UTILIZATION OF VARYING TRANSIENT RESPONSE TIMES IN GRAVIMETRIC AND IMPEDIMETRIC MULTIVARIATE GAS SENSOR WITH SINGLE POLYMERIC SENSING FILM FOR ENHANCED SELECTIVITY

Steven A. Schwartz[1,2], Luke A. Beardslee[2,3,4*], and Oliver Brand[1,2]*
[1]School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA
[2]Institute for Electronics and Nanotechnology, Georgia Institute of Technology, Atlanta, Georgia, USA
[3]Naval Submarine Medical Research Laboratory, Groton, Connecticut, USA
[4]Emory University School of Medicine, Atlanta, Georgia, USA
*Current Affiliation

ABSTRACT

We report on the ability to discriminate between multiple volatile organic compounds (VOCs) utilizing variations in the transient response times of the gravimetric and impedimetric responses of a single micromachined multivariate gas sensor. The novel resonant gravimetric microsensor with a collocated capacitive transducer based on an interdigitated electrode (IDE) enables the simultaneous observation of both mass loading and dielectric changes in the same polymeric sensing film upon sorption of analyte. A 2D dispersion of the multivariate responses demonstrates separation between aromatics and alcohols due to variations in the transient response times along with varying concentration-dependences of these responses.

KEYWORDS

Resonant gas sensor, multivariate sensor, multivariate gas sensor, selectivity enhancement, multivariate dispersion.

INTRODUCTION

Chemical sensing has applications ranging from home safety and health monitoring to industrial process monitoring, environmental hazardous monitoring, and homeland security. Many of these applications have relied (and often still rely) on laboratory or benchtop-sized analytical tools, such as gas chromatography - mass spectrometry (GC-MS) systems, which limits portability and in-field usability. To both increase the utility and ubiquity of chemical sensors, microelectromechanical systems (MEMS)-based chemical microsensors have been developed. MEMS-based gas sensors are often classified based on the sensor's transduction principle or the sensing material used to interact with the target chemical. Across all classes of chemical microsensors, high sensitivity, low limit of detection, long-term stability, and high selectivity are desired. Of these properties, selectivity remains the most difficult to improve due to the tradeoff with the reversibility of the analyte interaction with the sensing layer [1]. Therefore, methods of selectivity enhancement without tailoring the sensing layer chemistry are extremely desirable.

Among the many types of sensing materials, polymeric sensing films are a well-studied class for gas microsensors due to the tailorability of the material chemistry, ease of deposition, and partial selectivity to a wide variety of compounds. Moreover, polymeric-film based chemical sensors leverage absorption-based volumetric diffusion-limited processes, compared to adsorption-based surface interactions, enabling high sensitivities in microsensors for the detection of volatile organic compounds (VOCs). Of these polymer-based gas microsensors, two prominent subclasses are gravimetric and impedimetric sensors. Gravimetric microsensors, such as resonant gas sensors, detect mass changes upon sorption of an analyte into the sensing material. On the other hand, impedimetric sensors, including chemocapacitive and chemoresistive sensors, detect changes in the electrical properties of a sensing film due to analyte penetration.

The steady-state and transient responses have been characterized for polymer-coated gravimetric resonant devices [2] and for polymer-coated chemocapacitive sensors [3]; both sensor types demonstrate remarkable sensitivity to a wide variety of VOCs. However, in both cases, the selectivity of these sensors is limited for a single sensing film-transducer pair, because of the partial selectivity of the polymer coating itself. In univariate sensors, selectivity is often derived from the variation in sensitivities for each analyte which is a function of concentration [1,4]. Thus, quantification can only be performed in the case where the gases present are known a-priori. This is undesirable for many applications as there is often a need to quantify not only how much of something is in the air (quantification), but also what is in the air (speciation). To overcome the sensing-film based selectivity limitation, multivariate sensing in which a single sensor produces multiple outputs can be leveraged. A comprehensive review of multivariate gas sensors and the many combinations of transducers and signal types utilized can be found in [4].

