Research Report

A Chemical Sensor Based on a Microfabricated Cantilever Array with Simultaneous Resonance-Frequency and Bending Readout

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Abstract **-** We present a chemical sensor based on a microfabricated array of eight silicon cantilevers actuated at their resonance frequency and functionalized by polymer coatings. The operating principle relies on transduction of chemical or physical processes into a mechanical response. After exposure to analyte vapor, analyte molecules diffuse into the cantilever coating, which begins to swell. Jointly with the mass increase, a change of interfacial stress between coating und cantilever occurs, resulting in a bending of the cantilevers. Our setup allows the simultaneous detection of cantilever oscillation and bending of eight cantilevers by time-multiplexed optical beam deflection readout. The a.c. component of the cantilever response is demodulated, and the cantilever resonance frequency is tracked by a custom-built phase-locked loop. By filtering out the a.c. component (oscillation), the d.c. signal (bending) is extracted, yielding information on mass as well as surface stress changes simultaneously. Detection results of water, primary alcohols, alkanes and perfumes are presented.

1. Introduction

Miniaturization of chemical sensors [1-4] is a major requirement in industrial applications. Demands of increasing importance include very sensitive analyte detection, determination of physical properties on minute amounts of material, continuous quality and process control, measurement of small quantities, a versatile application range, the ability to tailor sensors to applications, and so forth. Miniaturization also entails greater complexity, higher functionality and compactness. Here we present a type of sensor that takes advantage of a transduction method different to those in other chemical sensors. Instead of detecting changes in e.g. electrical properties of sensor materials, we measure mechanical responses of thin beams of silicon, so-called microcantilevers, arranged in a microfabricated array. Each of these cantilevers is coated on one side with a sensor layer that shows an individual response to analyte molecules. To obtain information on the analyte, we investigate cantilever responses due to diffusion processes of the analyte in the sensor layer or chemical reactions with the sensor layer. The sensor layer transduces changes of its physical properties or energy transfers related to chemical reactions into a mechanical response. When the sensor layer is exposed to an analyte, the cantilevers mechanically respond by bending on the nanometer scale because of surface stress change or heat transfer and by mass change. The latter is detected by measuring resonance frequency shifts while actuating the cantilever (dynamic mode). Static deflection can be extracted from this signal by filtering out the a.c. component. The remaining d.c. signal reflects the bending due to surface stress change at the interface between cantilever and polymer layer during absorption of molecules. If heat transfer is involved (e.g. from chemical reactions or phase transitions), bimaterial effects such as cantilever bending due to temperature changes in the bimetallic structure occur in addition to the static deflection owing to surface stress changes.

Figure 1 shows the static and dynamic operation modes of the microcantilevers and a scanning electron micrograph of a cantilever array.

These cantilever-based sensor techniques are derived from the atomic force microscopy (AFM) [5] technique, which utilizes a sharp tip to scan a surface topography controlled by a feedback loop, e.g. by keeping the force between tip and surface constant. For the use as a chemical sensor, neither a tip nor a feedback loop is required. To obtain chemical functionality, free-standing cantilever beams are coated by sensor layers or samples are attached directly to the cantilever beam prior to exposure to the analyte vapor. The mechanical response in either the static mode (deflection) or the dynamic mode (shift of resonance frequency) is measured on the free-standing cantilever without resorting to a feedback loop.

Cantilever sensors can be employed in miniaturized versions of equivalent "classical" methods, often with increased sensitivity. Initial experiments on catalytical reactions [6] demonstrated that picojoule-level sensitivity in calorimetry can be achieved using the cantilever techniques. Calorimetric investigations of an alkane sample have been performed directly on the cantilever, an example being the study of solid-solid phase transitions in alkanes [7], down to the picomole level [8,9]. Single-cantilever sensors have been successfully used to study photothermal spectroscopy [10], surface stress [11-13] and infrared light absorption [14]. In the dynamic measuring mode, several operation conditions have been proposed, and tested. By determining the resonance frequency of the cantilever before and after mounting a small sample at the cantilever apex the mass of the sample can be measured with sub-picogram resolution. Subjecting the sample attached to the resonating cantilever to programmed heating in a controlled environment allows thermogravimetry on nanogram amounts of a sample [15]. By coating the

cantilever with a sensor layer, the resonating cantilever can detect a wide range of analyte concentrations in the environment.

In the so-called static mode the static deflection of the cantilever on exposure to an analyte is measured. This bending is caused by surface stress changes due to analyte interaction with the sensor coating of the cantilever [13]. Operating a cantilever in the static mode in liquids makes it possible to use the device as a biosensor. Detection of protein adsorption, antibody-antigen recognition, and DNA hybridization has been successfully demonstrated [16-17].

The use of cantilevers in arrays provides the capability of measuring differential responses, i.e. differences between cantilever responses. Some of the cantilevers are coated with sensor layers, such as metal coatings that react with analytes, whereas others are coated with a layer inert to the analytes presented, e.g. a gold layer. Reactions that affect the entire cantilever array, such as reactions on the uncoated back side of cantilevers as well as thermal drifts and calibration offsets, can be cancelled out using differential measurements [18-19].

2. Experimental

2.1 Cantilevers

A cantilever is characterized by its geometrical dimensions, its spring constant and its resonance frequency. The spring constant can be calculated in the following way [11]:

$$k = E t^3_{Cant} \, w_{Cant} \, (4 l^3_{Cant})^{-1}, \tag{1}$$

where t_{Cant}, w_{Cant} and l_{Cant} are the thickness, width and length of the cantilever, respectively, and E is the Young's modulus of the material used (Si). Equation (1) is only valid for $l_{Cant} \gg t_{Cant}$.

