Sensors and Actuators B 140 (2009) 490–499

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Selective detection of sulfur derivatives using microfabricated tuning fork-based sensors

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ARTICLE INFO

Article history:
Received 6 January 2009
Received in revised form 6 March 2009
Accepted 27 April 2009
Available online 7 May 2009

Keywords:
Sulfur derivatives
Thiols
Disulfides
Sulfides
Quartz tuning fork
Selective detection

ABSTRACT

The paper describes an integrated sensor system that can selectively and reversibly detect sulfur derivatives in the presence of interferent molecules. This is accomplished by integrating analyte-specific sensing materials with optimized filter materials. Microfabricated quartz tuning fork arrays are used to provide fast, accurate and low-cost transduction of the analyte binding events into electronic signals. The concept is demonstrated for detection of three sulfur derivatives—dimethyl disulfide, ethanethiol and methylsulfide.

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1. Introduction

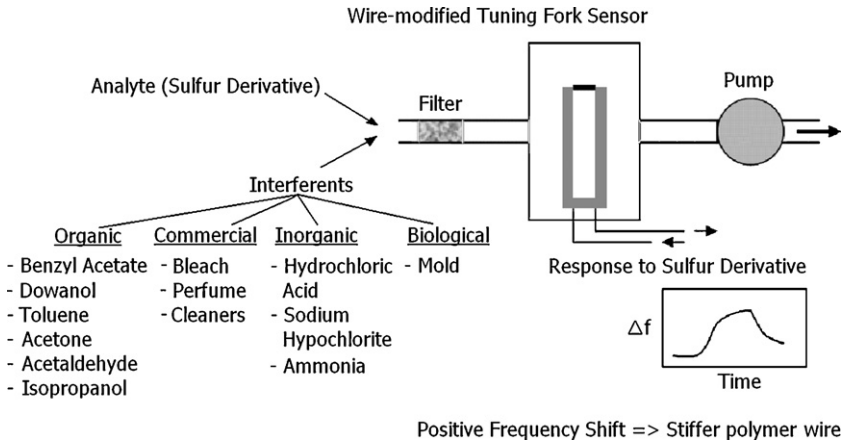
Many chemical sensors rely on molecular recognition, or specific binding of an analyte to a proper sensing material. Various materials, including organic molecules, conducting and non-conducting polymers and metal nanoparticles, are incorporated into sensors that are capable of transducing the binding event into a signal corresponding to an electrical, electrochemical, optical or mechanical property change [1]. An alternative approach is based on pattern recognition or electronic noses, using chem-resistors [2,3], colorimetric [4,5], surface plasmon resonance, microcantilever, surface acoustic wave and quartz crystal sensors [6]. The signals obtained from the electronic noses are analyzed with algorithms (e.g., principal component analysis [1,7,8], Fisher linear discriminant [7,8], hierarchical cluster analysis [4]) which, when combined with training using odor libraries, provide useful tools to identify specific odor patterns associated with particular tasks such as food quality control [6,7]. In spite of advances with these approaches, identifiying and detecting multiple trace analytes in a complex mixture of interferents still faces formidable challenges.

This paper presents an alternative strategy to improve selectivity and accuracy of detection of a particular chemical vapor or group of vapors, namely sulfur derivatives. In the current work, this technique has been optimized for indoor air analysis, such as inside a laboratory, or a household kitchen or bathroom. It includes: (1) a system-level approach that treats both an analyte-specific sensor and an interferent-filter with equal emphasis, (2) an efficient screening method to determine analyte-specific sensing and interferent filtering materials, and (3) a suitable transduction mechanism chosen based on the physical and chemical properties of the target analytes. We also emphasize the need of testing a sensor for its capability not only to sensitively detect a target analyte but also to reject common interferents. This concept is used to selectively detect sulfur derivatives (malodor molecules) at concentrations as low as several parts per million (ppm) in the presence of interferent molecules. A similar concept has been applied and succesfully proved in commercial sensors and to design sensors for breath analysis [9].

Organic sulfur compounds (OSCs) are commonly used as products in the manufacturing of wood pulp, fuels and detergents [10]. They are also released in various commercial processes and known to play a significant role in global temperature and acid precipitation [10]. In addition, OSCs are indicators of euthrophication, environmental pollution of natural water sources [3] and bad indoor ventilation. Release of OSCs also causes odor problems, and some of them are toxic in nature. Thus, it is important

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doi:10.1016/j.snb.2009.04.053



Scheme 1. Schematic representation of sulfur derivative sensing system. The device is an integration of sensitive sensing elements and a filter subsystem controlled with microcontrollers. Each sensing element consists of a tuning fork and a polymer wire stretched across the two prongs of the tuning fork. A specific interaction of an analyte changes the mechanical properties of the polymer wire. This is sensitively detected as a shift in the resonance frequency of the tuning fork. The filter subsystem is optimized to protect the sensing elements and to further improve their selectivity.

to detect and quantitatively assess the concentrations of these gases in ambient environments. Thiols and sulfides are often detected using gas chromatography (GC) [10]. While GC is a powerful and sensitive tool [11], it is still an expensive and user-dependent technique for real-time continuous monitoring purposes.

Scheme 1 illustrates the sensing device including an array of sensing elements made of microfabricated quartz tuning forks (QTF), a filter subsystem and sample delivery subsystem (a pump (shown) and valve) that are controlled with a microcontroller (not shown). Each QTF sensing element has a polymer wire stretched across the two prongs, and a specific binding of the target analyte triggers a change in the mechanical properties of the polymer wire, which is quickly and sensitively detected via a change in the resonance frequency of the QTF. Depending on the specific nature of interactions, the frequency can either increase or decrease, providing more selective detection than mass-loading based chemical sensors (described below). The filter subsystem not only protects the sensing elements from over exposure and fouling, but also further improves the selectivity of the entire sensor system especially in presence of high concentrations of interferent molecules often found in real work applications. The microcontroller provides intelligent control and consorted operations of the sampling, filtration and detection. Surface plasmon resonance imaging (SPRi) and QTF are used to screen various polymers for both the filter and sensing materials.

2. Experimental

2.1. Reagents

Analytes, dimethyldisulfide (DMS), methylsulfide and ethanethiol, and interferents, Dowanol TPM (a major component in cleaners), benzyl acetate (BA, a fragrance component), ammonia, hydrochloric acid, toluene, isopropanol, acetone and acetaldehyde were obtained from Sigma–Aldrich, Co. and used without further purification during the screening process and sensor performance evaluation. Other interferents from commercial products: general purpose cleaner (3M), bathroom desinfectant cleaner (3M), wax cleaner (Butchers® Amplify, 3M), body spray (Axe), body mist (Coty, US) were employed according to the manufacturer instructions or as per routine use. The products were applied on the floor and surfaces or on a person's body inside a small room (10 ft × 7.5 ft × 10 ft). Air samples in the room, containing realistic concentrations of these products, were collected for testing. Saturating vapors of mold obtained from a bath tub were collected in a Tedlar® bag and analyzed.

Filter and sensing materials studied in this work include ethyl cellulose (EC) with different substitution degrees: T-10 (S.D. = 50.6%), N-22 (S.D. = 49.0%) and N-7 (S.D. = 48.5%), hydroxypropyl cellulose (HPC) and sodium carboxymethyl cellulose (CMC) purchased from Hercules Inc. Aqualon Division. Other polymer materials include Wax (Apiezon®), polycarbonate (PC, Acros Organics), polystyrene (PS, Acros Organics), poly(methyl methacrylate) (PMMA, Acros Organics), Carbowax® (CW, MTO, Supelco), poly(vinyl chloride) (PVC, Sigma–Aldrich), Parafilm® M (PF, Sigma–Aldrich), Cytop® (Bellex International Co.), polyaniline (emeraldine salt, PANI, Aldrich), poly(3-hexylthiophene-2,5-diyl) (PHTP, Aldrich), poly(ethylene glycol) (PEG, Aldrich), poly(acrylic acid) (PAA, Aldrich), poly(diallyldimethylammonium chloride) (PDDA, Aldrich), poly(vinylsulfonic acid, sodium salt; PVS, Aldrich), poly(sodium-4-styrenesulfonate, PSS, Aldrich), methyl cellulose (MC, Sigma–Aldrich), polyethyleneimine (PEI, Aldrich), mercury chloride (Sigma–Aldrich) and gold (Kurt J. Lesker, Clairton, PA).

