative gravimetric sensitivity of a cantilever vibrating in any particular in-plane flexural mode, i.e., the gravimetric sensitivity divided by the resonance frequency of the flexural mode, is, in a first-order approximation, independent of the cantilever length and width, provided that the cantilever has a uniform cross-section and a uniform membrane coating thickness.

In the present study, a finite element approach (COMSOL, Stockholm, Sweden) has been used to model the gravimetric sensitivity of the in-plane mode cantilevers. Using a modal analysis, the in-plane resonance frequency of a polymer-coated silicon cantilever was calculated as a function of the polymer density. For 75  $\mu\text{m}$  wide, 400  $\mu\text{m}$  long, and 7.5  $\mu\text{m}$  thick silicon cantilevers, as also experimentally used in the present study, with a 0.7  $\mu\text{m}$  thermal oxide, a 1.2  $\mu\text{m}$   $\text{SiO}_2/\text{SiN}_x$  passivation layer, and a 0.3  $\mu\text{m}$  gold coating, the calculated gravimetric sensitivity is 30.2  $\text{Hz}/(\text{kg m}^{-3})$  in the case of a 2  $\mu\text{m}$  poly(ethylene-co-propylene) (EPCO) coating on both sides of the cantilever; the simulated first in-plane resonance frequency is 450.5 kHz in vacuum. The simulation does not account for changes in resonator stiffness due to the analyte absorption; while this is a reasonable assumption for the case of thin polymeric films on top of silicon resonators as studied herein, stiffness effects may substantially change the characteristics of a mass-sensitive sensor for other conditions.<sup>21</sup>

If the analyte concentration  $c_A$  is given in parts per million (v/v), the analyte sensitivity  $S_A$  may be calculated as

$$S_A = \frac{\partial \rho_L}{\partial c_A} = \rho \cdot K \cdot 10^{-6} \quad (3)$$

where  $\rho$  is the density of the analyte, and  $K$  is the partition coefficient of the particular analyte/membrane combination, i.e., the ratio of the analyte concentration in the sensitive film to the analyte concentration in the surrounding matrix. The factor  $10^{-6}$  accounts for the fact that  $c_A$  is given in parts per million. In the case of chlorobenzene detection ( $\rho = 1.11 \text{ g cm}^{-3}$ ) using an EPCO membrane, a liquid-phase partition coefficient of approximately 320<sup>26</sup> yields an analyte sensitivity of 0.36 ( $\text{kg m}^{-3}$ )/ppm. Similarly, calculated liquid-phase partition coefficients for poly(isobutylene) (PIB) and several other analytes have been reported in ref 27. For the cantilever tested in this work, the resulting chemical sensitivity for chlorobenzene becomes 11 Hz/ppm. As will be shown later (Figure 6c), this value is close to the experimentally determined sensitivity of 16 Hz/ppm. The discrepancy is likely attributed to a thicker polymer layer on the tested cantilever or due to a larger than expected partition coefficient. Theoretically, the chemical sensitivity may be improved using thicker sensing membranes. However, in the case of liquid-phase operation, membrane adhesion limits the possible thickness of the chemically sensitive polymer film. In the case of



**Figure 1.** SEM image of a 60  $\mu\text{m}$  wide and 400  $\mu\text{m}$  long cantilever with a 300 nm gold layer on the surface. The resistors for electro-thermal excitation and piezoresistive detection of in-plane vibrations (as well as the aluminum interconnects) are visible close to the cantilever's clamped edge at the bottom of the image. A detailed description of the piezoresistor layout can be found in ref 20.

the EPCO coating used here, the maximum film thickness without loss of adhesion was determined at approximately 2  $\mu\text{m}$ . By coating both sides of the cantilever, the overall film thickness could be doubled without adhesion loss.