The resonance frequency of a long and thin rectangular cantilever is calculated according to [11]

$$f_0 = (2\pi)^{-1} \, (E/\rho)^{-1/2} \, t_{Cant} \, l^2_{Cant}, \tag{2}$$

where ρ is the density of the cantilever material.

Absorption of analyte vapor in the sensor layer produces stress at the interface between the cantilever and the sensor layer, leading to a bending of the cantilever. Stoney's law [20] gives the dependence of the surface stress change on the bending radius of the cantilever:

$$\sigma = E \, t^2_{Cant} \, (6R(1-v))^{-1}, \tag{3}$$

where v is the Poisson's ratio of the cantilever material and R the bending radius of the cantilever. The following material constants for silicon have been used: $E = 1.7 \times 10^{11} \, Nm^{-2}$, $\rho = 2.33 \times 10^3 \, kgm^{-3}$, and $v = 0.25$.

Via the oscillation of the cantilever at its resonance frequency using an external piezoelectric crystal, small changes in cantilever mass can be detected. This implies its application as a highly sensitive microbalance capable of resolving mass changes in the sub-picogram range. The mass change depends on the resonance frequency of the oscillating cantilever in the following way:

$$\Delta m = k \, (4n\pi)^{-1} \, (f_1^{-2} - f_0^{-2}). \tag{4}$$

Here k denotes the spring constant of the cantilever, n is a geometry-dependent correction factor ($n = 0.24$ for rectangular cantilevers), f_0 is the resonance frequency prior to the experiment, and f_1 is the resonance frequency during the experiment. Equation (4) is only valid if the spring constant k does not change during the experiment. Diffusion of analyte molecules through the cantilever coating may change the elastic constants of the cantilever.

Cantilever sensor arrays have been microfabricated at the Micromechanics Department of IBM's Zurich Research Laboratory from silicon using combined dry and wet etching techniques. A series of eight cantilevers is assembled in a chip. The cantilever dimensions are chosen depending on the application. The length of the cantilevers was selected to be 500 μm, their width 100 μm. For operation in the dynamic mode, a thickness of 8.6 μm was chosen, resulting in a resonance frequency of approximately 50 kHz. For operation in the static mode, the thickness was selected to be approximately 1.2 μm. Eight cantilever sensors are linearly arranged at a pitch of 250 μm.

2.2 Measurement setup

The sensor array is placed in an analysis chamber that holds the components for detection of cantilever responses. These include optical cantilever-deflection detection by means of an array of vertical-cavity surface-emitting lasers (VCSEL, Avalon Photonics Zurich, Switzerland), collimation optics, and a position-sensitive detector (PSD, SiTek, Partille, Sweden). In addition, the measurement setup comprises a gas-handling system for controlling the gas flow through the analysis chamber, data-acquisition and control electronics, and a personal computer (PC) that controls the gas flow and cantilever readout. Figure 2 schematically shows the measurement setup. The analysis chamber consists of a small x-y positioning table for alignment of cantilevers and light sources, a piezoelectric crystal for actuation of the cantilever array, a tube containing the VCSEL light sources, collimation optics, and PSD including a current-voltage converter and preamplifier. Analyte vapor is introduced into the chamber via a sample port consisting of a vial containing the analyte. Two syringes are introduced in the sample headspace, one to blow dry nitrogen gas into the headspace regulated by a mass flow controller/meter (Bronkhorst HI-TEC, AK Ruurlo, The Netherlands), the other for probing the headspace. Two valves are used to allow the nitrogen gas flow to bypass the analyte headspace for purging the analyte chamber.

The deflection of the cantilever sensors is read out optically via a beam-deflection technique. A linear array of eight VCSEL is sequentially addressed in a time-multiplexing mode [18] such that at any time only one light source is switched on allowing the deflection of each cantilever to be determined sequentially using only one PSD. The switching frequency is typically 3 Hz. A collimation optics consisting of two achromatic doublets lenses produces a 1:1 projection of the light sources onto the cantilever sensors. The light is reflected off the cantilever surface and collected by a linear PSD. A two-stage preamplifier is mounted directly on the back side of the PSD to transform the currents produced by the incident light spot into voltages. This determines the position of the light spot on the PSD. The voltages are digitized by an analog-to-digital conversion board in the PC. The PC also controls the switching of the VCSEL light sources.

2.3 Detection electronics and software

The voltages indicating the position of the incident light spot on the PSD are amplified by a preamplifier. Electronics developed in-house is used for data acquisition, preprocessing and amplification. A microcontroller-based printed circuit board (PCB) controlled by software on the

PC converts the deflection signals into a digital format and sends commands for time-multiplexing of the VCSEL light sources and communication with the other PCBs via a bus system. A phase-locked loop (PLL) PCB is used for frequency demodulation in the dynamic mode. Additional boards are responsible for acquisition of static cantilever deflections and intensity control of the VCSEL light sources. The PCBs use memory in the microcontroller (memory mapping), which enables a high access speed and simplified programming procedures. The microcontroller also transmits commands for switching the valves.

The signal from the oscillating cantilever consists of an a.c. and a d.c. component. The resonance frequencies of the cantilevers are determined by demodulating the frequency of the cantilever response measured so as to obtain the a.c. component of the signal. The static deflection signal (d.c. component) is generated from the cantilever response by eliminating the a.c. component in the signal via lowpass filtering. The properties of the lowpass filter are chosen in such a way that the sampling theorem is fulfilled, i.e. no aliasing occurs. To compensate any individual initial bending of the cantilevers, an offset voltage is added to the d.c. component prior to measurements.