2.2. Surface plasmon resonance imaging (SPRi)

SPRi was used to perform initial screening of materials to identify differential affinities between representative components of malodor (DMS), cleaner (Dowanol) and a fragrance (BA). The principle of SPRi is explained elsewhere [12–16]. Briefly, a p-polarized collimated light beam from a 648 nm LED is directed through a prism onto a gold film (thickness ~50 nm) supported on a BK7 glass cover slide. The reflected light from the film is collected by a charge-coupled device (CCD) camera. The incident angle ($\theta_i \sim 43^\circ$) is chosen so that the light is partially absorbed by surface plasmons in the gold film. The absorption is extremely sensitive to changes in the refractive index and/or thickness of materials deposited on the gold surface, which can be detected and imaged by the CCD camera.

In order to use SPRi as a high throughput screening tool to determine interactions between various polymers and analyte/interferent molecules, low-concentration solutions (<200 μg/mL) of different polymers were manually deposited on the gold film using a microsyringe (0.1–0.6 μL), which resulted in formation of a patterned array of polymer films after evaporation of the solvent. The film thickness of each array element was estimated by comparing the measured SPR signals with those calculated using Winspall (http://www.mpip-mainz.mpg.de/knoll/soft/). Although

the film thickness can be varied over a wide range, only those with thicknesses less than 20 nm were evaluated since this range ensures linearity of the SPR response.

A flow cell made of Teflon® with inlet and outlet was used in the screening experiment. The analyte and interferent vapors (150 ppmV DMS, BA and Dowanol) were introduced into the cell with a Pocket Pump® (SKC Inc., Eighty Four, PA) at a rate of 200 mL/min and allowed to interact with the polymer array on the sensor surface for 9 min.

We note that since the gold films in the SPRi screening and the silver electrodes on QTFs (described below) are highly reactive to DMS, both the gold films and QTF electrodes were passivated by exposing them to saturated DMS vapors at room temperature for 30 min followed by thorough washing with acetone before experiments.

2.3. QTF sensor arrays

An array of QTFs was used both as an additional tool to screen sensing and filter materials and as the sensing platform for the detection of sulfur derivatives (Scheme 1). QTFs are piezoelectric devices that can be easily driven into resonance with an electrical signal. The resonant frequency f_0 is given by [17]

$$f_0 = \frac{1}{2}\sqrt{\frac{k'}{M}} \quad (1)$$

where k' and M are respectively the effective spring constant and mass. The QTFs used in our experiments have a resonance frequency of 32,768 Hz with dimensions: 4 mm × 0.35 mm × 0.6 mm for each prong (Newark Inone Electronics). The effective spring constants of these QTFs are ~20 kN/m and the thermal noise is as small as $\sim 4 \times 10^{-4}$ nm (root mean square oscillation amplitude of the prongs) at room temperature [18].

The outer packaging was removed and the QTFs were chemically modified with polymer wires stretched across their prongs using the following procedure [19]. First, a viscous solution of the polymer was prepared in DMS, and two small drops (~0.1 μL) of this solution were then placed on each of the two prongs of the tuning fork. Before the drops dried out, a syringe needle was dipped into one of the polymer solution drops and used to pull the drop to the second prong. Surface tension led to capillary thinning and formation of a stretched polymer wire (of diameter between hundreds of nm to tens of microns). This wire increased the effective spring constant of the QTF and consequently increased f_0. The polymer wire-modified QTFs were left to dry overnight before use. Typically, the quality factor (Q) [20] of the QTFs decreases from 8000–11,000 to 1000–3000 after the modifications. For mass loading applications, QTFs were simply coated with dilute polymer solutions (<0.35 μL).

A 0.2 V AC signal from a function generator (Stanford Research Systems, SRS DS345) was used to drive an array of wire-modified QTFs into oscillations. The electrical outputs from the oscillating QTFs were amplified with a current amplifier and sent to a lock-in amplifier (Stanford Research Systems, SRS SR830). The outputs from the lock-in amplifier were recorded as a function of excitation frequency with a digital oscilloscope (LeCroy Wavepro 950) with a noise level of 20 mHz per second of data acquisition. A gas diluter (Model 1010 from Custom Sensor Solutions Inc.) provided chemical vapor mixtures at different concentrations. Various flow rates, sample injection and purging times, and analyte concentrations were used in the experiments.

For quick screening of filter materials, QTFs were used as mass loading sensors. An array of 9 QTFs coated with different polymers (Table 1) was used to identify potential filter materials based on their specific interactions with various interferents (organics, commercial and mold). The initial selection of these polymer materials was based on the results of the SPRi screening process described earlier. The materials were coated on the QTFs using a spin coater (Model 6700, Speciality Coating Systems, Inc.). The QTF array was driven into resonance with a microcontroller-based circuit which recorded frequency of each tuning fork by counting the number of oscillations in a fixed time pulse. The frequency resolution is limited by control circuit noise level and is ~5 mHz for the digital control circuit indigenously developed by us. Vapors of different interferent chemicals were drawn into a 15 mL test chamber using a pump (~650 mL/min.). After establishing a baseline with ambient air, the array was subjected to a 200-s injection for each test vapor, followed by a 10-min purging period to allow the QTFs to recover to their original frequency.

Table 1
Polymers coated on QTF array for filter material screening.

Material	Coating mass (ng)[a]
T-10	5,198
N-22	6,212
N-7	6,563
PS	4,356
PC	10,780
PMMA	5,936
Wax	11,780
PVC	6,231
<Bare tuning fork>	–

[a] Calculated from the relationship between mass and coating frequency shift in a QTF (17 ng/Hz).

2.4. Interferent filter assembly

The filters were made by first coating clean glass fibers with solvent-based solutions of PVC or EC N-7. After the solvent was dried up, the coated fibers were packed into a clean glass tube. The filter was further baked in an isothermal oven at 60 °C for 30 min to release trapped solvent vapors.

3. Results and discussion

Our sensor system has two components that interact with chemical vapors—an adsorbing filter for a wide range of interferents and a QTF sensor array that responds to sulfur derivatives. Selecting suitable materials for both components is critical for selective and sensitive detections of analytes. We describe below the filter and sensing material screening results first and then discuss the performance of the sensor system.

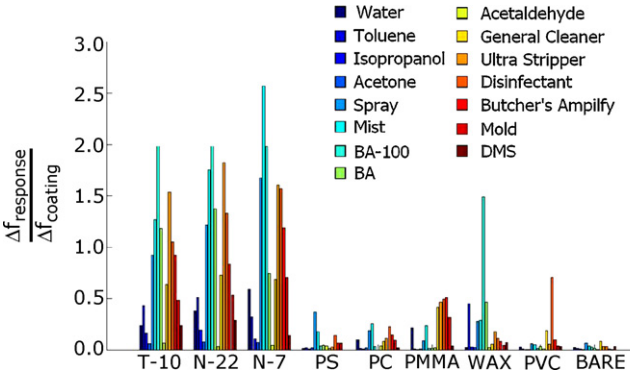


Fig. 1. Response of a QTF array to DMS and interferent molecules. Each QTF is coated with a separate material (listed along *X*-axis). Response is normalized by frequency shift due to mass of coating material on the QTF.