For a multivariate sensor with multiple outputs, with the sensor responses depending on the partition coefficient to varying degrees or a product of multiple material property relationships, additional selectivity can be derived by comparing variations in these relations. This is often visualized using a multi-dimensional dispersion in which data is plotted as a function of the sensor outputs rather than gas concentration [4] and has been demonstrated for the multivariate sensor used here [5]. However, this previous study only considered a comparison of the steady state data. In this paper, it is investigated if such variations hold true for transient characteristics of the sensor responses as well and if these variations are distinct from steady-state selectivity.

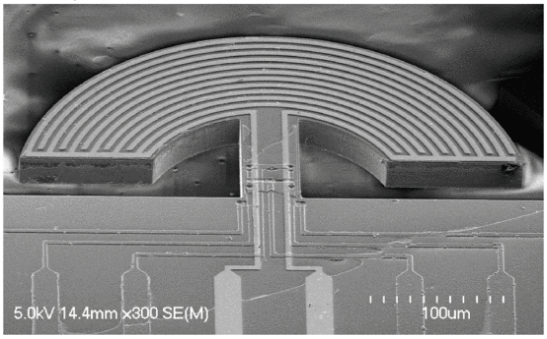

Figure 1: SEM image of gravimetric/impedimetric multi-sensor with hammerhead-shaped resonator and IDE on top of the semicircular annulus. Reprinted with permission [5].

SENSOR DESIGN & TESTING

Sensor Design & Characterization

The multivariate sensor builds on an established hammerhead-shaped resonator platform reported in [5,6], consisting of a semicircular annulus of 100/200μm inner/outer radius supported by a 100μm long and 45μm wide cantilever beam. An interdigitated