2.4 Data processing

As differences in cantilever responses might not be evident at first glance, refined procedures for data processing have to be applied, such as artificial neural networks (ANN). ANN approximate relations between input and output signals based on appropriate training procedures and a sufficient number of training data sets. Here we used a multilayer perceptron topology of the neural network and trained it with a backpropagation algorithm.

2.5 Cantilever functionalization

Cantilever arrays have been functionalized by coating individual cantilevers with a polymer layer having a thickness of 2-3 μm by spreading a droplet of polymer solution on each cantilever. Tables 1 and 2 summarize the cantilever coatings used in the experiments. Other cantilever arrays have been coated uniformly with polyvinylchloride (PVC).

2.6 Measurement procedure

2 ml of liquid analyte is filled into a vial closed by a septum. Analyte vapor in the vial headspace is extracted and transferred to the analyte chamber using a flow of dry nitrogen saturated with analyte vapor. The total flow (analyte vapor and dry nitrogen) through the analyte chamber is kept constant at a value of 100 ml/min, controlled by digital mass flow meters/controllers. In experiments "90% analyte" means that 90 ml/min dry nitrogen saturated with analyte vapor is added to 10 ml/min of dry nitrogen. To avoid delays in adjusting the gas flows, two electrically controlled three-terminal valves are used to direct the gas flow through the analyte vial or to bypass the vial. To avoid pressure changes, tube resistances have been selected to be equal in both paths. After typically 130 s of cleaning with dry nitrogen, the valves are switched to allow analyte vapor to be directed through the analyte chamber for 120 s. After this exposure step, dry nitrogen is allowed to flow through the analyte chamber during typically 300 s to purge chamber and tubes.

3. Results and Discussion

3.1 Water
Detection of water vapor plays an important role in many applications. To investigate which cantilever coatings are suitable for detecting water, a sensor array functionalized according to Table 1 was used. Figure 3 shows simultaneously acquired dynamic and static cantilever responses on exposure to various concentrations of water vapor. It is remarkable that certain sensors show quite a large response to water vapor (frequency shift up to 120 Hz and 250 nm deflection) whereas others do not. Especially cantilever coating consisting of polymers soluble in water, such as PVA, CMC and PVP, show large signals. The signals are produced by diffusion of analyte into the polymer layer, resulting in a swelling of the polymer. The mass increase implies a decrease in resonance frequency and a change in surface stress at the interface between the polymer and the cantilever surface, which results in a bending of the cantilever. The deflection signal increases owing to the compressive nature of the surface stress change on the functionalized surface of the cantilevers. After the flow of nitrogen gas saturated with analyte has been exchanged for a flow of dry nitrogen gas, the analyte diffused into the polymer layer begins to diffuse out of the polymer into the environment, leading to a decrease of mass on the cantilever: the resonance frequency increases. Simultaneously, the surface stress at the interface between polymer layer and cantilever is reduced, resulting in a decrease in deflection. Note that the dynamic and static responses do not reach a constant value for all concentrations and that the time constants differ in static and dynamic modes. This is due to the fact that the static response is dominated by stress change at the surface, and the dynamic response results from the diffusion of the analyte within the polymer, simultaneously with a partial dissolution of the polymer.

The chemical nature of the polymer layer is responsible for hydrophilicity, polarity and extent of swelling capability of the cantilever coating, producing various types of calibration curves depending on polymer material. Whereas polymers such as PVA, CMC and PVP strongly absorb water, other polymers such as PU, PS and PMMA are relatively insensitive against water exposure (maximum frequency shifts of typically 10 Hz and maximum deflections of 30 nm). The PVC-coated sensor exhibits a cantilever response in an intermediate range.

3.2 Primary alcohols
A standard system of analytes is the homologous series of primary alcohols. Based on the findings in the preceding section, all cantilevers in an array were coated with a PVC polymer layer to reduce the sensitivity against water on the one hand and to provide signals sufficiently large to be measured easily on the other hand. The analyte concentration was set to 90%. Typical cantilever responses measured are shown in Figure 4 for methanol, ethanol, 1-propanol and 1-butanol. The largest and fastest cantilever responses in both dynamic and static mode are observed in methanol, which is the smallest of the analyte molecules investigated. Methanol has the largest vapor pressure among the primary alcohols. The small size of the molecule implies short diffusion times within the polymer. After the experiment, the initial baseline level is reached again, proving the reversibility of the experiment.

To study the influence of the analyte concentration on the cantilever responses, we varied the analyte gas flow from 20 to 90 ml/min, in steps of 10 ml/min. The total flow through the analyte chamber was kept constant at a value of 100 ml/min by mixing the analyte gas flow with the corresponding amount of dry nitrogen gas. Figure 5 shows the dependence on analyte concentration of the cantilever responses in dynamic and static modes for a PVC-coated

cantilever. The measurable concentration range depends on the polymer material selected. For example, PMMA allows responses in the dynamic mode to be measured between 10 and 90% analyte. A chart plotting concentration vs. maximum frequency shift and concentration vs. maximum deflection reveals an increase in the magnitude of cantilever response with concentration (Figure 6). The dependence is linear for the deflection signal, and is strictly monotonous for the resonance frequency shift signal, but exhibits higher-order terms, such as a parabolic term. Such a deviation from the linear dependence may be interpreted as contributions due to changes in the elastic constants of the cantilever. A decrease in the cantilever spring constant owing to swelling of the polymer layer implies a softening of the coated cantilever. Such an effect would produce the observed increase in frequency shifts at high analyte concentrations.