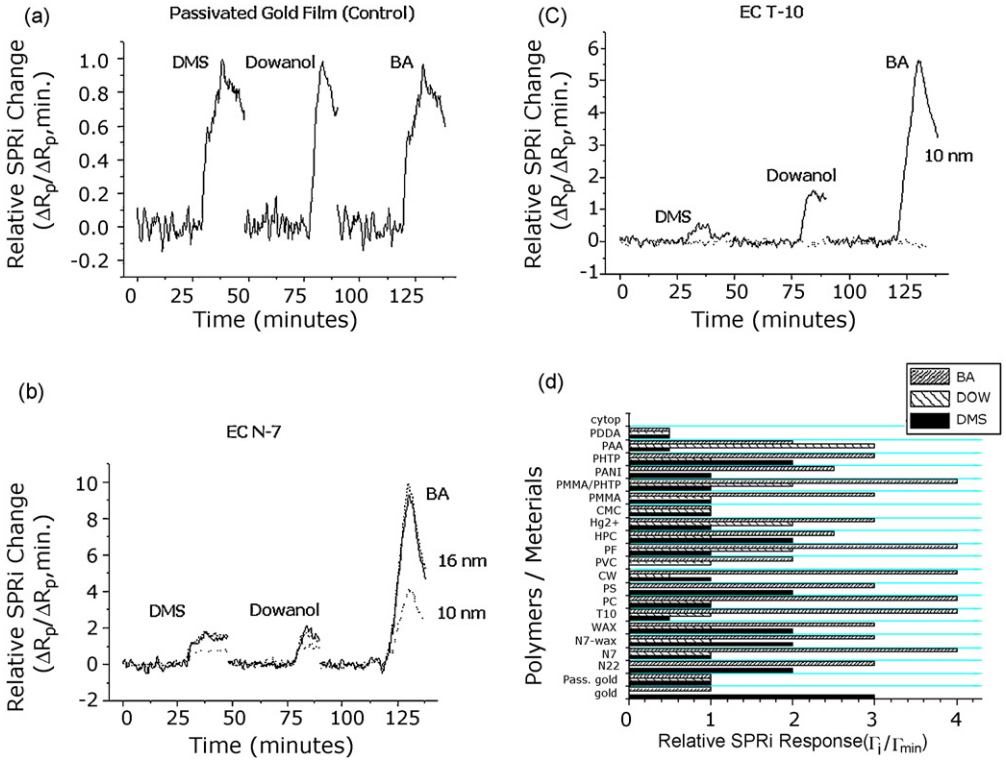


Fig. 2. SPRi response (reflectance change) to 150 ppmV vapors of analyte (DMS) and interferents (Dowanol, BA). (a) Response of passivated gold film (control). (b) Response of gold film patterned with EC-N7. (c) Response of gold film patterned with EC T-10. Pattern thickness is indicated next to the corresponding curve. (d) SPRi responses of 22 different polymers and materials to DMS, Dowanol and BA vapors (150 ppmV). SPRi response (*X*-axis) is explained in the text.

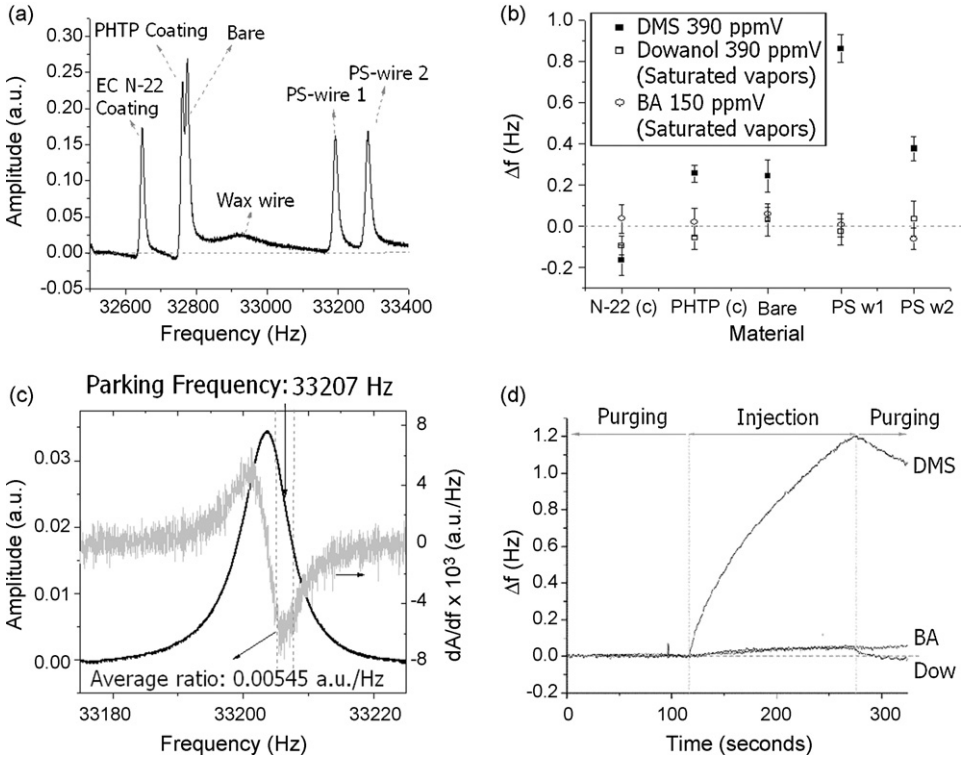


Fig. 3. (a) Frequency spectrum of a QTF array including 6 sensing elements: EC N-22 and PHTP-coated QTFs, wax-, PS1- and PS2-wire modified QTFs, and a bare control QTF. PS1 corresponds to QTF modified with 2 wires. (b) Resonance frequency shift pattern for each sensor in the QTF array with 390 ppmV DMS, 390 ppmV Dowanol and 150 ppmV BA. (c) Amplitude-frequency spectrum of PS-wire 1 QTF. Slope and derivative of the amplitude-frequency curve determine parking (or perturbation) frequency. (d) Frequency response of PS-wire 1 QTF on exposure to 390 ppmV DMS, 390 ppmV Dowanol and 150 ppmV BA. The QTF was parked at 33,207 Hz, and amplitude changes were recorded and converted to equivalent frequency changes by using the corresponding amplitude/frequency slope (0.00545 a.u./Hz) shown in (c).

3.1. Filter material screening

3.1.1. QTF arrays

As we have already mentioned, a QTF can detect a change either in the effective mass due to analyte adsorption or spring constant resulting from interactions of analytes with the polymer wires. The relationship between the measured resonance frequency shift of a QTF and changes in the effective mass and spring constant is described by [21]:

$$\Delta f(k', M) = \left(\frac{f_0}{2}\right)\left[\frac{\delta k'}{k'} - \frac{\delta M}{M}\right] \quad (2)$$

where $\Delta k'$ and ΔM denote the changes in the effective spring constant and mass, respectively. Our previous work [19,22,23] has determined that $\Delta k'$ is dominant when an analyte adsorbs onto a polymer wire stretched across QTF prongs, as ΔM is negligible when compared to the total mass of the QTF. We also found that detecting $\Delta k'$ can provide extra selectivity (see below).

When QTFs modified with polymer coating films are used to screen materials for filter design, Eq. (2) shows that frequency change is solely due to mass loading effect (δM), since $\delta k'$ is zero in this case. The resonance frequency decreases with an increase in the mass which provides a straightforward method to screen materials for filters. Rather than using multiple filters to target individual interferent molecules, a single filter that exhibits moderately high affinity for most interferents will make the sensor system more portable. More importantly, resistance associated with each successive filter will decrease the uniformity of air flow. A single filter using a mixture of different materials is another possible approach but was not explored in this study. The aim of the filter screening process is to find a single material for use as a general filter for the interferents involving organics, commercial products and mold.

