SANDIA REPORT
SAND2012-3744
Unlimited Release
Printed May 2012

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives

Christopher M. Brotherton and David R. Wheeler

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.osti.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online

SAND2012-3744
Unlimited Release
Printed May 2012

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives

Christopher M. Brotherton[1] and David R. Wheeler[2]

Contraband Detection[1], Materials Science[2]
Sandia National Laboratories

P.O. Box 5800

Albuquerque, New Mexico 87185-MS0782

Abstract

Field-structured chemiresistors (FSCRs) are polymer based sensors that exhibit a resistance change when exposed to an analyte of interest. The amount of resistance change depends on the polymer-analyte affinity. The affinity can be manipulated by modifying the polymer within the FSCRs. In this paper, we investigate the ability of chemically modified FSCRs to sense hydrogen peroxide vapor. Five chemical species were chosen based on their hydrophobicity or reactivity with hydrogen peroxide. Of the five investigated, FSCRs modified with allyl methyl sulfide exhibited a significant response to hydrogen peroxide vapor. Additionally, these same FSCRs were evaluated against a common interferrant in hydrogen peroxide detection, water vapor. For the conditions investigated, the FSCRs modified with allyl methyl sulfide were able to successfully distinguish between water vapor and hydrogen peroxide vapor. A portion of the results presented here will be submitted to the Sensors and Actuators journal.

Acknowledgments

The authors would like to acknowledge Mark Rodriguez for the XRF measurements, Cody Washburn for use of the FTIR, and Doug Read for his guidance and insight.

Contents

1. Introduction 7
2. Materials and Methods 8
   2.1 Sensor Fabrication 8
   2.2 Sensor Testing Apparatus 10
   2.3 Testing Procedure 10
3. Results and Discussion 11
   3.1 Polydimethylsiloxane (PDMS) 11
   3.2 Acrylic Acid (AA) 12
   3.3 1,4-diazabicyclo[2.2.2]octane (DABCO) 13
   3.4 2,6-diallyl-3,5-bis(trifluoromethyl)phenol (DBP) 14
   3.5 Allyl methyl sulfide (AMS) 14
4. Conclusion 17

Figures

Figure 1. Depiction of a typical hydrosilylation reaction. 8
Figure 2. The chemical structures of the materials incorporated into the elastomer of FSCRs: (a) acylic acid, (b) 1,4-diazabicyclo[2.2.2]octane, (c) 2,6-diallyl-3,5-bis(trifluoromethyl)phenol and (d) allyl methyl sulfide. 9
Figure 3. Experimental apparatus for testing FSCRs with both water and hydrogen peroxide vapor. 10
Figure 4. The percent resistivity change of the FSCRs is determined by comparing the baseline resistance with the change in resistance once exposed to the analyte vapor. 11
Figure 5. Example results for unmodified FSCRs exposed to water vapor. 12
Figure 6. FTIR results for the Si-H containing monomer with and without AA. The AA concentration listed here is with respect to the Si-H containing monomer. The final concentration within the sensor is half this value due to the addition of the vinyl-terminal PDMS used for curing. 13
Figure 7. XRF results for the Si-H containing material reacted with AMS overnight at 50C. The material contains 5 wt% AMS and 0.6 vol% Karstedt catalyst. These concentrations are with respect to the the Si-H containing material. The final concentrations within the sensors are half this value due to the addition of the vinyl-terminal PDMS used for curing. 15
Figure 8. Results for an FSCR modified with AMS and exposed to hydrogen peroxide vapor. Periodically, the sensors experience hypersensitivity resulting in significantly higher resistance values. 16
Figure 9. Results for FSCRs modified with 5 wt% AMS exposed to hydrogen peroxide vapor. The FSCRs experience both a break-in period and periodic hypersensitivity. 17

Nomenclature

AA	acrylic acid
AMS	allyl methyl sulfide
DABCO	1,4-diazabicyclo[2.2.2]octane
DBP	2,6-diallyl-3,5-bis(trifluoromethyl)phenol
FSCR	field-structured chemiresistors
FTIR	fourier transform infrared spectroscopy
PDMS	polydimethylsiloxane
VOC	volatile organic compound
XRF	x-ray fluorescence

1. Introduction

Typical chemiresistors are made up of an elastomer filled with a conductive material which is often carbon black. These resistors are then exposed to an analyte of interest that causes swelling within the chemiresistor. This swelling causes disruption in the conduction pathways within the elastomer resulting in an increase in the resistivity of the material. In order to differentiate analytes, arrays of chemiresistors made with different elastomers are used and pattern recognition is used to match the sensor responses with known analyte responses [1-12]. In addition to the equilibrium sensor response, work has also been performed investigating the kinetic response of chemiresistors when exposed to high vapor pressure materials [13-15]. Chemiresistors have been shown to be effective in a broad range of applications ranging from volatile organic compound (VOC) detection in soil and groundwater [16] to detection of land mines [17]. Additionally, the relative ease of construction and availability of materials make chemiresistors inexpensive, allowing both reusable and disposable applications to be considered.

Prior work using field-structured chemiresistors (FSCR) has shown them to be a responsive, versatile, and robust sensing technology. Differing from traditional chemiresistors, FSCRs use gold-coated magnetic particles suspended in an elastomer and cured in the presence of a magnetic field. The magnetic field causes the particles to align in chain-like structures that bridge electrodes and provide conduction pathways through the material. The electrodes allow the resistivity of the material to be measured continuously over the course of any experiment. With the particles aligned, only small amounts of swelling are necessary to separate the pathways and significantly increase the resistivity of the material. An additional advantage of FSCRs comes from the ability to tune the sensors for particular swelling ranges by controlling the stress within the elastomer. This tuning allows for particular concentration ranges of analyte to be targeted [18-20].