The analyte injection time determines the amount of analyte that is transferred to the cantilever array. If the amount of analyte is too large, the polymer layer might be saturated, and additional analyte will no longer produce an increase in the signal. We varied the injection time of methanol vapor into the analysis chamber from 60 to 200 s in steps of 20 s, using the same cantilever array with PVC coating on all cantilevers as above. As expected, an increase in frequency shift and deflection is observed with increasing injection time (Figure 7). This reflects the mass increase of analyte in the polymer. Whereas in the dynamic mode no saturation is observed, the static cantilever response levels off for longer injection times. As the interface area between cantilever surface and polymer layer is responsible for the static deflection signal, the range of useful injection times is smaller than in the dynamic mode, where the volume of the polymer layer determines the saturation limit.

In addition, the headspace volume, i.e. the volume above the liquid in the analyte vial filled with analyte vapor, could influence the cantilever responses. However, no dependence of the cantilever responses in dynamic or static modes was observed by varying the headspace volume by a factor of four. This implies that in all our experiments the headspace volume was sufficiently largeto be able to saturate the analyte gas flow with analyte.

3.3 Alkanes

In contrast to polar analytes, such as primary alcohols and water, alkanes are apolar molecules. This has an impact on the diffusion properties in the polymer. In this subsection the results on the homologous series of alkanes (hexane to dodecane) using PVC-coated cantilevers are presented. Figure 8 shows cantilever responses in dynamic and static mode for various alkanes. Interestingly, the maximum frequency shift does not increase in a monotonous way as a function of chain length. Moreover, the cantilever responses in dynamic mode can be divided into two groups of analytes: one group consisting of alkanes with an even number of carbon atoms, the other of alkanes having an odd number of carbon atoms. No such separation is observed in static mode. The reason for this splitting in the behaviour can be found in the differing structural and physical properties. Alkanes with an even number of carbon atoms exhibit higher melting points than those with an odd number of carbon atoms. A similar behaviour is also found for the boiling points. This implies a slightly larger vapor pressure for alkanes having an odd number of carbon atoms than for those having one carbon atom fewer. Alkanes with a shorter chain produce cantilever responses with larger frequency shift and deflection than alkanes with a longer chain do, as the former have a larger vapor pressure than the latter. This implies that the concentration of heptane is actually higher than that of hexane even though the analyte gas flows are adjusted to the same value (90 ml/min).

3.4 Perfume oils

An example for the characterization of complex analytes is the investigation of perfume oils (Spinnrad GmbH, Gelsenkirchen, Germany). We selected perfume samples with a standardized content of 2.5% perfume oil in ethanol: 'Rose', 'Camomile', 'Heliotropin', 'Corps' and 'Leather'. Of perfume oil, 100 µl was filled into a closed vial. A dry nitrogen gas flow of 80 µl/min was saturated with these analytes. A cantilever array functionalized as displayed in Table 1 was exposed to the analytes for 120 s. Figure 9 shows all the cantilever responses in the dynamic mode in one graph. The curves were normalized to the magnitude of sensor 3 for later use with neural network techniques. Every measurement produces a new curve, which is the data set for a neural network. Differences between individual perfume oils can be observed when comparing, for example, the responses of sensor 1. We observe that the curves measured are very similar for each of the analytes.

A feed forward neural network was trained with a set of five curves per analyte using a gradient descent momentum backpropagation algorithm with adaptive learning rate. The topology of the neural net is displayed in Table 3. The learning curve displaying the mean squared error during validation for the perfume training sets is shown in Figure 10(a). The neural net is able to gather information on analytes (training curve) and has the capability to generalize because the mean squared error of the validation curve decreases in a similar way as the training curve. If the neural net is presented one of the ten validation data sets (which have not been used for training), the neurons in the third layer produce a response. The validation data set shown in Figure 10(b) acquired on the heliotropin perfume oil produces a neural network response close to 1 for heliotropin, see Figure 10(c). This implies that the trained neural network is capable of identifying perfume vapors after presentation of the training sets.

4. Conclusion

We demonstrated the application of micromechanical cantilever arrays as chemical sensors using a setup for the simultaneous detection of resonance frequency and bending. Information on cantilever bending and resonance frequency shifts during exposure to analyte vapor can be used for qualitative and quantitative characterization and recognition of a variety of chemical substances, such as water, primary alcohols, and alkanes. Based on the pattern of cantilever responses, the setup can be used for the characterization of complex analytes, such as perfume oils. The discrimination power is greatly enhanced by the use of neural network techniques. Application areas of such sensors are mainly in quality and process control. The application of functionalized cantilever arrays as chemical sensors is only a first step towards a widespread use of micromechanical structures. Recent publications [16, 21-24] point out the large potential of biochemical applications using micromechanical sensors in liquids for the study of protein adsorption, antibody-antigen recognition, DNA hybridization, and rapid medical diagnostics. Sensing is not the only application of micromechanical stuctures. By using functionalized nanomechanical membranes as lid, a container could open in presence of drugs to release other substances very locally.

Acknowledgments

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**Table 1**: Cantilever coatings from polymer solutions.