The sensor's limit of detection given in eq 1 is particularly affected by the geometrical dependence of the minimal detectable frequency change  $\Delta f_{\min}$ .  $\Delta f_{\min}$  is generally improved (i.e., reduced) by increasing the quality factor of the resonance, which is the main motivation behind investigating in-plane rather than out-of-plane cantilever modes. The 400  $\mu\text{m}$  long cantilevers tested in this work exhibit  $Q$  factors around 40 in water. For a given cantilever thickness, the  $Q$  factor in water roughly increases with the square-root of the in-plane resonance frequency, and  $Q$  factors in the range of 60–70 in water for 200  $\mu\text{m}$  long cantilevers have recently been demonstrated.<sup>20</sup> These values favorably compare to values around 10 for cantilevers with similar dimensions but vibrating in out-of-plane flexural modes.<sup>18</sup> It should be noted that the  $Q$  factor in water is not substantially affected by the polymer coating, because of the dominating fluid damping. This is in contrast to cantilevers operated in air, where  $Q$  substantially decreases with increasing polymer thickness.<sup>14</sup>

## EXPERIMENTAL SECTION

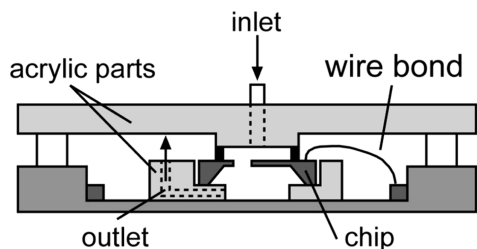
**Cantilever Fabrication.** With the above considerations in mind, thermally excited and piezoresistively detected single crystal silicon cantilevers were fabricated using a CMOS compatible bulk micromachining process described elsewhere.<sup>28</sup> Figure 1 shows

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**Figure 2.** Schematic cross-section of packaging concept with fluid flow through the etch opening in the sensor chip (top to bottom).

a scanning electron microscopy (SEM) image of a fabricated cantilever. The U-shaped piezoresistive Wheatstone bridge is configured such that the in-plane mode of the cantilever is preferentially detected over the out-of-plane mode and that a possible thermal signal from the heating resistors is suppressed.<sup>20</sup> The resistor placement was optimized by analyzing the stress distribution of both the in-plane and out-of-plane mode shapes using finite element simulations (COMSOL, Stockholm, Sweden).

**Experimental Setup.** Once fabricated and diced, the devices were wire bonded and packaged using acrylic manifolds, which were fabricated with a stereolithography tool. For creating a flow cell, an acrylic manifold is first glued into a standard 28-pin dual-in-line (DIL) package. The cantilever chip is placed over a silicone gasket in the bottom manifold, forming a seal when the entire system is assembled. The die is then wire bonded, and an acrylic ring is glued to the surface of the chip after wire bonding. A top manifold screws down to threaded inserts glued to the DIL package allowing a gasket to seal against the acrylic ring, thereby creating the flow cell (Figure 2). The design of the flow cell allows fluid flow from the top to the bottom of the sensor chip through the bulk micromachined opening. Luer-lok fittings are used to connect the flow cell to a three-way "T" that is connected to two syringe pumps. Fluid exits the flow cell through a piece of silicone tubing routed through the top manifold.

For electrical operation, the cantilevers were placed in an amplifying feedback loop that has previously been described.<sup>28,29</sup> Phase adjustments and signal gain adjustments are set to ensure device oscillation. A Schmidt trigger at the output of the circuit creates a square wave that allows the frequency to be read using a digital counter. A gate time of one second is used for measurement, but further averaging using a data evaluation software (MATLAB, MathWorks, Natick, MA) allows studying the effect of varying gate times. All of the measurements were done using 75  $\mu\text{m}$  wide, 400  $\mu\text{m}$  long, and 7.5  $\mu\text{m}$  thick cantilevers covered by 0.7  $\mu\text{m}$  of thermal oxide and an approximately 1.2  $\mu\text{m}$  thick silicon dioxide and silicon nitride passivation layer; the cantilevers also had an approximately 300 nm thick gold layer deposited at the surface. (See Figure 1.) For liquid operation, the heating resistors were biased with 4 V DC, which was superposed with a 2 V peak-to-peak AC signal; the bias used for the Wheatstone bridge was 2 V. The two excitation resistors and four Wheatstone bridge resistors all have a resistance of approximately 400–450  $\Omega$ . The quality factor of the EPCO-coated cantilever was measured in water after packaging and was determined to be around 40.