In this paper, we tailor FSCR sensors for detection of hydrogen peroxide. Hydrogen peroxide is a strong oxidizer used in a broad range of applications such as bleaching and disinfection. However, concentrated hydrogen peroxide can also be used as an energetic material when mixed with an appropriate fuel. Detection of hydrogen peroxide/fuel mixtures is complicated by the fact that hydrogen peroxide is often encountered in legitimate health and beauty products resulting in a high occurrence of false positives. To be effective as a sensor, a FSCR must be able to detect hydrogen peroxide at relevant concentrations. An additional complication of detecting hydrogen peroxide results from its similarity with water. Typically, the analyte of interest absorbs into the elastomer of the chemiresistor and causes the material to swell. The amount of swelling is dictated by the interactions between the elastomer and the analyte as well as the analyte concentration. If the interactions between the elastomer and hydrogen peroxide are not significantly different than that with water, detection with a single elastomer becomes impossible. Typical measures of elastomer/solvent interaction are solubility parameters. The Hansen solubility parameters for water and hydrogen peroxide are 47.8 and 47.0, respectively, suggesting that the interactions of these two materials with an elastomer would be very difficult to differentiate unless the sensor has sufficient selectivity or an array of different sensor materials are used [21]. Alternatively, the reactive nature of hydrogen peroxide can be used to irreversibly alter the elastomer resulting in a change to the solubility parameter of the elastomer and potentially increasing the response to the hydrogen peroxide analyte.

2. Materials and Methods

2.1 Sensor Fabrication

In this work, we focus on polydimethylsiloxane (PDMS) based FSCRs and incorporate various chemical species into the crosslinked elastomer via catalytic hydrosilylation. Catalytic hydrosilylation is the reaction of a Si-H bond with an unsaturated organic compound (see Figure 1) [22-24]. Hydrosilylation is a common reaction used for crosslinking PDMS where two parts (part a is a vinyl-terminated PDMS and part b is a multifunctional Si-H containing siloxane polymer) are mixed and heated. One way of incorporating other chemical compounds into the PDMS used for FSCRs requires the reaction of the multifunctional Si-H containing polymer with a vinyl-terminated species first. Incorporation of the chemical species into the Si-H containing siloxane polymer is then verified using either FTIR or X-ray fluorescence. Once that reaction is complete, the modified polymer can then be reacted in equal parts with the vinyl-terminated PDMS to crosslink the material and form an elastomer.

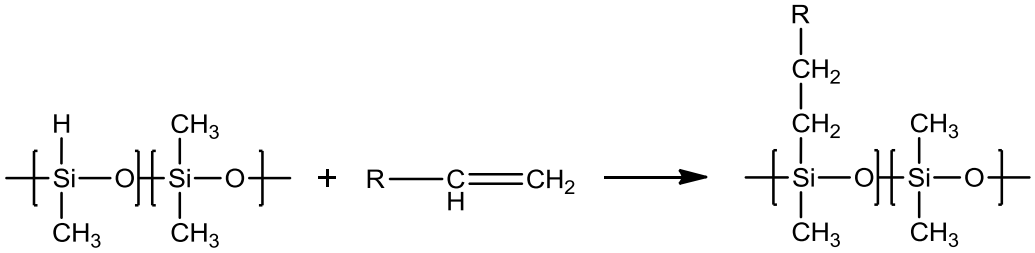

Figure 1. Depiction of a typical hydrosilylation reaction.

The chemical species chosen to modify the elastomer of the FSCRs appear in Figure 2. Acrylic acid (AA) was selected to manipulate the hydrophobicity of the FSCR elastomer and 1,4-diazabicyclo[2.2.2]octane (DABCO), 2,6-diallyl-3,5-bis(trifluoromethyl)phenol (DBP) and allyl methyl sulfide (AMS) were selected based on their reactivity with hydrogen peroxide. All of the analytes are from Fisher Chemicals (A.C.S. certified reagent grade). The concentration of the chemical species that can be incorporated into the elastomer is limited by the concentration of Si-H bonds available. If all of the Si-H bonds are reacted with the chemical species of interest, the elastomer will not crosslink resulting in a liquid material.

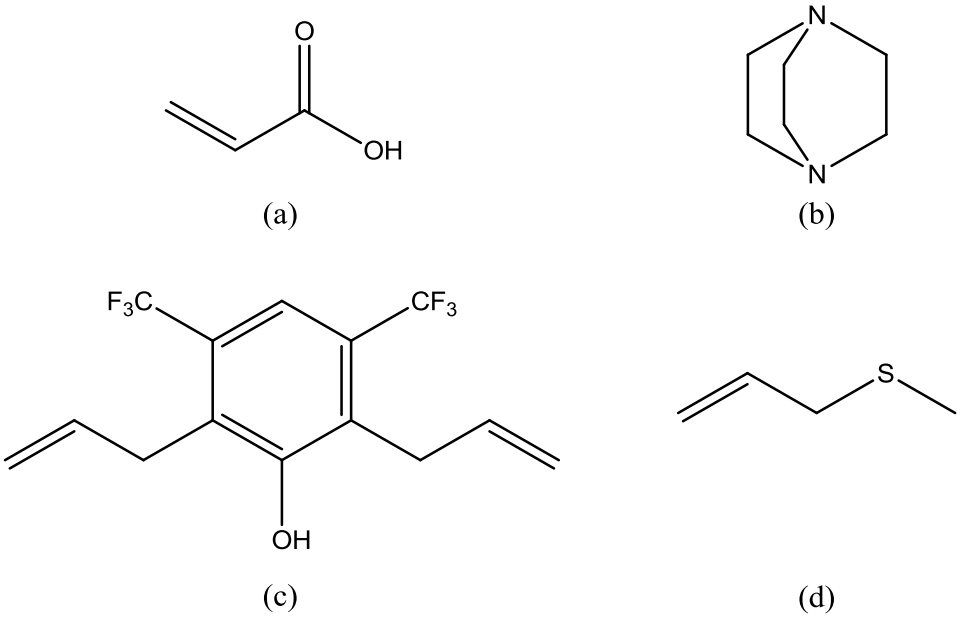

Figure 2. The chemical structures of the materials incorporated into the elastomer of FSCRs: (a) acylic acid, (b) 1,4-diazabicyclo[2.2.2]octane, (c) 2,6-diallyl-3,5-bis(trifluoromethyl)phenol and (d) allyl methyl sulfide.