Cantilever	Coating (5mg/ml solvent)		Solvent
1	CMC	Carboxymethylcellulose	Water
2	PVA	Polyvinylalcohol	Water
3	PVP	Polyvinylpyridine	Ethanol
4	PVC	Polyvinylchloride	Aceton
5	PU	Polyurethane	Dichloromethane
6	PU	Polyurethane	Dichloromethane
7	PS	Polystyrene	Toluene
8	PMMA	Polymethylmethacrylate	Toluene

Table 2: Cantilever coatings from polymer solutions.

Cantilever	Coating (5mg/ml solvent)		Solvent
1	PMMA	Polymethylmethacrylate	Toluene
2	PMMA	Polymethylmethacrylate	Toluene
3	PMMA	Polymethylmethacrylate	Toluene
4	PS	Polystyrene	Toluene
5	PS	Polystyrene	Toluene
6	PU	Polyurethane	Dichloromethane
7	PU	Polyurethane	Dichloromethane
8	PU	Polyurethane	Dichloromethane

Table 3: Parameters of the feedforward net.

Layer	Number of neurons	Activation function
1	15	tangent function
2	4	tangent function
3	5	logistic function
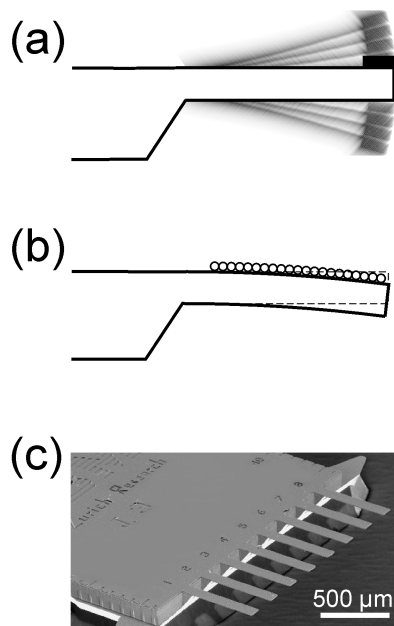