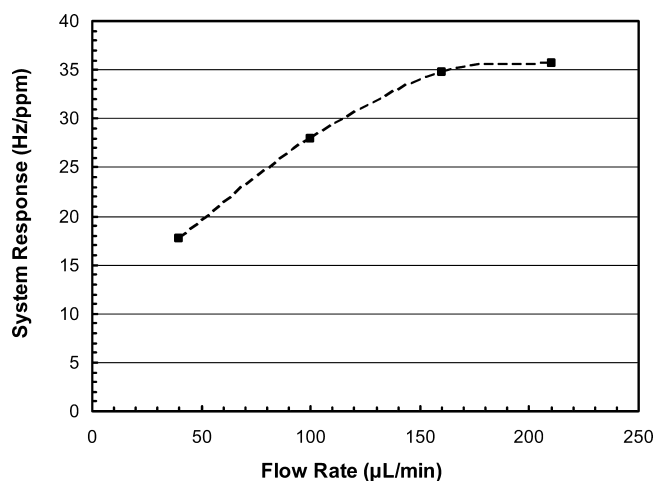
**Reagents and Solutions.** *m*-Xylene (99.9+%, HPLC grade), trichloroethylene (99.5+%, HPLC grade), benzene (99.5% HPLC grade), dichloropropane (99.5% HPLC grade), epichlorohydrin (99.5% HPLC grade), dichlorobenzene (99.5% HPLC grade), tetrachloroethylene (99.5% HPLC grade), ethylbenzene (99% GC grade), and chlorobenzene (99.5+%, HPLC grade) were purchased from Sigma-Aldrich (St. Louis, MO). Chloroform (99.5% spectrophotometric grade) was purchased from Alpha Aesar (Ward Hill, MA). Toluene (ACS grade) was purchased from EMD (Gibbstown, NJ). Carbontetrachloride (certified ACS grade) was purchased from Fisher Scientific (Houston, TX). All chemicals were used as supplied. Deionized water ( $R = 18.2 \text{ M}\Omega \cdot \text{cm}$  at 25  $^{\circ}\text{C}$ ) was used for preparation of all solutions and for equilibration/regeneration of the sensing membranes. Poly(isobutylene) (PIB) and poly(ethylene-*co*-propylene) (EPCO) were purchased from Sigma-Aldrich (St. Louis, MO). Toluene was used as a solvent to prepare the polymer solutions. Hexamethyldisiloxane (HMDS, 100%) was purchased from Shin-Etsu MicroSi (Phoenix, AZ) and was used as supplied.

The sample solutions were individually prepared just prior to analysis by dissolving known amounts of the volatile organics in degassed and deionized water. The 1% (w/v) PIB and EPCO polymer solutions used in this work were dissolved in toluene at constant stirring for 4 h.

**Coating Procedure.** The polymer solutions were applied to the cantilever surface by spray coating using an air brush. For coating the cantilevers with polymer, the following procedure was used: each cantilever die was first packaged and tested, and the glue-on ring was put in place (see above). The cantilevers were thoroughly cleaned after the fabrication process to ensure that no organics remained at the surface. They were stored until use in a drybox in a nitrogen atmosphere. The cantilevers were tested after packaging to verify that they were operating properly. The cantilever die was then removed from the package, and a drop of HMDS acting as an adhesion promoter was placed at the surface and allowed to dry. The cantilevers were then spray coated on both sides. Test samples were simultaneously coated for polymer thickness measurement. After coating, the chips were annealed for 5 min in a toluene atmosphere to improve the film uniformity. The bond pads were masked off using tape during spray coating. After coating, the chips were again wire bonded into the package with the acrylic manifolds. Measurements of the obtained polymer thickness were performed on simultaneously coated test samples; the PIB coating was around 0.25  $\mu\text{m}$  thick on both sides, and the EPCO coating was 2  $\mu\text{m}$  thick on both sides. In contrast to PIB, it was found that EPCO layers could be applied up to a thickness of 2  $\mu\text{m}$  without delamination.