978-1-940470-04-7/HH2022/$25©2022TRF
DOI 10.31438/trf.hh2022.38

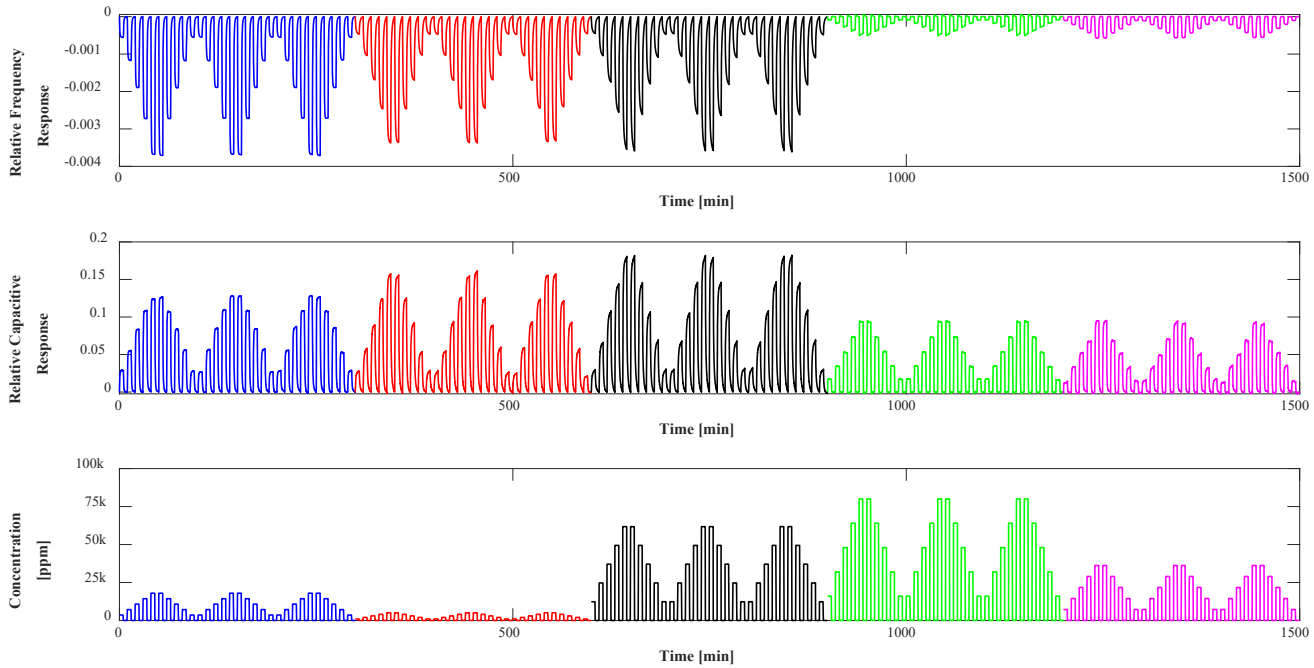

Figure 2: Timeseries of baseline corrected multisensor responses, i.e., measured relative frequency change and relative capacitance change, as well as respective exposure concentrations when exposing the PECH-coated sensor to different concentrations of the 5 tested gases: toluene (blue), m-xylene (red), ethylbenzene (black), methanol (green), ethanol (pink).

electrode (IDE) structure is overlayed on the surface of the device, enabling multivariate sensing using a single polymeric film (Figure 1). In this IDE structure both the electrode width and edge-to-edge spacing are 2µm. The resonator-based gravimetric sensor utilizes thermal excitation and piezoresistive sensing and is operated at its in-plane resonance mode using a closed-loop circuit, with the frequency being read out by a frequency counter. The capacitance of the IDE is simultaneously monitored using a high-precision LCR meter. For this work, an approximately 2µm sensing film of polyepichlorohydrin (PECH) was deposited on the annulus region of the device via spray coating with a shadow mask.

Gas Testing Procedure

The device was tested utilizing a custom-built gas measurement setup described in [5,6]. This measurement setup enables in-flow gas testing of chemical sensor devices with automated concentration ramping and exposure/purge cycling capabilities. Analyte concentration generation is performed using a temperature-controlled bubbler-vaporizer setup in which the saturated partial pressure of the target VOC is generated and then diluted through the control of flow rates in the system's gas lines via multiple mass flow controllers. Exposure/purge cycling is performed through the use of a 4-way solenoid valve enabling rapid transition between the analyte-filled exposure line and a purging line of pure carrier gas. The use of the solenoid valve and minimal headspace of the flow cell enables near ideal concentration stepping, minimizing systemic error in the transient response characteristic.

GAS SENSING MEASUREMENTS

Gas Testing Timeseries Data

Figure 2 shows the representative timeseries data collected from the multivariate sensor when exposed to different concentrations of five gases consisting of two VOC subclasses, aromatics and alcohols. Toluene, m-xylene, and ethylbenzene were the aromatic hydrocarbons selected as they are part of the BEXT class of industrial gases involved in the petroleum and plastics industry, while the alcohols, methanol and ethanol, were selected due to their heavy use as industrial solvents in chemical plants and consumer-use items such as windshield wiper fluid and industrial cleaners. Each gas was tested at five concentrations utilizing the bubbler-based gas measurement setup. For each analyte gas, the sensor is subsequently exposed to multiple cycles of increasing and decreasing analyte concentrations, with each 5-minutes analyte exposure followed by a corresponding purge of similar length using UHP nitrogen. The data highlights the repeatability of the sensor response, as well as the characteristic diffusion-limited response patterns for the different analytes. It should be noted that while the transient responses here are created using the test setup, similar transients can be generated by rapidly heating/cooling the sensor [7].

The sensor responses are displayed in relative quantities, enabling an improved comparison of the results for each gas test which were performed separately and consecutively over the course of a week with minimal changes in the baseline signal. The data shown here has been concatenated into a single timeseries to improve visualization of the variation in responses to each gas. Additionally, the data has been baseline corrected to remove signal drift.

Transient Response Analysis

In this work, the T_{90} response time, defined by the time it takes to reach 90% of the steady-state response, has been explored as it had been identified before as a useful metric to improve gas discrimination in polymer-based impedimetric sensors [3]. Figure 3 shows the extracted T_{90} for each sensor response as a function of analyte concentrations for the five gases. For this data set the last available datapoint at the end of the five-minute period was used in place of saturation limit as some gases do no reach full saturation of their gravimetric response within the five-minute period (see Figure 2). The response time for a particular analyte depends on the analyte concentration, as noted previously [2,3,8] for gas sensors utilizing polymeric films. The data was fit with a second-order polynomial demonstrating the quadratic dependence of the T_{90} response time on