Figure 1: (a) Static mode. The cantilever bends owing to adsorption of analyte molecules and change of surface stress at the cantilever surface. (b) Dynamic mode. Absorption of analyte molecules in a sensor layer lead to shift in resonance frequency. (c) Scanning electron micrograph of a cantilever array.
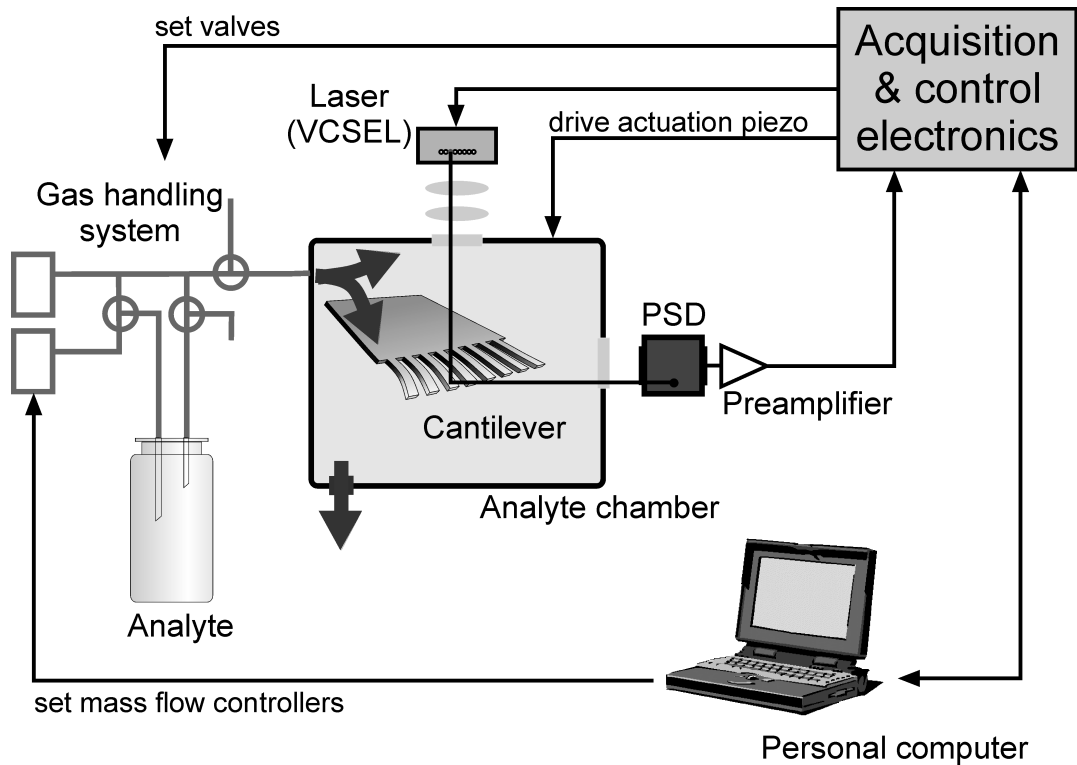
Figure 2: Schematic of the measurement setup.
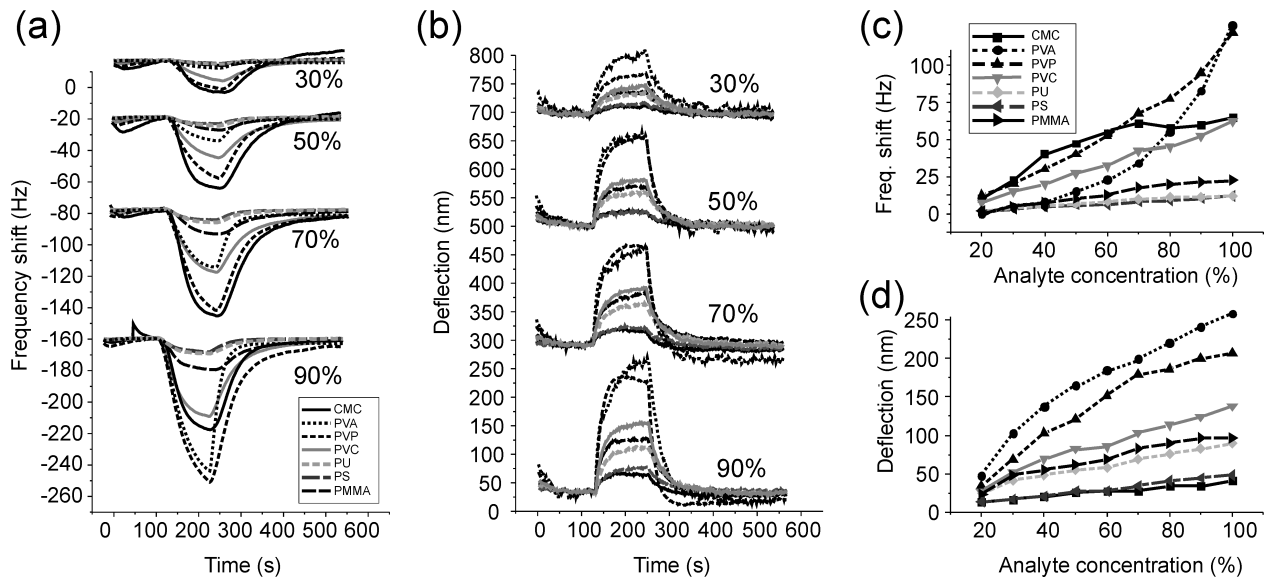
Figure 3: Cantilever responses (a) in dynamic and (b) in static mode on exposure to various concentrations of water vapor. (c) Dependence of the maximum frequency shift on water vapor concentration and (d) maximum deflection at a given concentration.
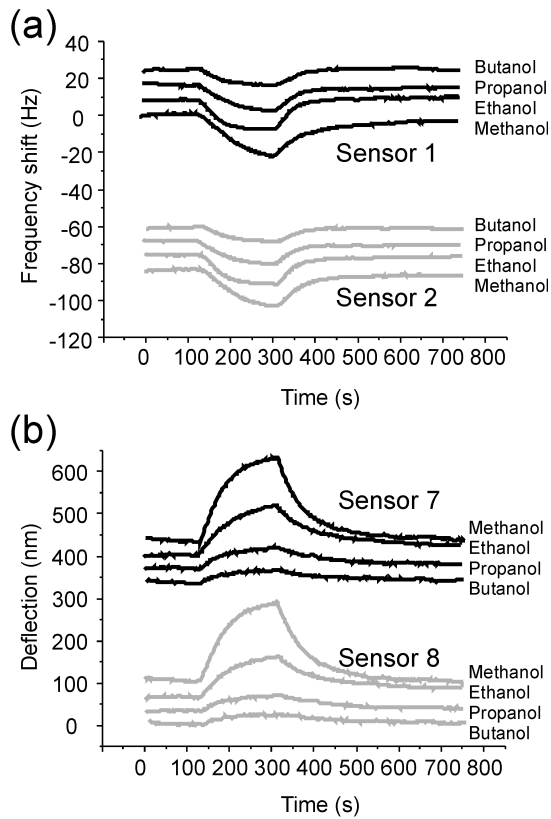
Figure 4: Cantilever responses to various primary alcohols (a) in dynamic and (b) in static mode. The concentration for all analytes was set to 90%.
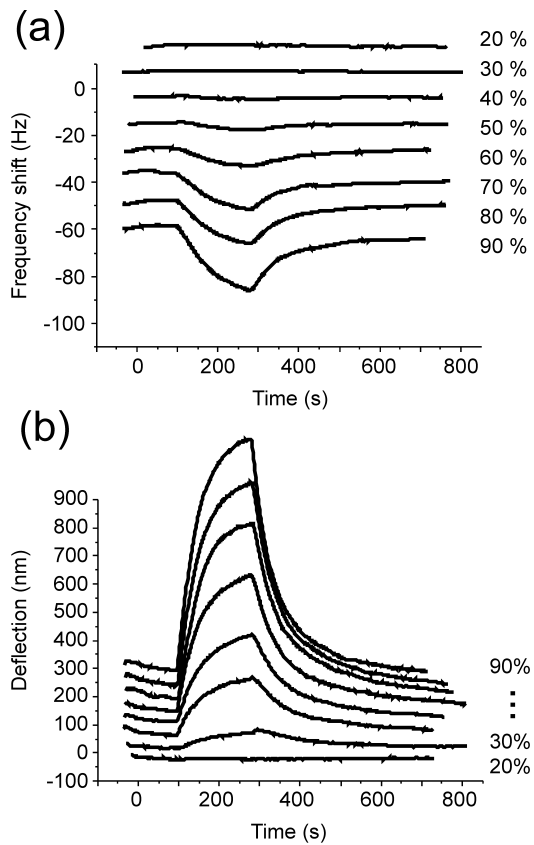