**Testing Procedure.** Prior to testing, each packaged die was baked for 20 min at 110  $^{\circ}\text{C}$  to remove any remaining solvent or moisture from the polymer membrane and to further improve film adhesion. Before use, each analyte solution was constantly stirred for at least 30 min. The analyte solution was loaded into a 5 mL glass syringe, which was connected to a T fitting, as described above. A second syringe pump containing water was also connected to the remaining port of the T fitting. Polyetheretherketone (PEEK) tubing and fittings were used for all connections in order to avoid memory effects. Finally, the dependence of the system response on the flow rate was investigated, as discussed below.

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**Figure 3.** System response as a function of the analyte flow rate for an EPCO-coated cantilever exposed to a 75 ppm *m*-xylene solution.

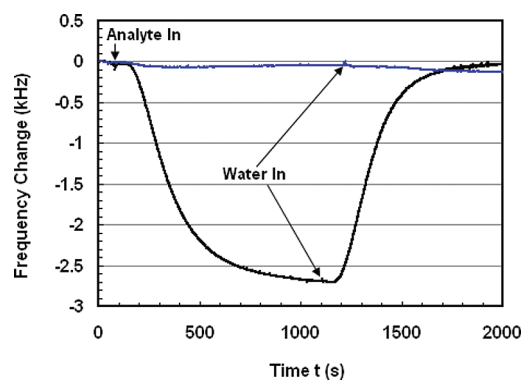
A flow rate of 200  $\mu\text{L}/\text{min}$  was used for all measurements. An upper limit estimate on the final volume of the flow cell is 40  $\mu\text{L}$ ; thus, the volume of fluid within the flow cell is replaced at least 5 times every minute.

## RESULTS AND DISCUSSION

Figure 3 presents the effect of the flow rate on the system response, i.e., the measured frequency change for a given analyte concentration. The measurements were performed using an EPCO-coated cantilever and a 75 ppm *m*-xylene solution. The system response increases with increasing flow rate and finally levels off at higher flow rates. For the measurements shown in Figure 3, analyte and water were each flowed for 15–20 min during the experiments to reach a steady response; this corresponds to passing at least 75 sample volumes through the flow cell. The data in Figure 3 suggests that, at lower flow rates, mass delivery to the measurement chamber is not fast enough to compensate for absorption by the packaging materials. During spray coating, not only the cantilever but also the entire chip surface is partially coated; thus, the chemically sensitive polymer is present throughout the package, not just at the cantilever surface. In addition to the actual polymer sensing film, the acrylic manifolds and also the silicone gasket material at the inlet and beneath the die may absorb analyte, thereby changing the solution concentration encountered by the cantilever especially at low flow rates.

At higher flow rates, mass delivery to the flow cell is sufficiently high to compensate for any absorption within the flow cell, and the sensor response thus becomes independent of the flow rate and can be considered to be the true chemical sensor sensitivity. On the basis of these results, a flow rate of 200  $\mu\text{L}/\text{min}$  was selected for all measurements. It should be noted that, despite possible analyte enrichment, silicone gaskets and acrylic parts were used here, as they provide excellent sealing to the die and allow for simple manufacturing, respectively; however, in a final device design, the cantilever die would be glued into the manifold and packaged using, e.g., epoxy, thereby rendering the entire package more chemically inert.