The FSCRs are constructed using a mixture of a two-part, addition-cure material PDMS (Gelest Inc. optical encapsulent 41, PP2-OE41), one of the chemical species described above and 10 micron gold-coated nickel particles (Sulzer Metco E-Fill 2755). The mixture is then deposited on a nonconductive substrate with two gold electrode pads spaced 1 mm apart. The mixture is deposited in order to span the 1 mm gap. The sensors are then cured for 24 hours in a ~750 G uniaxial magnetic field. The sensors are oriented so that the nickel particles within the elastomer align into a chain-like network that bridges the two electrodes. The concentration of the chemical species, particles and cure temperature are varied.

In addition to modifying with chemical species, the properties of the FSCRs can be manipulated by varying the particle concentration and cure temperature. Particle concentration affects the sensitivity of the sensors to swelling. As the concentration of particles increases, the number of conduction pathways throughout the material also increases, requiring a larger amount of swelling to break enough conduction pathways to result in a measurable change in resistivity. The advantage to increased particle concentration is the increased likelihood that the conduction pathways will form within the material resulting in a sensor with a baseline resistivity that is not infinite. Additionally, the stress incorporated into the sensor material is affected by the cure temperature. As the cure temperature increases, the crosslinking proceeds at a quicker pace and results in an increased amount of stress within the elastomer and a stiffer material. As the stiffness increases, a larger amount of analyte is necessary to cause a measurable amount of change in the resistivity due to swelling. However, sensors cured at elevated temperatures are more likely to contract when cooled, resulting in a higher probability that the baseline resistivity of the sensor is not infinite.

2.2 Sensor Testing Apparatus

The sensors are tested using the apparatus shown in Figure 3. The apparatus consists of a tank of high-purity nitrogen (Matheson Tri-Gas) that is split into two separate streams each controlled using mass flow controllers (Aalborg GFC17). One stream is bubbled through a container of either DI water or a 30 wt% solution of hydrogen peroxide. This analyte stream is then recombined with the stream of nitrogen. The flow rates of each stream can be manipulated in order to obtain the vapor concentration of interest. The individual sensors are housed in a chemically-resistant chamber that allows for electrical contact to be made with each of the two conductive pads on the sensor. The resistance of the sensors is monitored continuously during the experiment using Keithley picoammeters (model 6487). In the current configuration, four sensors can be tested simultaneously. The bubbler as wells as the sensor housing are contained within a temperature controlled container. The temperature is controlled using a recirculated water bath (Polysciences 9102A111B). The entire system is controlled using custom LabView software that allows for automated testing.

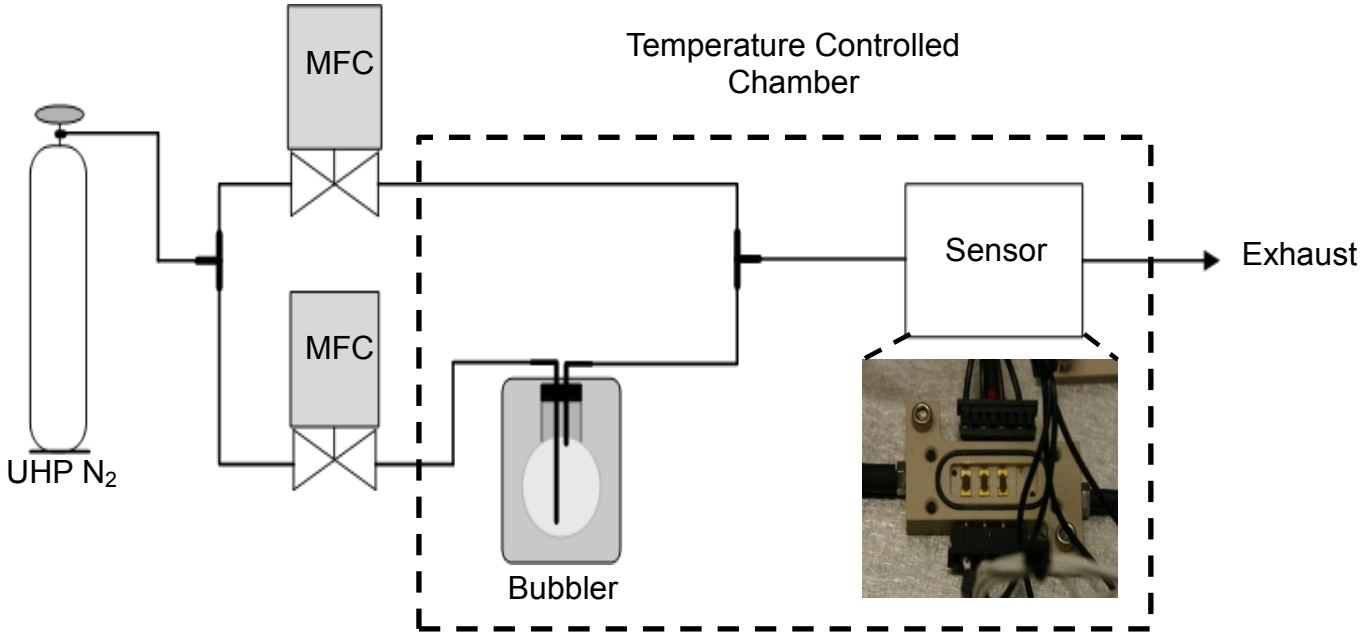

Figure 3. Experimental apparatus for testing FSCRs with both water and hydrogen peroxide vapor.