Figure 5: Cantilever responses for various methanol vapor concentration (a) in dynamic and (b) in static mode.
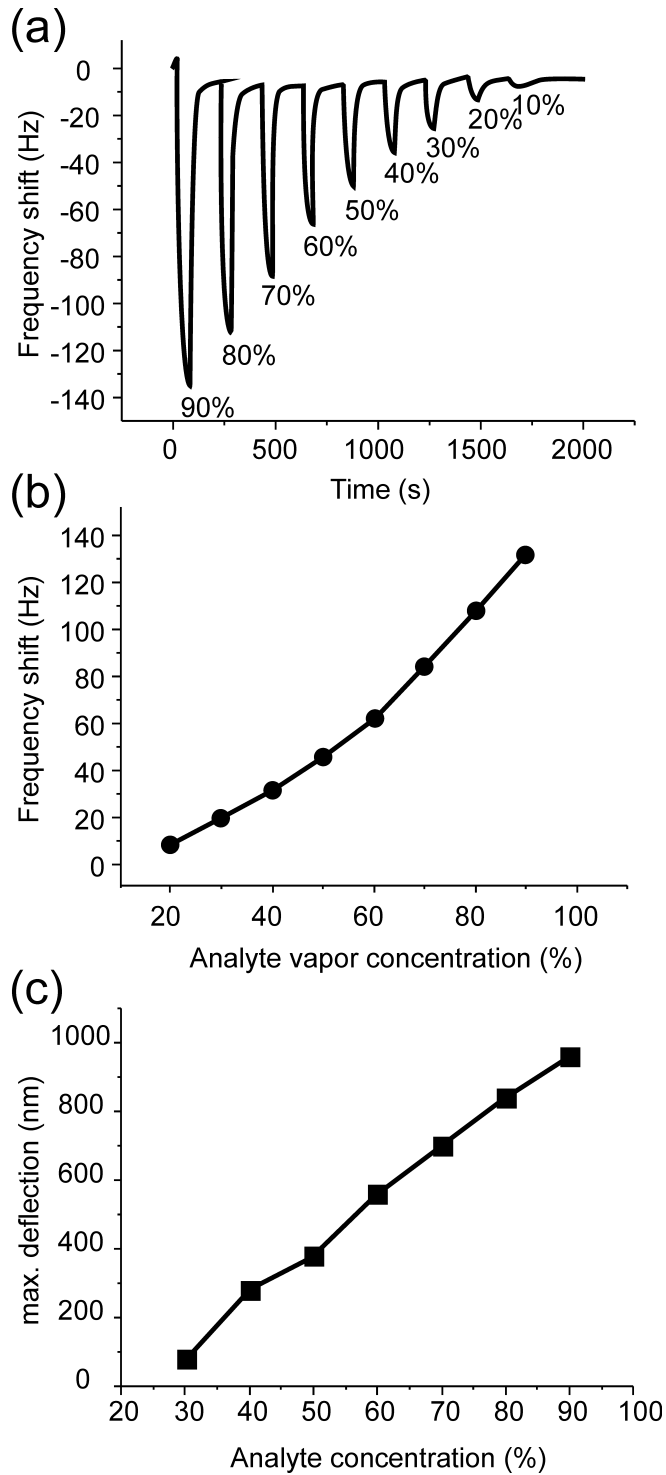
Figure 6: (a) Cantilever response of a PMMA coated cantilever in dynamic mode on various ethanol concentrations. (b) Maximum frequency shift plotted against ethanol concentration.
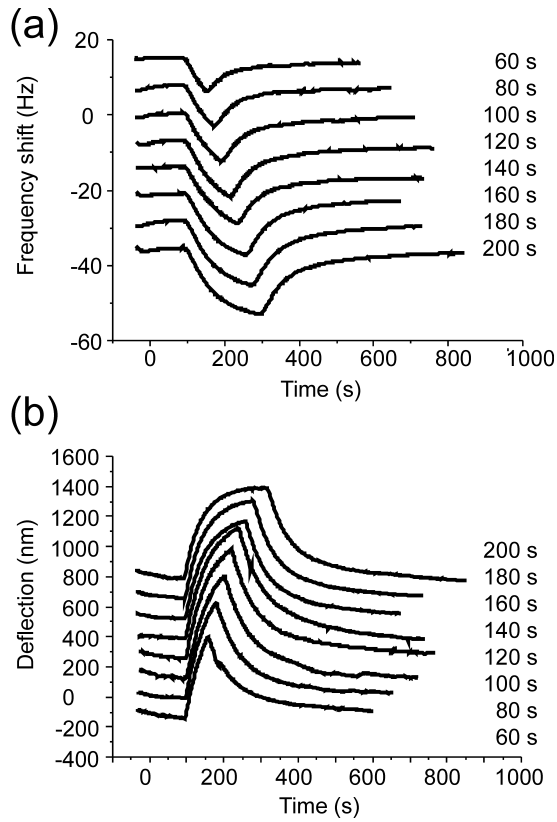
Figure 7: Cantilever responses for various analyte injection times (a) in dynamic and (b) in static mode. The cantilever coating is PVC and the analyte is methanol at a relative concentration of 90% in dry nitrogen.
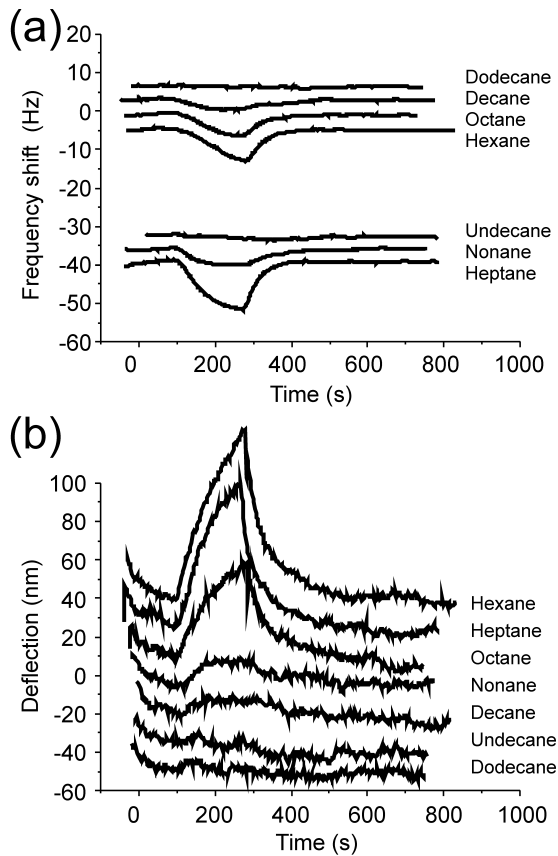