Figure 4 compares the frequency change of an uncoated 45  $\mu\text{m}$  wide, 200  $\mu\text{m}$  long, and 7.5  $\mu\text{m}$  thick cantilever to that of an

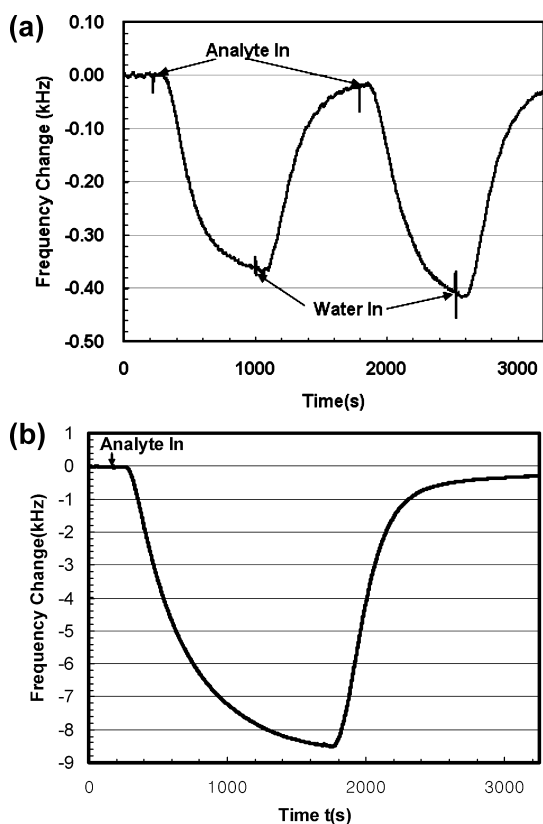


**Figure 4.** Frequency change of an uncoated 45  $\mu\text{m}$  wide, 200  $\mu\text{m}$  long reference cantilever (blue line) and a 75  $\mu\text{m}$  wide, 400  $\mu\text{m}$  long EPCO-coated cantilever to subsequent flow of 75 ppm *m*-xylene solution (starting at analyte in) and DI water (starting at water in). The uncoated device had a resonance frequency of 1090 kHz in water, and the coated device had a resonance frequency of 426 kHz in water.

EPCO-coated (2  $\mu\text{m}$  coating on each side of the cantilever) 75  $\mu\text{m}$  wide, 400  $\mu\text{m}$  long, and 7.5  $\mu\text{m}$  thick cantilever, each exposed to a 75 ppm *m*-xylene solution at a flow rate of 200  $\mu\text{L}/\text{min}$ . Clearly, the response of the uncoated cantilever is substantially smaller than that of the coated device, indicating that the measured frequency changes are caused by analyte partitioning into the polymeric sensing material and not due to, e.g., a density or viscosity change of the surrounding fluid. The small frequency drift evident for the uncoated reference cantilever is most likely due to a thermal drift. It should be noted that the control measurement should ideally be done with a cantilever of the same size as the sensing cantilever; due to design constraints, however, no two identical cantilevers were available at the time of testing.