2.3 Testing Procedure

Typical tests consist of cycling the sensors between pure nitrogen and either nitrogen with saturated DI water or hydrogen peroxide vapor. The tests take place at 20 C and the temperature is held constant throughout the entire experiment. Each step in the cycle occurs for 20 minutes, allowing for the sensor and the chemical vapor to come to equilibrium. After 20 minutes the resistance of the sensors is taken. The values of the final one minute (one per second) of the 20 minute step are averaged to determine the resistance value. The resistance for the sensor when in equilibrium with nitrogen is the baseline resistance (R_b). The resistance for the sensor after exposure to the nitrogen + vapor is compared with the baseline resistance to give a change in

resistance (ΔR). The ratio of those values multiplied by 100% describes the percent resistivity change upon exposure to the analyte. An illustration of this analysis is depicted in Figure 4. The testing is repeated to ensure that each sensor is exposed to a minimum of five cycles to capture repeatability.

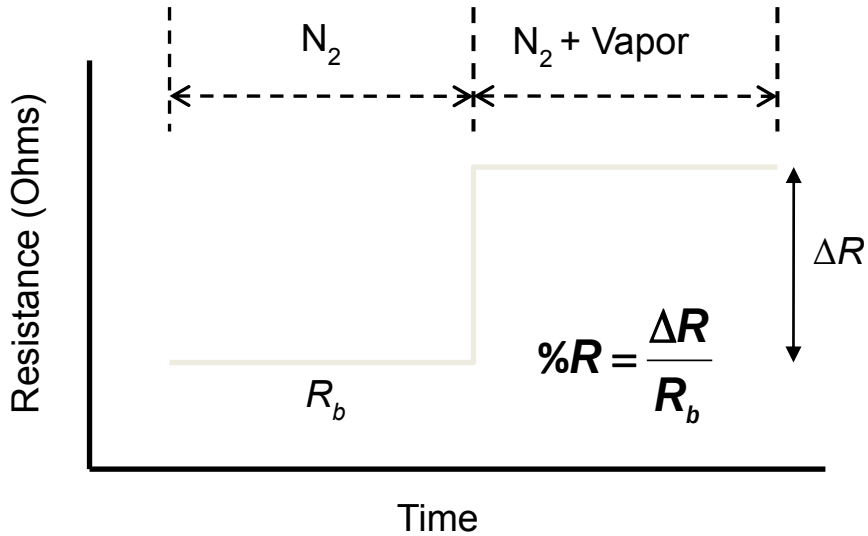

Figure 4. The percent resistivity change of the FSCRs is determined by comparing the baseline resistance with the change in resistance once exposed to the analyte vapor.

3. Results and Discussion

3.1 Polydimethylsiloxane (PDMS)

To establish a control, sensors fabricated without an additional chemical species were evaluated by exposing them to both DI water and hydrogen peroxide vapor. The elastomer was prepared according to the manufacturer's instructions (equal parts a and b) and mixed with gold-coated nickel particles to produce a 15 wt% mixture. The mixture was cured at 50 C. Typical results are shown in Figure 5. Exposure to either water or hydrogen peroxide both resulted in a percent resistivity change of 10%, illustrating that the PDMS material used in the sensors does not exhibit statistically different behavior for nitrogen with either water or hydrogen peroxide vapor.

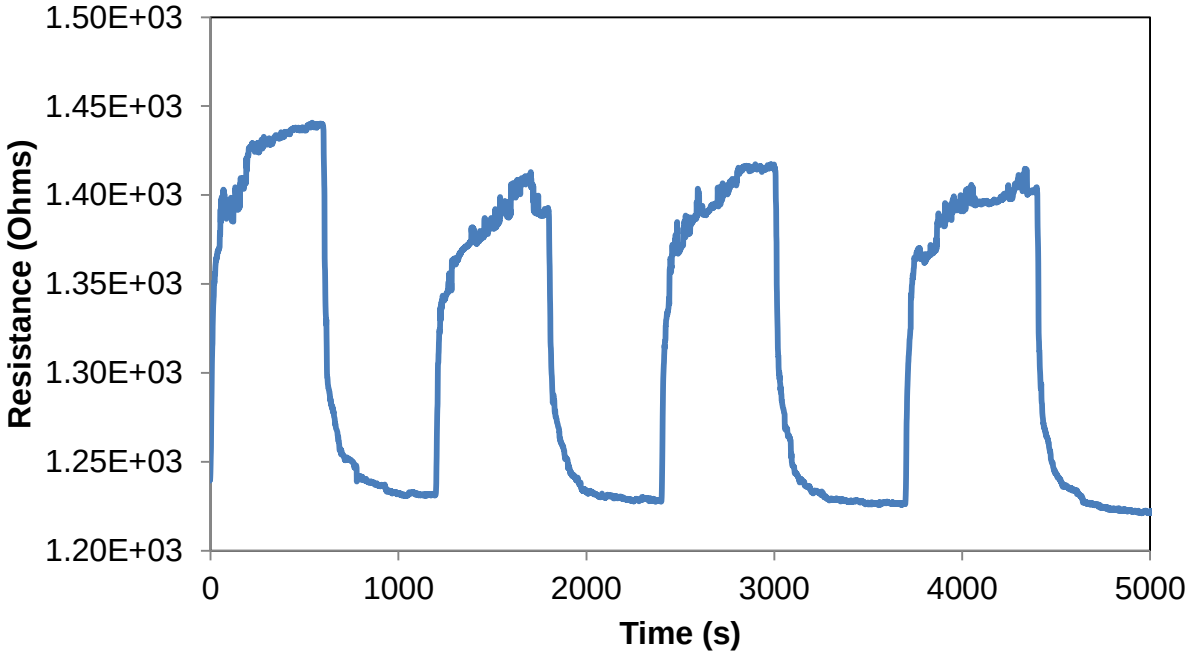

Figure 5. Example results for unmodified FSCRs exposed to water vapor.