Figure 8: Cantilever responses of a PVC-coated cantilever to various alkanes (a) in dynamic and (b) in static mode.
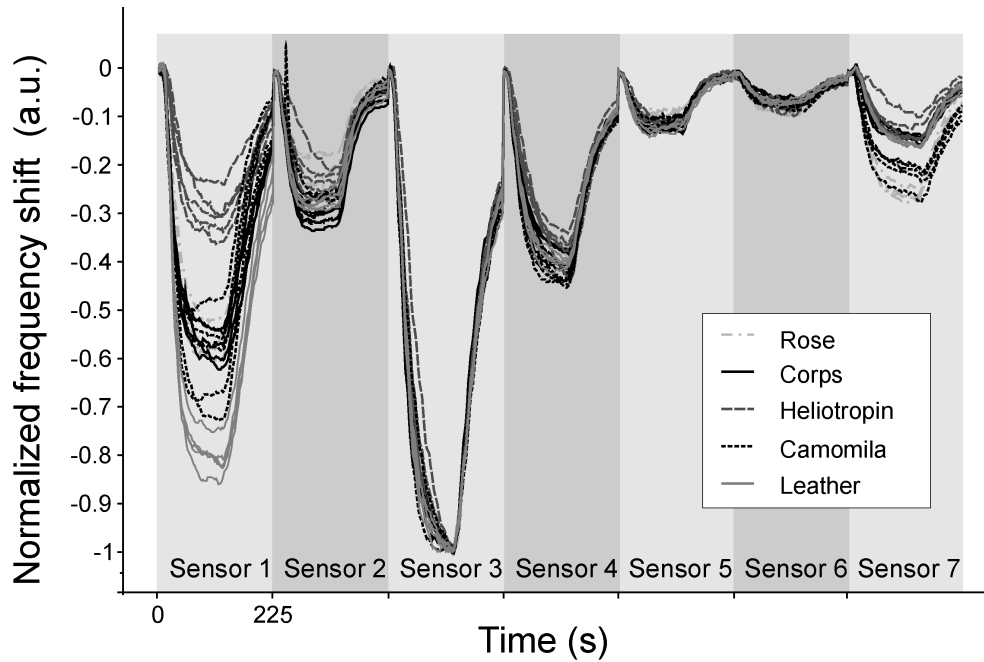
Figure 9: Cantilever responses in dynamic mode to various perfume oils. The responses are normalized by the response of sensor 3.
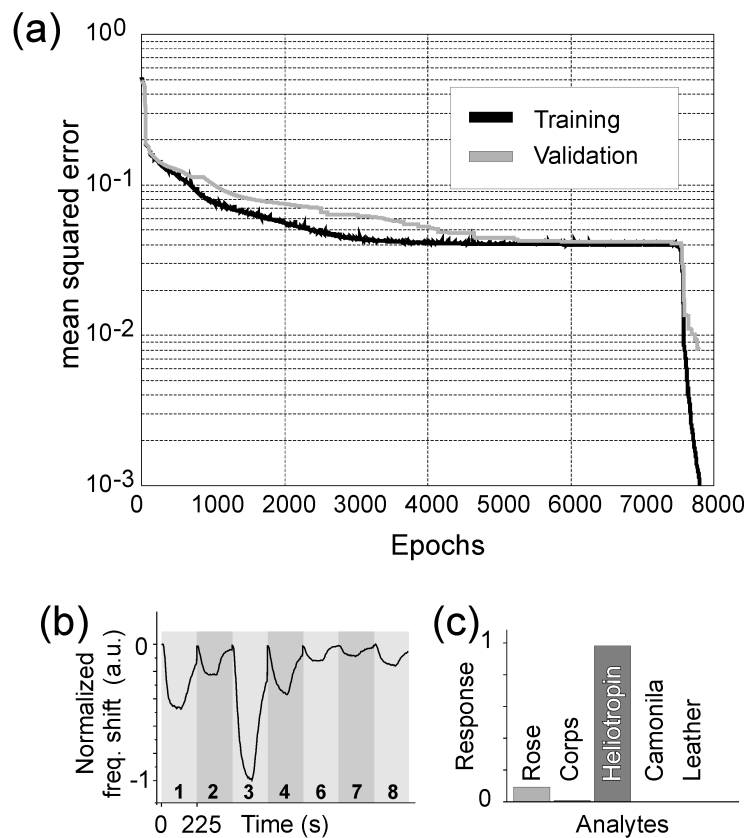

Figure 10: (a) Learning curve of a neural network while adaption of weight factors for recognition of perfume oils and corresponding validation curve. (b) Validation data set (cantilever responses) presented to the neural network. (c) Correct recognition of the analyte (heliotropin).