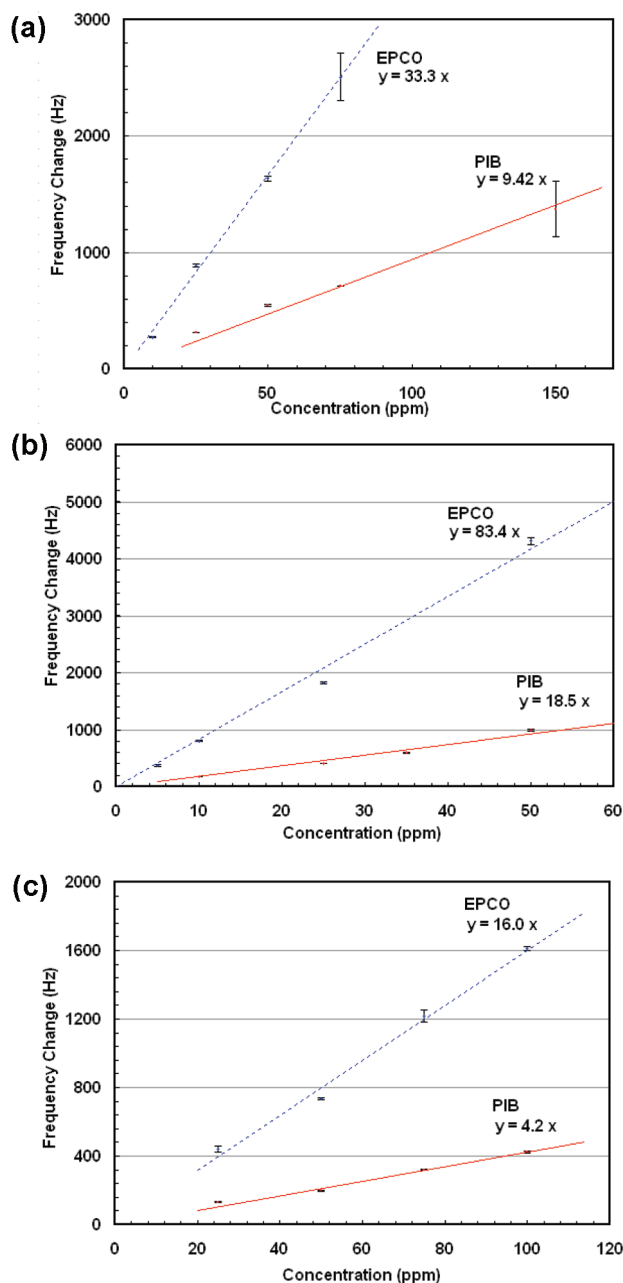
Figure 5a shows a sample measurement for an EPCO-coated cantilever, i.e., the frequency change of the cantilever following two subsequent exposures to a 5 ppm tetrachloroethylene solution. After exposing the sensor to the analyte solution for approximately 800 s, the measurement chamber is flushed with DI water for approximately 800 s. When conducting these measurements, the syringe pumps were switched from analyte solution to DI water and vice versa once the measured frequency change was <30 Hz within 3 min, indicating that the analyte concentration within the polymer layer was largely in equilibrium with the analyte concentration in the solution. The recorded data shows the signal transients during analyte absorption and desorption cycles. The baseline drift is mainly caused by temperature effects and may be considered negligible compared to the magnitude of the analyte response. Thermal drifts may be further minimized by appropriate measures for temperature stabilization, e.g., via thermoelectric heating/cooling. The measured frequency shift in response to a 5 ppm tetrachloroethylene solution was approximately 370 Hz, which yields a sensor sensitivity of approximately 75 Hz/ppm. A detailed estimation of the limit of detection (LOD) is given below.

Figure 5b shows an EPCO coated-cantilever responding to 100 ppm dichlorobenzene, yielding a frequency shift of 8.5 kHz at a base frequency of 426 kHz in water and a sensitivity of 85 Hz/ppm. An exponential fit of the absorption transient results in a time constant of 408 s with an approximately 1600 s long absorption period; thus, the frequency change was recorded over periods of at least 4 times the time constant.



**Figure 5.** (a) Response of EPCO-coated cantilever, i.e., frequency change vs time, to two subsequent exposures to a 5 ppm tetrachloroethylene solution. The resulting sensitivity is approximately 75 Hz/ppm. The spikes at the top and bottom of the peaks are due to pressure transients when the pumps are switched. (b) Response of EPCO-coated cantilever, i.e., frequency change vs time, to an exposure to a 100 ppm dichlorobenzene solution. The resulting sensitivity is approximately 85 Hz/ppm. The device tested here had a resonance frequency of 426 kHz in water.