3.2 Acrylic Acid (AA)

Sensors were evaluated with 0.25, 0.5 and 1 wt% acrylic acid and cured overnight at 50 C. Additionally, 30 µL of Karstedt catalyst (0.15 vol%) was added to the mixture to increase reactivity. The incorporation of the acrylic acid into the Si-H containing polymer was verified using FTIR (Nicolet 6700). Example FTIR data for both the virgin Si-H containing polymer and the 10 wt% acrylic acid concentration appears in Figure 6. The 10 wt% AA concentration is with respect to the Si-H containing monomer. The final concentration within the sensor is half this value due to the addition of the vinyl-terminal PDMS used for curing. The curves are offset to aid in the identification of the relevant peaks. The disappearance of the Si-H peak (2100-2360 cm^{-1}) and the appearance of the carboxylic acid peak (1705-1720 cm^{-1}) illustrates that the AA is incorporated into the elastomer by reacting with the Si-H groups [25]. The disappearance of the Si-H groups also dictates the maximum concentration of the AA that can be incorporated since there must be Si-H groups present in order to crosslink the material for use in a sensor. Therefore, only sensor concentrations of AA <5 wt% are considered.

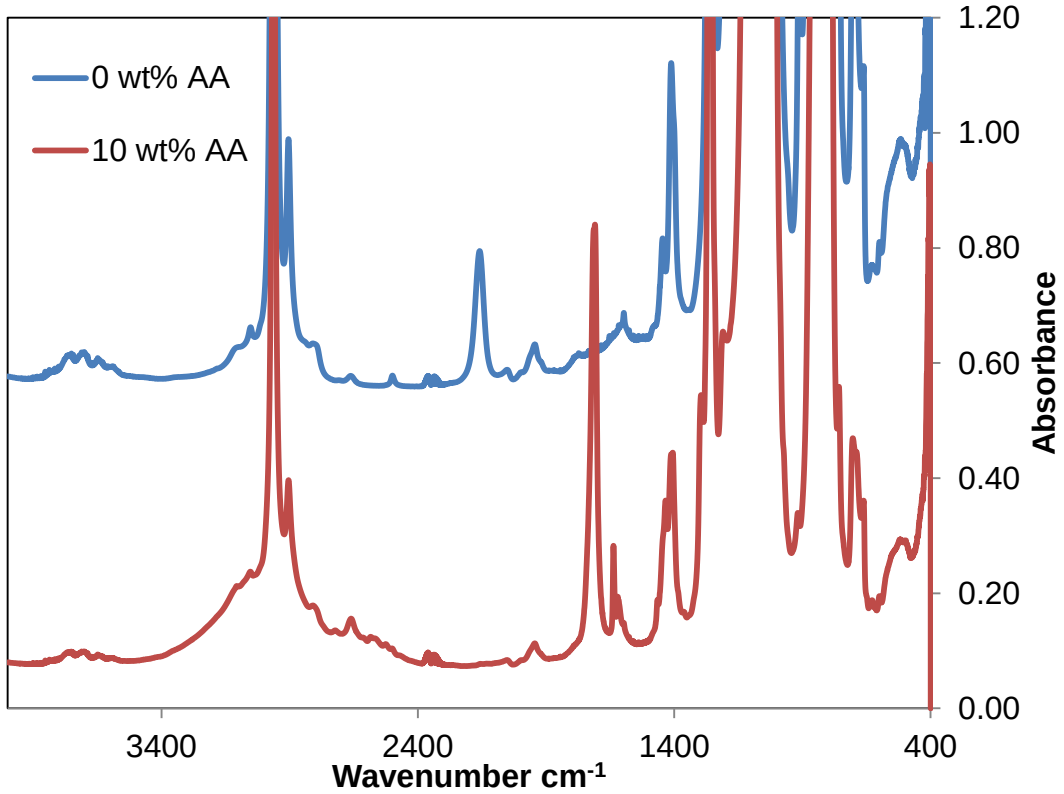

Figure 6. FTIR results for the Si-H containing monomer with and without AA. The AA concentration listed here is with respect to the Si-H containing monomer. The final concentration within the sensor is half this value due to the addition of the vinyl-terminal PDMS used for curing.

All of the concentrations of AA considered produced sensors with a wide range response to water vapor. The percent resistivity change varied from 4 to 40% and did not correlate with the concentration of AA in the sensor. Given the large standard deviation of the response, sensors made with AA were not tested with hydrogen peroxide since the probability that the response to water would be statistically different from the response with hydrogen peroxide, given a reasonable number of sensors, is low.

3.3 1,4-diazabicyclo[2.2.2]octane (DABCO)

DABCO was selected due to the reaction it will undergo when exposed to hydrogen peroxide resulting in a DABCO-hydrogen peroxide complex [26]. Since DABCO does not contain a vinyl bond, it is not expected to covalently bond with the PDMS material in the sensor. Instead, the resulting sensor is a mixture of the DABCO surrounded by crosslinked material. Sensors made with 5 wt% DABCO and 25 wt% gold-coated nickel particles were cured overnight at 80 C and tested with both water and hydrogen peroxide vapor. In both cases, the resulting sensors did not exhibit a response statistically different from zero for either water or hydrogen peroxide vapor. These results suggest that either the reaction between the DABCO and hydrogen peroxide did not take place over the time span of the experiment or that the reaction had only a negligible

effect on the elastomer that did not result in physical change (swelling or contraction) to the elastomer material.

3.4 2,6-diallyl-3,5-bis(trifluoromethyl)phenol (DBP)

DBP was selected due to the presence of vinyl bonds capable of reacting with the Si-H bonds in the elastomer and the potential for reaction with hydrogen peroxide [27]. Incorporation of DBP with the Si-H containing elastomer was verified using FTIR to identify the reduction in the Si-H peak after the reaction and the increase in the OH peak from the DBP molecule. Sensors were made with 0.5, 1.0, 2.0 and 5.0 wt% DBP, 25 wt% gold-coated nickel particles, and 0.15 vol% Karstedt catalyst. Cure temperatures of 22 C (room temp) to 50 C were also investigated. The lower temperatures were selected to reduce the stiffness of the elastomer and potentially increase the sensitivity of the elastomer to physical changes due to reaction. Under all conditions, the percent resistivity change for sensors made with DBP for both water and hydrogen peroxide vapor is less than 5%. This suggests that the reaction between the DBP and hydrogen peroxide did not proceed at a sufficient rate to be captured over the course of the exposure experiment.