The QTF array in Table 1 was exposed to analyte and interferent vapors, and the response of the array is summarized in Fig. 1. The frequency change of each QTF in the array is normalized by the frequency shift due to the coating mass of the polymer. A bare QTF was used as control. It was observed that all three ethyl cellulose polymers (EC N-22, EC N-7 and EC T-10) recorded highest changes in frequency when exposed to chemicals containing BA derivatives (spray, mist) and Dowanol derivatives (cleaners and disinfectants). Of the EC polymers, EC N-7 demonstrated least affinity for DMS. From the combined SPRi and QTF screening results, two materials were selected for further testing—PVC to filter out BA and Dowanol specifically (see below), and EC N-7 as a general filter.

3.1.2. SPRi

As discussed before, SPRi-based screening was carried out by patterning polymers on the gold film and exposing them to vapors of the analyte, DMS, and interferent molecules at known concentrations. Fig. 2(a)–(c) shows the SPRi responses of a passivated gold film (which acts as a control) and two polymer-modified gold films (EC N-7, EC T-10) to vapors of DMS, Dowanol and BA (150 ppmV). In the control experiment (Fig. 2(a)), the three chemicals caused similar SPR responses. In the case of polymer modified gold films (Fig. 2(b) and (c)), the responses to analyte and interferent molecules are different due to each material's unique affinity to the chemical vapors. This interaction was determined from the SPRi responses ((R_p, the change in optical reflectance), which is related to the surface coverage of adsorbed molecules (Γ) [12,24].

Fig. 2(b) and (c) shows that (1) for a given polymer, SPRi responses normalized by the polymer thicknesses are constant and reproducible. This is expected because the polymer films are thin (<20 nm) as compared to the decay length (~200 nm) of the evanescent field, and the SPRi response is linearly proportional to the adsorbed materials. Fig. 2(d) is a comparison of relative reflectance changes ($\Delta R_{p,i}/\Delta R_{p,min} = \Gamma_i/\Gamma_{min}$) of DMS, Dowanol and BA on different polymers. To simplify data interpretation, the reflectance change of the molecule with lowest response ($\Delta R_{p,min}$) was taken as unity and the $\Delta R_p/\Delta R_{p,min}$ ratios were rounded off. Hydrophilic polymers (PSS, PVS, PEI, PEG and MC) did not show affinity for any of the tested molecules and are excluded from Fig. 2(d). Several conclusions can be drawn from the SPRi screening results:

1. PVC absorbs both interferents (Dowanol, BA) but does not interact with DMS. Thus, it is a good candidate for the filter material;
2. EC T-10 and N-7, PF, CW and a mixture of PMMA/PHTP show high affinity for BA vapors;

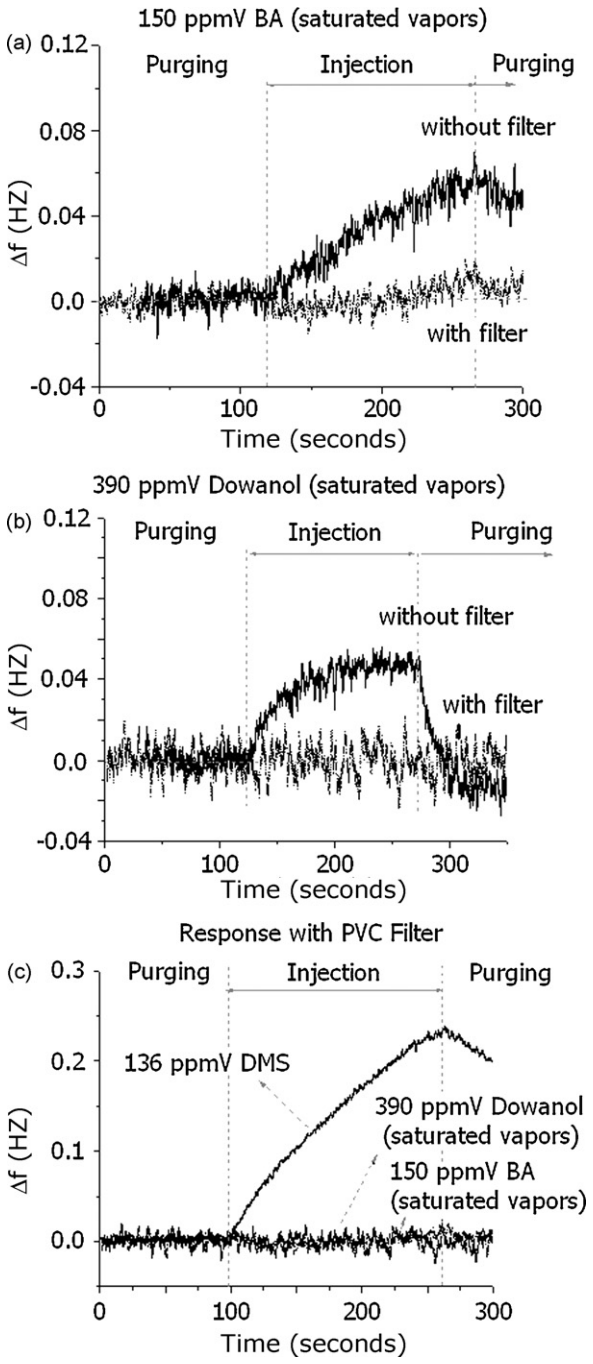


Fig. 4. (a) and (b) Responses of a PS-wire QTF to saturated vapors of BA and Dowanol with and without a PVC filter. (c) Selective detection of DMS with the PVC filter in the presence of BA and Dowanol vapors.

3. PAA is a good sorbent for selective adsorption of Dowanol;
4. PS, Wax, EC N-22 and PHTP can be used as sensing materials to detect DMS when used in combination with filter materials mentioned above (1–3).

It was also observed that DMS has faster adsorption kinetics than Dowanol and BA, on PHTP, at a similar concentration (not shown). This is important especially if this material is to be used in differential adsorption kinetics detection methods.

It should be noted that DMS showed, as expected, a strong irreversible binding on bare gold surface, while BA and Dowanol did not. Although this material could be a choice for selective detection of sulfur derivatives against interferents, it was excluded because of the irreversible response (see Section 3.5 real sample analysis).