For direct quantification of *m*-xylene, trichloroethylene, and chlorobenzene in water using PIB and EPCO sensing layers, six calibration curves were obtained (Figure 6a,b,c). For each analyte, four concentrations in the range of 0 to 150 ppm(v/v) were analyzed in duplicate with error bars representing the calculated standard deviation. The achieved chemical sensitivities were derived from linear regressions  $y = mx$  with zero intercept and are provided in Figure 6a,b,c. The goodness of the fit ( $R^2$ ) is typically around 0.99. Evaluating Figure 6a,b,c, it appears that the EPCO polymer layer provides superior enrichment properties for the tested analytes in contrast to PIB. However, the EPCO membrane thickness was 8 times the PIB membrane thickness due to better film adhesion of EPCO, and thus, the obtained sensitivities need to be normalized by the film thickness for comparison. Given the experimental results, it is evident that EPCO provides favorable properties as a sensing membrane given the increased membrane thickness that may be applied and the resulting increase in sensitivity. Analyzing Figure 6a, it is evident that the error bars for the highest concentration of *m*-xylene for both EPCO and PIB layers are significantly larger than the error bars at lower concentrations. This is attributed to the polymer layer approaching saturation and, thus, producing less repeatable results. Otherwise, the error bars for the measurements shown



**Figure 6.** Measured frequency change of EPCO-(blue symbols) and PIB-coated (red symbols) cantilevers as a function of (a) *m*-xylene, (b) tetrachloroethylene, and (c) chlorobenzene concentration in water. The lines are linear fits to the measurement data according to the equation given in the graph.

in Figure 6b,c are minimal, thereby indicating excellent measurement reproducibility.

The measurements used to create the calibration curves were performed in random order, sometimes with higher concentration solutions being measured before lower concentrations or vice versa. A flow rate of 200  $\mu\text{L}/\text{min}$  was used for all the measurements. The random order of the measurement helps to address the concern that the materials used for packaging may be absorbing analyte and changing the concentrations within the flow cell. If this were the case, linear calibration curves could not be created from the data, due to the fact that a lower concentration solution measurement after a higher concentration one would result in analyte desorption from the packaging during the lower

**Table 1. Calculated Limits of Detection for Volatile Organics Measured in Water Based on the Presented Measurements**

chemical	EPCO LOD (ppb)	PIB LOD (ppb)
<i>m</i> -xylene	113	289
tetrachloroethylene	46	170
chlorobenzene	224	690
chloroform	3600	5800
ethylbenzene	144	570
toluene	376	1100
epichlorohydrin	10 900	25 000
dichlorobenzene	43	(not tested)
trichloroethylene	341	(not tested)
benzene	1400	(not tested)
dichloropropane	980	(not tested)
carbontetrachloride	216	(not tested)

concentration measurement. This, in turn, would make the concentration higher than expected and make the response inconsistent with other measurements. The ability to establish robust calibrations confirms that at a 200  $\mu\text{L}/\text{min}$  flow rate true chemical sensitivities of the sensors are recorded and that sorption into packaging materials is not affecting the sensor response. Moreover, the excellent measurement repeatability observed when establishing the calibration curves provides evidence that these microresonators may be successfully applied for the quantification of volatile organic compounds (VOCs) for in situ water monitoring applications.

The obtained experimental results are summarized in Table 1. The EPCO-coated device provided a frequency stability of 1.1 Hz, and the PIB-coated device had a stability of 1.0 Hz, both determined using the Allan variance method at a gate time of roughly 4 s in water. While all the measurements were performed at a gate time of 1 s, the data was averaged for a 4 s gate time using MATLAB (Mathworks, Natick, MA). Limits of detection were calculated using eq 1 shown above. While for the analytes shown in Figure 6a,b,c detailed calibration curves were established, the response to further analytes was tested during single measurements for estimating the achievable sensitivity. It is important to note that the calculated limits of detection are specific to the system tested here and further optimization using, e.g., alternative cantilever geometries may allow for further lowering the achieved limits of detection. Additionally, several analytes were tested at the same concentration with both PIB and EPCO and yielded different transient response characteristics. For example, the EPCO coated device gave a full response to 75 ppm *m*-xylene in around 21 min, while the PIB coated device took 12 min. Comparison of the response times and other characteristics of the transient responses may yield additional information that could be used to distinguish between different analytes.<sup>30</sup>