3.5 Allyl methyl sulfide (AMS)

AMS was selected due to the presence of a vinyl bond that can be used to covalently bind the molecule to the elastomer and the reaction of sulfides to sulfoxides and sulfones with hydrogen peroxide [22-24]. The sulfoxides/sulfones will effectively lower the hydrophobicity of the sensor resulting in increased swelling and therefore an increase in resistivity of the sensor when exposed to polar molecules. To incorporate the AMS into the elastomer, AMS was reacted overnight with the Si-H containing elastomer (5 wt% AMS) at 50 C and a Karstedt catalyst concentration of 0.6 vol%. The AMS and catalyst concentrations listed here are with respect to the Si-H containing monomer. The final concentrations within the sensors are half these values due to the addition of the vinyl-terminal PDMS used for curing. A higher catalyst concentration was necessary (typically 0.3 vol%) due to catalyst poisoning by the sulfide. Incorporation of the AMS into the Si-H containing polymer was determined using both FTIR and x-ray fluorescence (XRF) (Bruker M4 Tornado). FTIR was used to verify the decrease in the concentration of Si-H bonds within the material and XRF was used to measure the concentration of sulfur in the reacted material. XRF results appear in Figure 7 and the resulting concentration of sulfur in the material was 2.95 ± 1.46 wt%.

Figure 7. XRF results for the Si-H containing material reacted with AMS overnight at 50C. The material contains 5 wt% AMS and 0.6 vol% Karstedt catalyst. These concentrations are with respect to the the Si-H containing material. The final concentrations within the sensors are half this value due to the addition of the vinyl-terminal PDMS used for curing.

Sensors were then made with 2.5 wt% AMS, gold-coated nickel particles at a concentration of 25 wt%, a Karstedt catalyst concentration of 0.6 vol% and a cure temperature of 80 C. Percent resistivity change experiments were performed at 20 C. The percent resistivity change of these resistors upon exposure with water vapor prior to hydrogen peroxide vapor exposure is less than 2%. Including AMS into the PDMS elastomer lowers the response to water vapor due to the increase in hydrophobicity of the material. Typical results with hydrogen peroxide vapor are illustrated in Figure 8. The results illustrate the typical cycling of the sensors between pure nitrogen and nitrogen with hydrogen peroxide vapor. The initial percent resistivity change is 5%, but increases with each cycle. With continued cycling, the percent resistivity change can increase above 50%. These results suggest that the elastomer material is reacting with the hydrogen peroxide vapor and becoming more hydrophilic. However the reaction proceeds slowly and multiple cycles are needed for the reaction to complete.

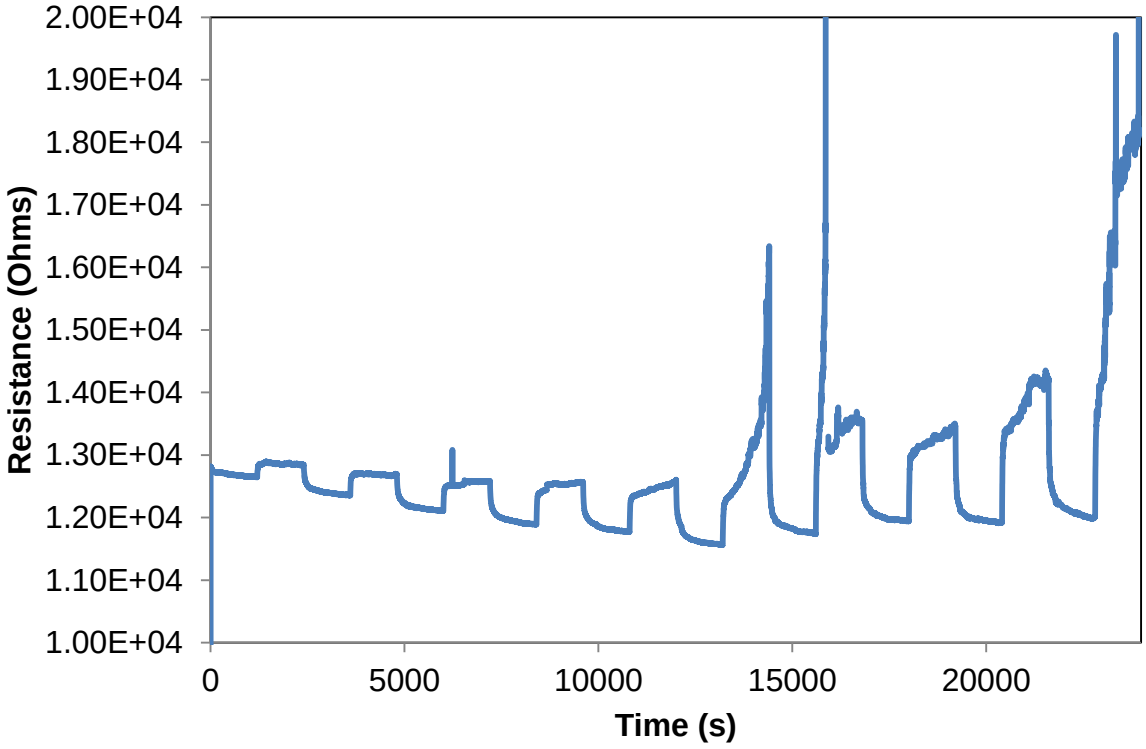

Figure 8. Results for an FSCR modified with AMS and exposed to hydrogen peroxide vapor. Periodically, the sensors experience hypersensitivity resulting in significantly higher resistance values.