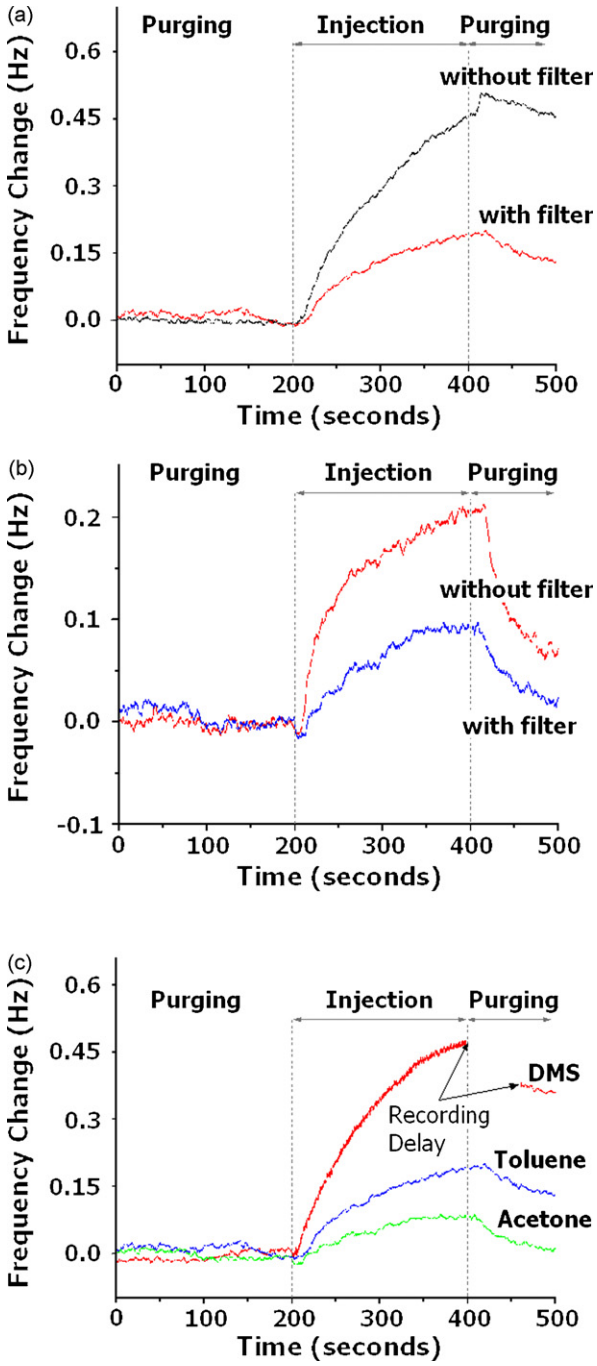


Fig. 5. Response of a PS-wire QTF sensor with and without an EC N-7 filter to 148 ppmV of (a) toluene and (b) acetone (c) response of the sensor with the EC N-7 filter to 148 ppmV of analyte (DMS) in the presence of interferents at same concentration.

3.2. Sensor material screening for detection of sulfur derivatives

After identifying the optimal materials for the filter subsystem, focus was shifted to studying the interactions of the materials with the analyte vapors. As mentioned before, sulfur derivatives are responsible for indoor and outdoor malodors, and many of them are toxic in nature [25,26]. Assessment of their levels is an important step towards providing healthy indoor and outdoor environments. This section describes the effects of DMS and some common indoor interferents on the mechanical properties of modified QTF sensors. QTFs are very sensitive and inexpensive resonators that can be modified for sensing applications [19,22,23,27–29]. By monitoring changes in the resonance frequencies of modified QTFs due to chemical vapors, it is possible to study the effects of these vapors on the effective spring constants of the QTFs [19,22].

QTF arrays were modified with materials that had been classified as sensitive to DMS during the SPR screening process (previous section). Fig. 3(a) illustrates the frequency spectrum of a QTF array consisting of 6 sensing elements: EC N-22 and PHTP-coated QTFs, wax-, PS1- and PS2-wire modified QTFs, and a bare control QTF. Each peak in the spectrum is the response of one sensing element. Fig. 3(b) shows the response of the QTF array to DMS, Dowanol (390 ppmV each) and BA (150 ppmV). Note that both Dowanol and BA were saturated vapors in air. The *Q*-factor of the wax-polymer

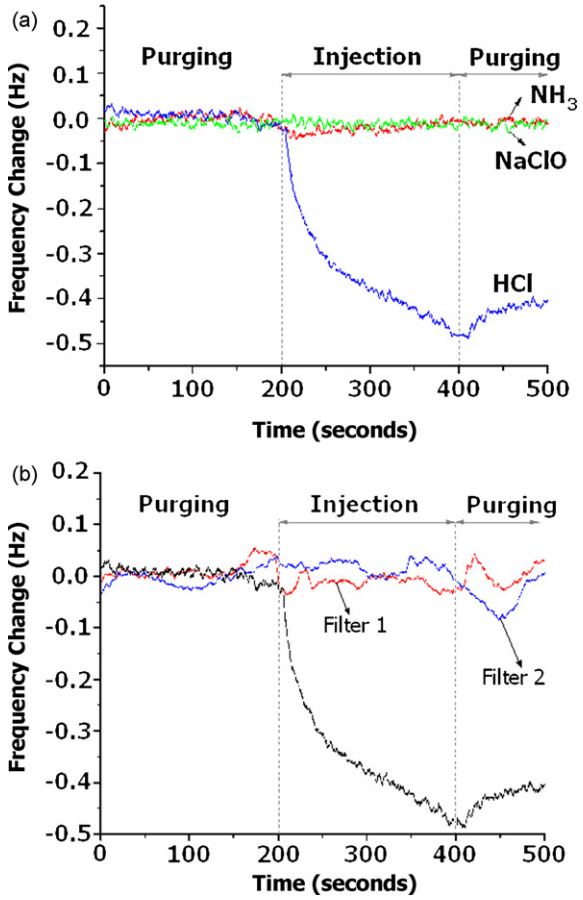


Fig. 6. (a) Response of a PS-wire QTF sensor to HCl, ammonia (NH_3) and sodium hypochlorite (NaClO, bleach). Neither NH_3 nor NaClO shows significant adsorption on PS-wire. (b) Response of the sensor to HCl vapor, using pH paper filters. Filter 1 (0.132 g) is sufficient to prevent HCl from reaching the sensing chamber. Filter 2 uses 0.2 g of pH paper.

Table 2
Percentage frequency change ($\Delta f_{interferent}/\Delta f_{DMS} \times 100$) values for the interferents listed in Scheme 1, both in the absence and presence of filters.

Interferent	Type	Filter	Response without filter (%)	Response with filter (%)
Ammonia[a]	Inorganic	–	<3	–
Hydrochloric acid[a]	Inorganic	pH paper	99	4
Sodium hypochlorite[a]	Inorganic	–	<3	–
Benzyl acetate[a]	Organic	EC N-7	83	6
Isopropanol[a]	Organic	EC N-7	7	7
Toluene[a]	Organic	EC N-7	73	44
Acetone[a]	Organic	EC N-7	42	17
Acetaldehyde[b]	Organic	EC N-7	<3	<3
General cleaner[b]	Commercial	EC N-7	7	<3
Disinfectant[b]	Commercial	EC N-7	<3	<3
Mist[b]	Commercial	EC N-7	<3	<3
Spray[b]	Commercial	EC N-7	5	<3
Mold[b]	Biological	EC N-7	23	14

[a] These chemicals were all tested at the same concentration as DMS (148 ppmV).
[b] Exact concentration could not be determined for these interferents. The amount used for testing was determined according to practical considerations or manufacturer-recommended use so that their final concentrations represent realistic conditions.

modified QTF was too small (broad peak in Fig. 3(a)) for accurate measurements. Significant positive frequency shifts were observed for the PS-wire modified QTFs in the presence of DMS, indicating that the analyte increased the effective spring constant of the PS wire. This is interesting because most analytes soften the polymer wires and decrease their spring constants, leading to negative frequency shifts. The positive frequency shift was confirmed in another experiment, in which a PS-wire QTF was excited at a frequency fixed near the resonance peak and the change in the amplitude due to the shift in the resonance frequency was monitored (Fig. 3(d)). As shown in Fig. 3(c)), the resonance frequency shift is linearly proportional to the amplitude change within a certain frequency window (marked between dashed lines).

3.3. Integrated operation of sensing and filter subsystems

So far, all experiments in this work had been directly concerned with identification of suitable materials for analyte sensing and interferents' adsorption. Having selected PS as a sensing material and PVC, EC N-7 for filtering, the filters were characterized by performing detection of DMS in the presence of saturated vapors of interferent molecules, including Dowanol and BA as well as realistic concentrations of general interferents. A filter was placed in the path of air flow before the sensing chamber (shown in Scheme 1) with the intention of trapping interferent molecules and allowing only the analyte to pass through.