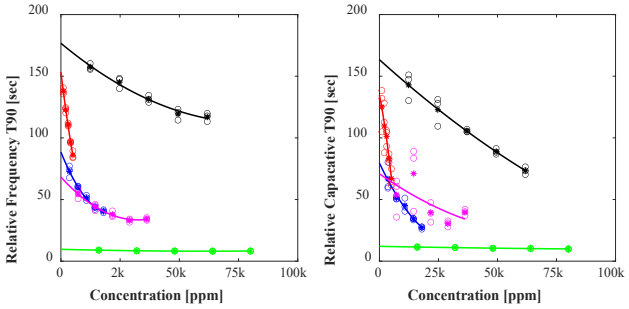

Figure 3: T_{90} response times extracted from gravimetric (frequency) and impedimetric (capacitance) responses as a function of analyte concentration for five tested gases: toluene (blue), m-xylene (red), ethylbenzene (black), methanol (green), ethanol (pink).

analyte concentration. There is both noticeable separation of analytes based on their transient response time and noticeable variation in their concentration dependence. This separation provides a means of selectivity and gas identification if the concentration is known.

To provide a means for gas identification without the need for a-priori knowledge of the gas or concentration information, a 2D dispersion of the frequency response times versus the capacitive response times is shown in Figure 4(B), along with the 2D dispersion of the steady-state responses for comparison in Figure 4(A). For the steady-state dispersion, the aromatics and alcohols are well separated at high concentrations, but the discriminatory power of this dispersion fades as the analyte concentration approaches zero. This limitation was not observed for the 2D dispersion of the transient response times as all five gases are spatially separated and their intercepts do not converge to zero. Notably, these curves do not lay on the x=y line as would be expected if the transient behavior was the same for both sensor responses. In particular, it was observed that, for the aromatics, the capacitive response is faster than the gravimetric/frequency response, while this behavior is reversed for the alcohols. Thus, both 2D dispersions provide discrimination of the five gases with separation/clustering of the aromatic and alcohols.

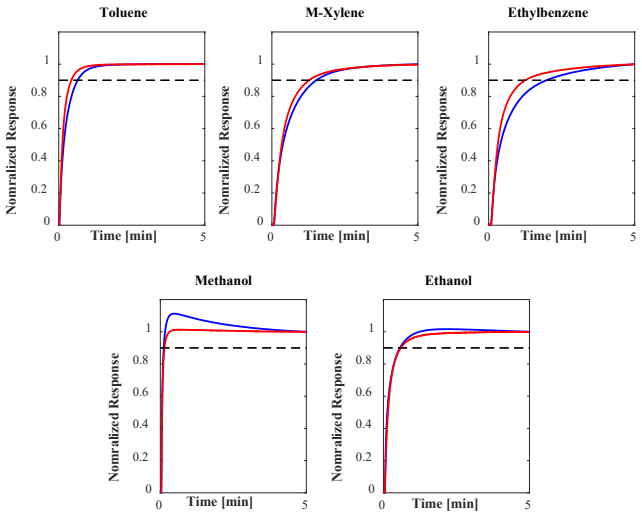

Figure 5: Comparison of normalized gravimetric (blue) and impedimetric (red) transient responses at maximum concentrations for all 5 tested gases with T_{90} reference line (black, dashed).