From the presented data, the distinct advantages of the use of the in-plane mode are evident. The estimated LODs around 100 ppb represent a roughly 1 order of magnitude improvement compared to values reported for out-of-plane cantilevers in water.<sup>18</sup> From eq 3, the limit of detection for a resonant sensor is a function of the short-term frequency stability divided by the sensitivity. Using the first in-plane mode results in a significant improvement

in both sensitivity and stability. The determined quality factors in liquid for in-plane mode cantilevers were 4 times higher than those reported for out-of-plane mode devices in liquid. In addition, as evidenced by the reduced frequency shift in liquid compared to air (5–10% for the in-plane mode vs 50% for the out-of-plane mode), the added fluid mass affects the device performance much less for in-plane mode devices. Thus, compared to out-of-plane cantilevers, the gravimetric sensitivity of the in-plane cantilevers is substantially improved when immersed in water. In summary, the achieved improvement in LOD is attributed to both improved chemical sensor sensitivity and improved frequency stability for in-plane cantilevers in water-based solutions.

## CONCLUSIONS

The results presented here demonstrate a limit of detection enhancement by roughly 1 order of magnitude compared to previously reported cantilever-based sensing devices fabricated in silicon for the detection of volatile organics in water.<sup>13,18</sup> Although the achieved limits of detection are not yet as low as previously reported measurements using surface acoustic wave (SAW) devices,<sup>23</sup> they do approach the same order of magnitude. The two main advantages of the system presented here are (1) that the fabrication process allows a single silicon substrate to comprise cantilevers and the readout circuitry allowing for highly parallel batch fabrication methods to manufacture the sensors and (2) that the cantilevers themselves have a very small footprint allowing them to be arrayed and used in embedded applications. While the current experiments were not performed using fully integrated circuitry, the electronics to operate the tested devices have been fabricated as a single integrated circuit (IC) and have already been proven for chemical sensor testing in the gas phase.<sup>31</sup>

Further improvements of the present chemical sensing system will consist of using more chemically inert materials for the packaging and combining the cantilever with an integrated circuit for closed-loop operation, as well as using laterally vibrating cantilever geometries exhibiting higher *Q* factors. Specifically, improvements to the packaging include (1) coating the acrylic manifolds with parylene to prevent analyte absorption, (2) attaching the die to the bottom manifold using epoxy instead of silicone, and (3) using a fluorosilicone gasket to seal to the ring on the top of the die.

Future work will focus on translating this technology into a hand-held field measurement system. The major aspects to address are improving the selectivity toward different analytes using cantilever arrays with different chemically sensitive coatings and reducing baseline drifts resulting from environmental parameters such as temperature. A valid concern for the system as presented in this work is that it would be nearly impossible to quantify the components in a complex mixture of volatile organics dissolved in water. As mentioned above, an array approach using partially selective layers and a properly trained algorithm could overcome this problem.<sup>30,32</sup> Additional approaches to making a selective array are using multiple sensor types in one package<sup>33</sup> or improving the molecular recognition by, e.g., molecular

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imprinting of the sensing film;<sup>34,35</sup> implementing these improvements may further enhance the versatility of such compact sensing platforms.

In conclusion, polymer-coated, laterally excited cantilevers show potential for low-level detection of volatile organic contaminants in water. Due to their small size, ease of manufacturing,

and their ability to be integrated with CMOS circuitry, the cantilevers presented here could be integrated into a low-cost hand-held device or deployed as part of an embedded sensing system for monitoring water quality in a wide variety of measurement scenarios.

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