Fig. 4(a) and (b) shows the responses of a PS-wire modified QTF to saturated vapors of Dowanol and BA, both with and without a PVC filter in place. Frequency shift for a particular QTF is measured relative to a baseline, which is obtained by placing a zeroing filter in the air flow path to the sensor. This zeroing filter (made of Purafil) is used to obtain a baseline that is free of sulfur derivatives and other interferents, and reflects the drift of the QTF over time. Typical drift signals were several times smaller (~10) than the response signals assessed from low ppmV levels of sulfur derivatives within 10 min of testing (sampling and purging) time. The data in Fig. 4 clearly demonstrates the effectiveness of PVC as the filter material and the finding is consistent with the reported study of PVC interactions with ether-bond molecules [30]. Fig. 4(c) shows overall response of the sensor to DMS and to saturating vapors of Dowanol and BA, which further demonstrates selective detection of DMS.

The filter screening data also show that EC N-7 interacts with most interferents studied here. EC N-7 was characterized as a filter material in two cases. The first case applied to interferents whose concentrations could be accurately determined. This included single chemical component interferents, such as isopropanol (ISP), acetone, and toluene. The second case involved interferents that were either a complex chemical mixture (like cleaners, which contain Dowanol; or spray and mist, which contain BA) or chemicals with high vapor pressures, such as acetaldehyde. Fig. 5(a and b) compare the responses of the PS-wire QTF sensor to 148 ppmV of toluene and acetone, with and without an EC N-7 filter. Results of the PS-wire QTF sensor performance and EC-N7 filter with analyte (DMS) and interferents present are highlighted in Fig. 5(c). In agreement with the screening data, the EC N-7 filter absorbs interferents to a large extent while allowing DMS to pass through to the sensor elements.

While EC N-7 and PVC proved to be good for filtering out organic interferents (such as acetone and toluene or Dowanol and BA, respectively), their affinities for inorganic vapors like hydrochloric acid (HCl) were limited (not shown). Instead, filter materials based on their acidic/basic natures were found to be better choices for the inorganic vapors. The response of the PS-wire QTF sensor to HCl, NH_3 and NaClO (from bleach) at 148 ppmV concentration in the absence of filters is shown in Fig. 6(a). It was observed that the effects of NH_3 and NaClO on the PS-wire QTF were insignificant. On the other hand, HCl induced a negative frequency change of relatively high magnitude, which is indicative of polymer wire softening. Fig. 6(b) demonstrates the effectiveness of pH paper as a filter for HCl. As with the polymer materials used to filter out organic and commercial products, the pH paper filters were re-usable, with QTF sensor frequencies recovering to their original values after the system being purged with clean air. Table 2 summarizes the performance of the filters. For each interferent, the frequency change from interferent vapors relative to the frequency change due to DMS is used to measure effectiveness of the filter for that interferent. All three filters (PVC, EC N-7 and pH paper), placed before the sensing chamber, caused this ratio to decrease for each interferent introduced into the system. This substantiated the choice of these materials as filter materials. It should be noted that filter characterization experiments were carried out in environments where relative humidity variations were as high as 35%.

3.4. Analytical characterization of the sensor

After optimizing the filtration system and sensing platform, it was necessary to determine the reproducibility, stability, detection limit, dynamic range and specificity of the entire system.

3.4.1. Reproducibility

The responses of the PS-wire QTF sensor to four consecutive injections of DMS (390 ppmV) on the same day and under nearly identical conditions of flow rate and relative humidity were found

to be highly reproducible with a relative error of ~7%. A similar level of reproducibility was observed between responses to DMS (390 ppmV) on two consecutive days (not shown). Importantly, the responses of two different PS-wire QTF sensors to DMS were found to be within 15% of each other. The kinetics of the adsorption–desorption process of DMS on PS is [22]:

$$\mathrm{DMS} + \mathrm{PS} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{DMS} - \mathrm{PS} \quad (3)$$

k_a and k_d are the adsorption and desorption kinetics constants, respectively. Along with dissociation constant K_D, their values were estimated for future injection and purging times. The results were: $k_a = 3.0\ (\mathrm{S.D.} = 1) \times 10^{-5}\ \mathrm{s}^{-1}\ \mathrm{ppmV}^{-1}$, $k_d = 1.4\ (\mathrm{S.D.} = 0.2) \times 10^{-3}\ \mathrm{s}^{-1}$ and $K_D = 47\ (\mathrm{S.D.} = 10)$ ppmV. Relative errors were less than 14% and 20% for kinetics parameters and thermodynamic constant, respectively.

3.4.2. Reusability, calibration and dynamic range

In order to test for reusability of the PS-wire QTF, the sensor was exposed to 50 consecutive injections of 24 ppmV DMS after exposure to a single injection at high concentration (394 ppmV), and the response was found to be within 10% (Fig. 7(a), inset), demonstrating good reversibility after intense use.

The PS-wire QTF response was tested as a function of analyte concentration (Fig. 7(b) and (c)). The frequency change of the sensor was linearly proportional to the logarithm of DMS concentration, which is consistent with the Langmuir-like adsorption features of the analyte molecules on the sensing polymer. The reproducibility of sensitivity (defined as the slope of the semi-logarithmic plot) was found to be 11% (for a flow rate of 0.7 L/min) and 7% (0.3 L/min) in three different runs for each flow rate.

3.4.3. Detection limits

Detection limit was calculated as the concentration of the analyte that caused a frequency shift in the sensor equal to three times the signal noise level. Without a filter, minimum detection limit of PS-wire QTF sensor for DMS was found to be 750 ppbV for 200-s injections at 0.66 L/min. When a PVC filter was used, minimum detection limit for DMS in the presence of saturating vapors of interferents (390 ppmV Dowanol and 150 ppmV BA) was estimated to be 4.6 ppmV. In this case, injections were of 150-s duration at 0.25 L/min.

3.4.4. Sensor lifetime and stability

Besides good analytical performance, highly reproducible and reversible response as shown in previous sections, the PS-wire QTF sensors showed high robustness with long-term use and environmental stress. The sensors maintained its quality factor within a 16% variation over a testing period of 15 months under hundreds of cycles of use and diverse ambient conditions (Fig. 8(a)). Along this line, a high immunity towards humidity was also observed with changes in quality factors and intrinsic sensitivities (amplitude/frequency slope) smaller than 1% between 10% and 100% relative humidity (Fig. 8(b)).

3.4.5. Specificity to sulfur derivatives

The PS-wire QTF sensor is sensitive to sulfur derivatives. Response of the sensor was determined for two sulfur derivatives (other than DMS): methylsulfide and ethanethiol. Exact concentrations of these compounds were difficult to determine due to their volatile natures. However, it was observed that the PS-wire QTF responded in a similar manner to all three analytes, showing that they all have a similar effect on the PS-wire (i.e. increasing its effective spring constant k'). Although the EC N-7 filter showed a relatively higher affinity for ethanethiol and methylsulfide than for DMS, the sensor exhibited a clear response to all three analytes