In order to decrease the reaction time, the concentration of AMS in the elastomer was increased to 5 wt%. The concentration of the gold-coated nickel particles, Karstedt catalyst concentration, cure temperature, and experimental temperature were not changed. Sample results are illustrated in Figure 9. Many of the sensors with increased AMS concentration exhibited a break-in period that varied from sensor to sensor. During the break-in period the response to the hydrogen peroxide vapor varied significantly and the reason for the response variability is currently not understood. After the break-in period, the sensors had percent resistivity changes up to 32%. The response to water vapor for these sensors is less than 3%. The necessary reaction time for the sensors with 5 wt% AMS is not significantly different from the sensors made with 2.5 wt% AMS. Future experiments should focus on increasing the concentration of AMS above 5 wt%, but Si-H bond concentrations in the elastomer may also have to increase to ensure that the material will have enough for crosslinking.

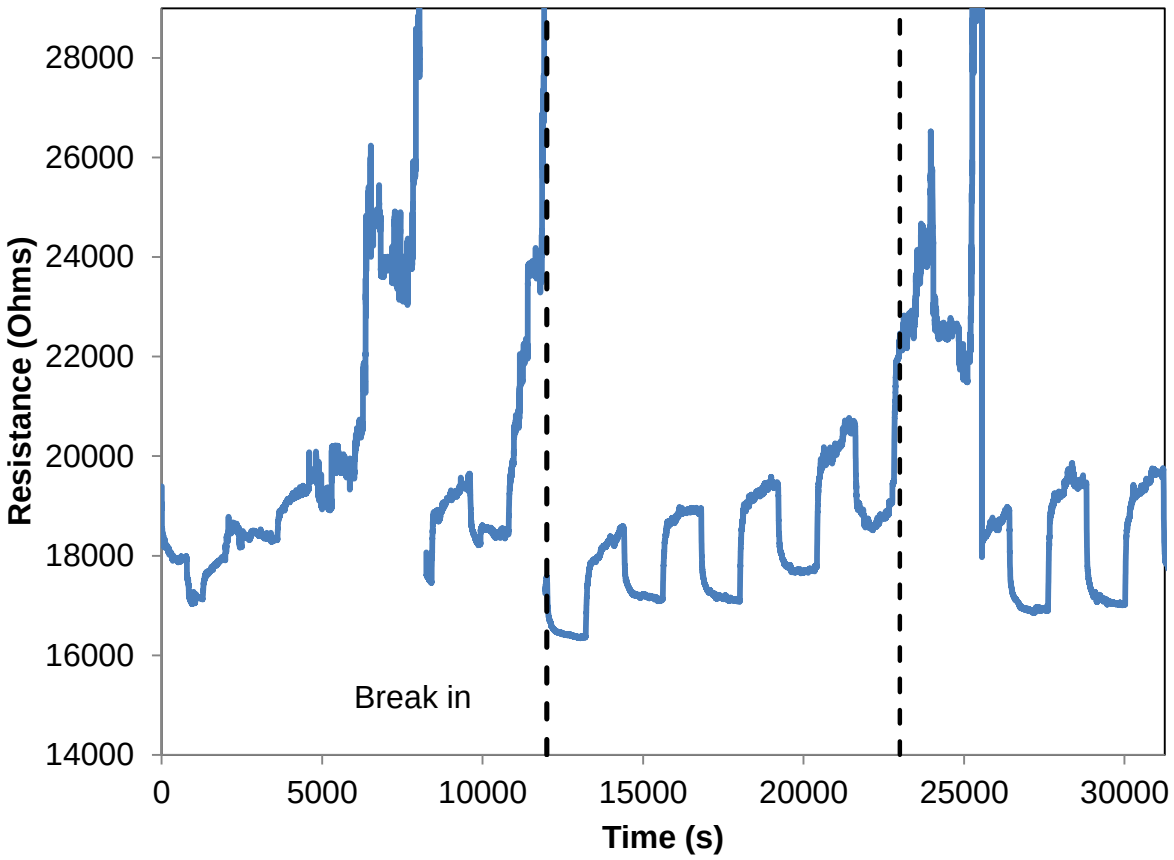

Figure 9. Results for FSCRs modified with 5 wt% AMS exposed to hydrogen peroxide vapor. The FSCRs experience both a break-in period and periodic hypersensitivity.

Increasing the experimental temperature from 20 C to 30 C was also considered in order to increase the rate of reaction between the AMS and the hydrogen peroxide vapor. The increase in temperature causes thermal expansion within the elastomer causing the sensors to be nonconductive. To offset this, the concentration of gold-coated nickel particles was increased from 25 wt% to 35 wt%. The increased particle concentration did increase the probability of the sensors being conductive, but the resulting sensors had a widely varying response to both water and hydrogen peroxide vapor. Due to this variability, additional experiments were not performed.

4. Conclusion

We have studied FSCRs with chemically modified elastomers to determine their effectiveness sensing hydrogen peroxide vapor. Of the chemical species used to modify the elastomer, only one (AMS) was able to sense hydrogen peroxide and differentiate between water and hydrogen peroxide vapor. Using the AMS-modified elastomers, the FSCRs demonstrated an increased resistivity that increased with each cycle. Under some conditions, the FSCRs experienced a

break-in period that lasted up to five cycles before exhibiting consistent behavior. Periodically, the FSCRs would experience hypersensitivity resulting in a large resistance. The onset of this hypersensitivity varied from sensor to sensor and often the sensors would return to a usable state after multiple cycles. The reasons for this hypersensitivity are not yet understood. In an attempt to increase the reaction rate of the hydrogen peroxide with the FSCRs, an increase in AMS concentration and an increase in the operation temperature were considered. Neither of these changes produced a significant decrease in the reaction time. We suggest that future efforts focus on decreasing the reaction time by increasing the AMS concentration higher than 5 wt%. Elastomers with an increased Si-H bond concentration will need to be used in order to ensure a crosslinked material.