In Figure 5, the transient response for each analyte was further

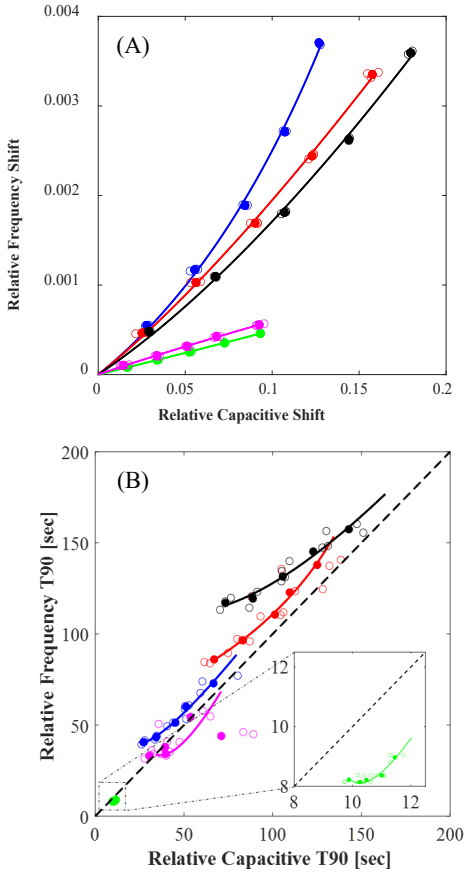

Figure 4: 2D dispersions of the (A) multisensor steady-state response and (B) T_{90} response data extracted from the gravimetric (frequency) and impedimetric (capacitance) responses. In (B) identical T_{90} response times for both signals would fall onto the dashed x=y line. Open circles represent extracted T_{90}, while closed circles represent averages for multiple measurements. Color coding as in Figure 2 & 3.

investigated by comparing the normalized responses of the two sensor outputs at all time points within a single 5-minute exposure at the maximum concentration of each gas. It can be clearly seen that for aromatics the capacitive transient response is quicker whereas for the alcohols the opposite is true. Moreover, in the gravimetric response of the alcohols, the normalized response exceeds a value of 1 which is an indication that the gravimetric response had a maximum within the exposure cycle rather than at the end. This is confirmed in Figure 2 if one zooms in on an individual relative frequency response of an alcohol. Further experimental investigation into this behavior is warranted.

DISCUSSION

The following discussion of the observed phenomena considers the literature for transient responses in polymer-coated sensors [2,3,8,9]. The transient responses of both transduction mechanisms are based on diffusion. Thereby, the gravimetric response can be directly related to the fractional mass uptake due to analyte diffusion into the sensing film, while the capacitive response is composed of contributions from both dielectric property changes of the sensing film due to incorporation of polarizable analyte into the polymer matrix and the swelling of the polymer [3,9]. Moreover, local dielectric property changes due to analyte diffusion into the sensing film create a spatially varying contribution to the sensor's capacitive

response due to the fact that the fringing of the electric field in the IDE creates non-uniform field density which is largest close to the electrode edges. Swelling-based contributions to the capacitive response are mainly due to the increase in the sensing film height which causes the volumetric replacement of air with its lower dielectric constant with sensing film with higher dielectric constant. It has been shown that 95% of all electric field lines of an IDE-based capacitor are contained within ½ the periodicity of the electrodes [10]; for the IDE in this paper, this critical thickness would be 4μm. Importantly, swelling is only important for thin sensing films, i.e., sensing film thicknesses smaller than this critical thickness, as is the case in this work.

The gravimetric sensor detects a mass change as soon as the analyte molecule enters the sensing film. In contrast, the capacitive response contribution due to the dielectric constant change of an analyte molecule increases as the analyte diffuses deeper into the sensing film due to the non-uniform electric field distribution. As a result, the capacitive response due dielectric property changes should always slower than the gravimetric response. How can we then explain the observed faster capacitive response in case of the aromatics? It is believed that the swelling-based contributions to the capacitive response provide a means for the transient response to be "front-loaded": the initial sensing film surface is closer to the electrodes and is pushed further away into lower electric field regions due to swelling. Thus, the swelling-based component to the capacitive signal is strongest at the beginning of the analyte diffusion. If this swelling-based contribution to the capacitive sensitivity dominates the capacitive response, like in the case of the aromatics, then it is possible for the capacitive response to respond faster than its gravimetric counterpart.

The implications of this are three-fold. First, for capacitive sensors with thin polymer coatings three components can contribute to the capacitive sensitivity of the device, yielding three sources for selectivity: (1) the partition coefficient, (2) the relationship of the dielectric constants of the sensing film-analyte pair, (3) the effects of the analyte-dependent swelling behavior. The second implication is that the enhanced selectivity due to the multivariate sensor does not come at the expense of additional sensor response time. In fact, the enhanced selectivity should be more pronounced for thinner sensing films where all above components contribute to the sensor response. The third implication is that the thickness of the polymer film can be used as an additional mechanism to tune the variation in multivariate responses and, thus, the discriminatory performance.