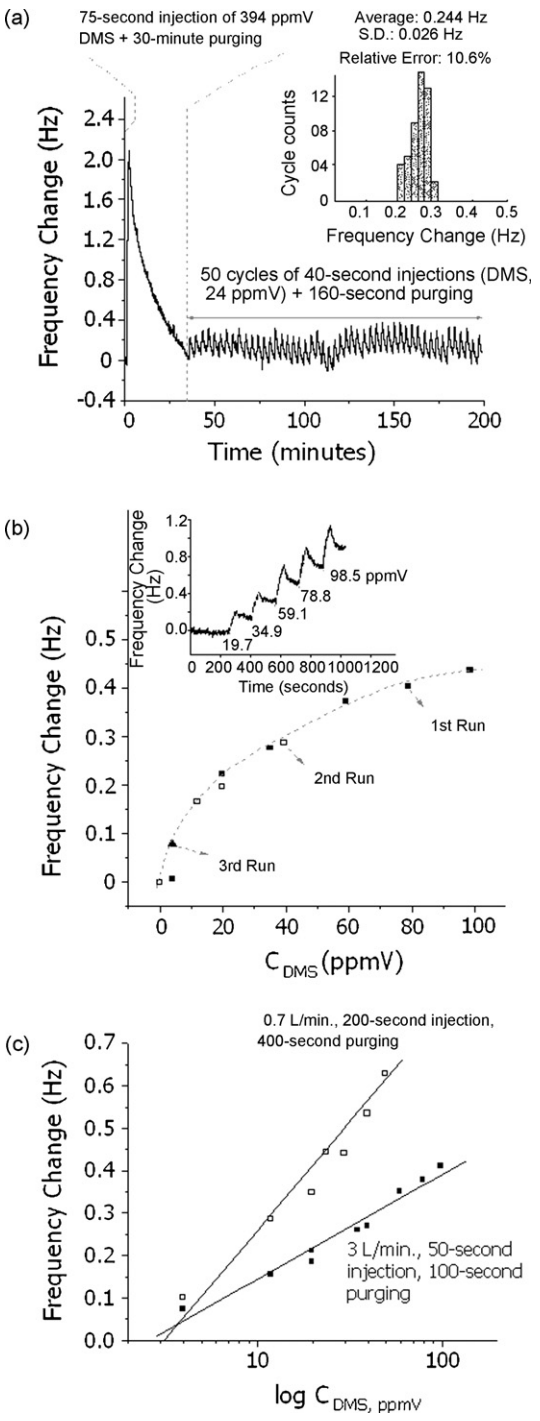


Fig. 7. PS-wire QTF sensor characterization. (a) Stability of PS-wire QTF over 50 cycles of 40-s injections of DMS (24 ppmV) after an initial injection of 394 ppmV DMS followed by recovery. Statistical data for the 40-s injections included in inset. (b) Calibration data (frequency change vs. DMS concentration) for PS-wire QTF sensor from three independent runs of increasing DMS concentrations with 50-s injections. Inset: response curve shows increasing frequency shift towards successive 50s-injections of increasing concentrations DMS followed by purging periods. Injected concentrations are marked. Flow rate: 3 L min^{-1}. (c) Comparison of calibration data for different flow rates.

even with the filter present. Table 3 summarizes response of the sensor system to all 3 sulfur derivatives. We noted that in the case of ethanethiol, absorption of analyte by sensor is as high as 48%. However, this sensor system is intended to be a semi-quantitative tool that detects the presence of sulfur compounds in an indoor environment (see Section 3.5 real sample testing).

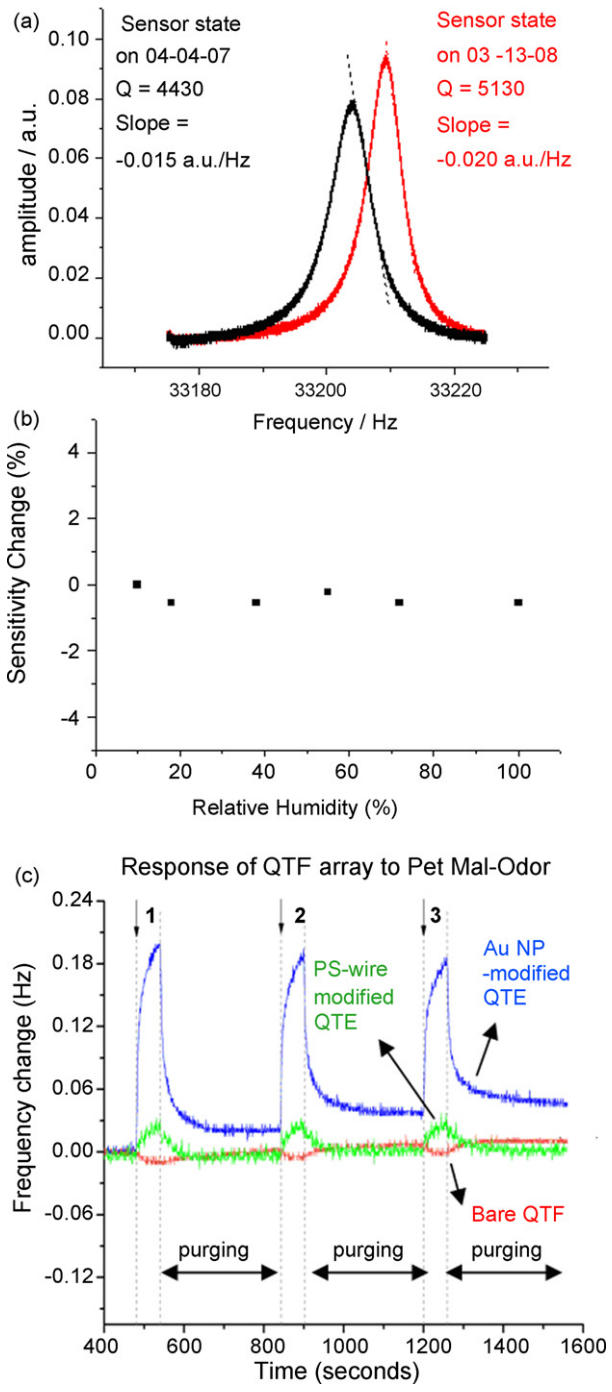


Fig. 8. (a) Spectrum of a TF sensor before and after 15 months of intensive use in ambient conditions. Only a 16% change of the TF quality factor (Q) was observed. (b) Percentage of sensitivity change of a TF upon 10–100% RH exposure. (c) Response of a QTF array with unmodified (bare) and modified (PS-wire and Au NP) sensors towards injections (1–3) of a commercial malodor sample (from cat) diluted 7000 times in ambient air. The PS-wire sensor demonstrates reproducible detection with successive injections, while Au NP sensor shows decreasing response due to cumulative quasi-reversible sensor recovery.

3.5. Real sample testing

PS-wire QTF sensors were exposed to malodor samples to test their capability to identify the presence of sulfur-containing components. From a series of commercial malodor samples (Robertet Fragrances, Inc.; bathroom, kitchen and pet), the PS-wire QTF sensor could positively detect the presence of sulfur compounds from pet malodor, matching the qualitative diagnosis performed by human testers who could discriminate the characteristic odor of sulfur derivatives.

Table 3
Response of PS-wire QTF to sulfur derivatives.

Analyte	Response without filter (Hz)	Response with filter (Hz)
Dimethyldisulfide (DMS)	0.97	0.91
Ethanethiol[a]	0.76	0.37
Methylsulfide[a]	0.64	0.36

[a] The concentration of these compounds was less than DMS concentration due to their high vapor pressure. The standard deviation for each of these responses was found to be less than 12% for consecutive measurements made on the same analyte sample, whose analyte concentration in the sample bag may vary over time.

The sulfur-compound positive sample was also utilized to compare the recovery capability of our proposed PS-wire based sensor to another sensor based on gold nanoparticles, a typical well-known sulfur binding material. A sensor array based on PS-wire QTF, gold nanoparticle (Au NP)-QTF and a bare QTF was built and tested for this purpose. Fig. 8(c) shows the response of this array towards three successive injections of the pet malodor separated by intermitent purging periods with ambient air. Despite the fact that Au NP-QTF produced a high response, a systematic decrease of the response associated with a cumulative quasi-reversible recovery was observed. On the contrary, the response of the PS-wire QTF sensor showed full recovery, confirming the advantage of using a optimized reversible binding chemistry to produce long lasting sensors for sulfur derivative detection. Furthermore, sulfur derivative concentrations in a real malodor sample with high background of glycols were estimated from our PS-wire QTF sensor and showed good agreement with total sulfur derivative concentrations assessed from GC/MS tests.