References

[1] 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.
[2] S.V. Patel, M.W. Jenkins, R.C. Hughes, W.G. Yelton, A.J. Ricco, Differentiation of chemical components in a binary solvent vapor mixture using carbon/polymer composite-based chemiresistors, Analytical Chemistry, 72 (2000) 1532-1542.
[3] T. Gao, E.S. Tillman, N.S. Lewis, Detection and classification of volativle organic amines and carboxylic acids using arrays of carbon black-dendrimer composite vapor detectors, Chemistry of Materials, 17 (2005) 2904-2911.
[4] T. Gao, M.D. Woodka, B.S. Brunschwig, N.S. Lewis, Chemiresistor for array-based vapor sensing using composites of carbon black with low volatility organic molecules, Chemistry of Materials, 18 (2006) 5193-5202.
[5] B.J. Doleman, M.C. Lonergan, E.J. Severin, T.P. Vaid, N.S. Lewis, Quantitative study of the resolving power of arrays of carbon black-polymer composites in various vapor-sensing tasks, Analytical Chemistry, 70 (1998) 4177-4190.
[6] B.C. Sisk, N.S. Lewis, Estimation of chemical and physical characteristics of analyte vapors through analysis of the response data of arrays of polymer-carbon black composite vapor detectors, Sensors and Actuators B, 96 (2003) 268-282.
[7] B.C. Sisk, N.S. Lewis, Vapor sensing using polymer/carbon black composites in the percolative conduction regime, Langmuir, 22 (2006) 7928-7935.
[8] B.C. Sisk, N.S. Lewis, Comparison of analytical methods and calibration methods for correction of detector response drift in arrays of carbon black-polymer composite vapor detectors, Sensors and Actuators B, 104 (2005) 249-268.
[9] M. De Wit, E. Vanneste, H.J. Geise, L.J. Nagels, Chemiresistive sensors of electrically conducting poly(2,5-thienylene vinylene) and copolymers: their responses to nine organic vapours, Sensors and Actuators B, 50 (1998) 164-172.
[10] E.S. Tillman, M.E. Koscho, R.H. Grubbs, N.S. Lewis, Enhanced sensitivity to and classification of volatile carboxylic acids using arrays of linear poly(ethylenimine)-carbon black composite vapors detectors, Analytical Chemistry, 75 (2003) 1748-1753.
[11] T.P. Vaid, M.C. Burl, N.S. Lewis, Comparison of the performance of different discrimination algorithms in analyte discrimination tasks using an array of carbon black-polymer composite vapor detectors, Analytical Chemistry, 73 (2001) 321-331.
[12] M.E. Koscho, R.H. Grubbs, N.S. Lewis, Properties of vapor detector arrays fromed through plasticization of carbon black-organic polymer composites, Analytical Chemistry, 74 (2002) 1307-1315.
[13] S.M. Briglin, N.S. Lewis, Characterization of the temporal response profile of carbon black-polymer composite detector to volatile organic vapors, Journal of Physical Chemsitry, 107 (2003) 11031-11042.
[14] M.D. Woodka, B.S. Brunschwig, N.S. Lewis, Use of spatiotemporal response information from sorption-based sensor arrays to identify and quantify the composition of analyte mixtures, Langmuir, 23 (2007) 13232-13241.
[15] D.H. Read, J. Martin, Analyte discrimination from chemiresistor repsonse kinetics, Analytical Chemistry, 82 (2010) 6969-6975.
[16] C.K. Ho, R.C. Hughes, *In-situ* chemiresistor sensor package for real-time detection of volatile organic compounds in soil and groundwater, Sensors, 2 (2002) 23-34.

[17] S.M. Briglin, M.C. Burl, M.S. Freund, N.S. Lewis, A. Matzger, D.N. Ortiz, P. Tokumaru, Progress in use of carbon black-polymer composite vapor detector arrays for land mine detection, in: A.C. Dubey, J.F. Harvey, J.T. Broach, R.E. Dugan (Eds.) Detection and remediation technologies for mines and minelike targets, Proceedings of SPIE, 2000.
[18] J. Martin, R. Anderson, J. Odinek, D. Adolf, J. Williamson, Controlling percolation in field-structured particle composites: Observations of giant thermoresistance, piezoresistance, and chemiresistance, Physical Review B, 67 (2003).
[19] D.H. Read, J.E. Martin, Field-structured chemiresistors, Advanced Functional Materials, 20 (2010) 1577-1584.
[20] D.H. Read, J.E. Martin, Master transduction curve for field-structured chemiresistor calibration, Analytical Chemistry, 82 (2010) 5375-5379.
[21] C.M. Hansen, Hansen Solubility Parameters: A User's Handbook, 2nd. ed., 2007.
[22] M. Cui, Z. Li, X. Huang, J. Xi, X. Tang, S. Zheng, Polysilaethers bearing Si-H and its functionalization via hydrosilylation with acrylic acid, Polymer, 46 (2005) 9162-9169.
[23] V.V. Kaverin, I.M. Salimgareeva, I.V. Kovaleva, V.P. Yur'ev, Hydrosilylation of diallyl sulfide with trichlorosilane, Russian Chemical Bulletin, 30 (1980) 1741-1743.
[24] R.N. Meals, Hydrosilylation in the synthesis of organosilanes, Pure and Applied Chemistry, 13 (1966) 141-158.
[25] A.J. Gordon, R.A. Ford, The chemist's companion: a handbook of practical data, techniques, and references, Wiley, 1972.
[26] P. Dembech, A. Ricci, G. Seconi, M. Taddei, Bis(trimethylsilyl) Peroxide (BTMSPO), Organic Syntheses, 74 (1997) 84.
[27] P.R. Lewis, R.P. Manginell, D.R. Adkins, R.J. Kottenstette, D.R. Wheeler, S.S. Sokolowski, D.E. Trudell, J.E. Byrnes, M. Okandan, J.M. Bauer, R.G. Manley, G.C. Frye-Mason, Recent advancements in the gas-phase MicroChemLab, IEEE Sensors Journal, 6 (2006) 784-795.

Distribution

1	MS0782	Christopher M. Brotherton	6633 (electronic copy)
1	MS0892	David R. Wheeler	1714 (electronic copy)
1	MS0899	Technical Library	9536 (electronic copy)

Sandia National Laboratories