CONCLUSION

Through the use of a novel micromachined multivariate sensor with a single polymeric sensing film, the transient behavior of gravimetric and capacitive sensor responses was investigated. Comparison of the transient sensor responses in 2D dispersion showed enhanced discriminatory ability compared to steady-state response alone, as the discriminatory power of the steady-state dispersion is concentration dependent while the transient response time dispersion is not. Observations of a counter-intuitive "front-loaded" transient behavior in which the capacitive response time was faster than the gravimetric response times for aromatics were noted and investigated within the framework of existing literature. The mechanism for this response time enhancement is hypothesized to be the result of swelling-induced changes in the capacitive response due to the use of a thin sensing film. Furthermore, this work highlights the ability of the multisensor to enhance selectivity not only through use of the steady-state dispersions but also transient response time dispersions at no additional cost to the sensor designer. Finally, this work may pave the way for future work targeting enhanced selectivity mechanisms with drastically improving sensor response times, which is a critical for monitoring VOCs in industrial environments and closed operational settings.

ACKNOWLEDGEMENTS

This work was funded in part by the U.S. Defense Health Agency, US Navy J9 Sustainment (Naval Submarine Medical Research Laboratory work unit F1811). The work was performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (ECCS-2025462).

The views expressed in this conference proceeding reflect the results of research conducted by the author(s) and do not necessarily reflect the official policy or position of the Department of the Navy, Department of Defense, nor the U.S. Government. LAB has been an employee of the U.S. Government. This work was prepared as part of his official duties. Title 17 U.S.C §105 provides that 'Copyright protection under this title is not available for any work of the United States Government'. Title 17 U.S.C §101 defines a U.S. Government work as a work prepared by an employee of the U.S. Government as part of that person's official duties.

REFERENCES

[1] J. Janata, Principles of Chemical Sensors, Springer, New York, 2009.

[2] J-J. Su, C. Carron, S. Truax, K. S. Demirci, L. A. Beardslee, and O. Brand, "Assessing polymer sorption kinetics using micromachined resonators," Int. Solid-State Sensors, Actuators and Microsystems Conf. (Transducers 2011), IEEE (2011) pp. 1420-1423.

[3] A. Kummer, T. Burg, and A. Hierlemann, "Transient signal analysis using complementary metal oxide semiconductor capacitive chemical microsensors," *Analytical Chemistry*, 78, 279-290 (2006).

[4] R. A. Potyrailo, "Multivariable sensors for ubiquitous monitoring of gases in the era of internet of things and industrial internet," *Chemical Rev.*, 116, 11877-11923 (2016).

[5] S. A. Schwartz., O. Brand, and L. A. Beardslee, "Micromachined mass-sensitive and capacitive chemical multisensor using single polymeric sensing film," IEEE Int. Conf. on Micro Electro Mechanical Systems (MEMS), IEEE (2020) pp. 721-724.

[6] L.A. Beardslee, C. Carron, K. S. Demirci, J. Lehman, S. Schwartz, I. Dufour, S. M. Heinrich, F. Josse, and O. Brand, "In-plane vibration of hammerhead resonators for chemical sensing applications," *ACS Sensors*, 5, 73-82 (2019).

[7] C. Carron, P. Getz, S. M. Heinrich, F. Josse, and O. Brand, "Cantilever-based resonant microsensors with integrated temperature modulation for transient chemical analysis." Int. Solid-State Sensors, Actuators and Microsystems Conf. (Transducers 2015), IEEE (2015), pp. 1511-1514.

[8] J. Comyn, ed, *Polymer Permeability*, Springer, 2012.

[9] A. M Kummer, "Tuning sensitivity and discrimination performance of CMOS capacitive chemical microsensor systems," PhD Thesis, ETH Zurich, 2004.

[10] P. Van Gerwen, W. Laureyn, W. Laureys, G. Huyberechts, M. Op De Beeck, K. Baert, J. Suls, W. Sansen, P. Jacobs, L. Hermans, and R. Mertens, "Nanoscaled interdigitated electrode arrays for biochemical sensors," *Sensors and Actuators B: Chemical*, 49, 73-80 (1998).

CONTACT

*Oliver Brand, tel: +1-404-894-9425, oliver.brand@ece.gatech.edu