4. Conclusions

This work has demonstrated a system-level approach for designing a sensor system that exhibits reversible, sensitive and selective detection of sulfur derivatives in the presence of saturating and realistic concentration of interferents. Specific interactions of analyte molecules with polymer wires cause changes in the mechanical properties of the wires which are amplified and detected by microfabricated tuning fork sensors. Proper filter materials are used to protect the sensing elements and to further improve the selectivity of the entire system which provides robust and reversible analyte detection. The integration of the sensor and filter components and the equal emphasis on the two components are critical for the success of the approach. The work underscores the necessity of testing interferent species while developing sensitive sensing elements if one wishes to detect trace analytes in complex environments. The device consists of low cost and miniaturized components which is ideal for many indoor applications.

Acknowledgements

The authors thank K. Foley for useful discussions about Surface Plasmon Resonance imaging. This work was supported by NIH (U01 ES0106064-01).

References

[1] E.J. Severin, B.J. Doleman, N.S. Lewis, An investigation of the concentration dependence and response to analyte mixtures of carbon black/insulating organic polymer composite vapor detectors, Analytical Chemistry 72 (2000) 658–668.
[2] T. Zhang, M.B. Nix, B.Y. Yoo, M.A. Deshusses, N.V. Myung, Electrochemically functionalized single-walled carbon nanotube gas sensor, Electroanalysis 18 (2006) 1153–1158.

[3] A.F. Bouwman, D.P. Van Vuuren, R.G. Derwent, M. Posch, A global analysis of acidification and eutrophication of terrestrial ecosystems, Water Air and Soil Pollution 141 (2002) 349–382.
[4] M.C. Janzen, J.B. Ponder, D.P. Bailey, C.K. Ingison, K.S. Suslick, Colorimetric sensor arrays for volatile organic compounds, Analytical Chemistry 78 (2006) 3591–3600.
[5] B. Johnson-White, M. Zeinali, K.M. Shaffer, C.H. Patterson, P.T. Charles, M.A. Markowitz, Detection of organics using porphyrin embedded nanoporous organosilicas, Biosensors & Bioelectronics 22 (2007) 1154–1162.
[6] K.J. Albert, N.S. Lewis, C.L. Schauer, G.A. Sotzing, S.E. Stitzel, T.P. Vaid, D.R. Walt, Cross-reactive chemical sensor arrays, Chemical Reviews 100 (2000) 2595–2626.
[7] T.P. Vaid, M.C. Burl, N.S. Lewis, Comparison of the performance of different discriminant algorithms in analyte discrimination tasks using an array of carbon black-polymer composite vapor detectors, Analytical Chemistry 73 (2001) 321–331.
[8] W. Wu, Y. Mallet, B. Walczak, W. Penninckx, D.L. Massart, S. Heuerding, F. Erni, Comparison of regularized discriminant analysis, linear discriminant analysis and quadratic discriminant analysis, applied to NIR data, Analytica Chimica Acta 329 (1996) 257–265.
[9] D.L.A. Fernandes, T.A. Rolo, J.A.B.P. Oliveira, M.T.S.R. Gomes, A new analytical system based on an acoustic wave sensor for halitosis evaluation, Sensors and Actuators B (2008), on line.
[10] K. Beiner, P. Popp, R. Wennrich, Selective enrichment of sulfides, thiols and methylthiophosphates from water samples on metal-loaded cation-exchange materials for gas chromatographic analysis, Journal of Chromatography A 968 (2002) 171–176.
[11] Q.Y. Zhong, W.H. Steinecker, E.T. Zellers, Meso-scale VOC-mixture analyzer with tunable separation and microsensor array detection, Rare Metal Materials and Engineering 35 (2006) 61–64.
[12] C.T. Campbell, G. Kim, SPR microscopy and its applications to high-throughput analyses of biomolecular binding events and their kinetics, Biomaterials 28 (2007) 2380–2392.
[13] T.M. Chinowsky, M.S. Grow, K.S. Johnston, K. Nelson, T. Edwards, E. Fu, P. Yager, Compact, high performance surface plasmon resonance imaging system, Biosensors & Bioelectronics 22 (2007) 2208–2215.
[14] Y. Li, H.J. Lee, R.M. Corn, Detection of protein biomarkers using RNA aptamer microarrays and enzymatically amplified surface plasmon resonance imaging, Analytical Chemistry 79 (2007) 1082–1088.
[15] M. Piliarik, H. Vaisocherova, J. Homola, A new surface plasmon resonance sensor for high-throughput screening applications, Biosensors & Bioelectronics 20 (2005) 2104–2110.
[16] N. Ly, K. Foley, N.J. Tao, Integrated label-free protein detection and separation in real time using confined surface plasmon resonance imaging, Analytical Chemistry 79 (2007) 2546–2551.
[17] C. Ziegler, Nanotechnologies for the biosciences, Analytical and Bioanalytical Chemistry 379 (2004) 903–913.
[18] R.D. Grober, J. Acimovic, J. Schuck, D. Hessman, P.J. Kindlemann, J. Hespanha, A.S. Morse, K. Karrai, I. Tiemann, S. Manus, Fundamental limits to force detection using quartz tuning forks, Review of Scientific Instruments 71 (2000) 2776–2780.
[19] M.H. Ren, E.S. Forzani, N.J. Tao, Chemical sensor based on microfabricated wristwatch tuning forks, Analytical Chemistry 77 (2005) 2700–2707.
[20] J.M. Friedt, E. Carry, Introduction to the quartz tuning fork, American Journal of Physics 75 (2007) 415–422.
[21] K.M. Hansen, T. Thundat, Microcantilever biosensors, Methods 37 (2005) 57–64.
[22] S. Boussaad, N.J. Tao, Polymer wire chemical sensor using a microfabricated tuning fork, Nano Letters 3 (2003) 1173–1176.
[23] F. Tsow, N. Tao, Microfabricated tuning fork temperature and infrared sensor, Applied Physics Letters 90 (2007).
[24] J.S. Shumaker-Parry, R. Aebersold, C.T. Campbell, Parallel, quantitative measurement of protein binding to a 120-element double-stranded DNA array in real time using surface plasmon resonance microscopy, Analytical Chemistry 76 (2004) 2071–2082.
[25] K.H. Kim, E.C. Jeon, Y.J. Choi, Y.S. Koo, The emission characteristics and the related malodor intensities of gaseous reduced sulfur compounds (RSC) in a large industrial complex, Atmospheric Environment 40 (2006) 4478–4490.
[26] C. Segala, D. Poizeau, J.M. Mace, Odors and health: a descriptive epidemiological study around a wastewater treatment plant, Revue D Epidemiologie Et De Sante Publique 51 (2003) 201–214.
[27] J. Zhang, S. O'Shea, Tuning forks as micromechanical mass sensitive sensors for bio- or liquid detection, Sensors and Actuators B-Chemical 94 (2003) 65–72.
[28] X.F. Zhou, T. Jiang, J. Zhang, X.H. Wang, Z.Q. Zhu, Humidity sensor based on quartz tuning fork coated with sol–gel-derived nanocrystalline zinc oxide thin film, Sensors and Actuators B-Chemical 123 (2007) 299–305.
[29] S.H. Guan, Frequency encoding of resonant mass sensors for chemical vapor detection, Analytical Chemistry 75 (2003) 4551–4557.
[30] E.K. Nefso, S.E. Burns, Comparison of the equilibrium sorption of five organic compounds to HDPE, PP, and PVC geomembranes, Geotextiles and Geomembranes 25 (2007) 360–365.

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