Talanta xxx (2008) xxx–xxx

Contents lists available at ScienceDirect

Talanta

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

Detection of methyl salicylate using polymer-filled chemicapacitors

Sanjay V. Patel*, Stephen T. Hobson, Sabina Cemalovic, Todd E. Mlsna

Seacoast Science, Inc., 2151 Las Palmas Drive Suite C, Carlsbad, CA 92011, United States

ARTICLE INFO

Article history:
Received 21 February 2008
Received in revised form 16 April 2008
Accepted 17 April 2008
Available online xxx

Keywords:
Capacitance measurement
Chemical transducers
Methyl salicylate
Microsensors
Sensor array
Man-in-Simulant Test

ABSTRACT

Methyl salicylate (MeS) is used as a chemical warfare agent simulant to test chemical protective garments and other individual personal protective gear. The accurate and real-time detection of this analyte is advantageous for various testing regimes. This paper reports the results of MeS vapor exposures on polymer-filled capacitance-based sensors at temperatures ranging from 15 °C to 50 °C under dry and humid conditions. Multiple capacitors were arranged in an array on a silicon chip each having a different sorptive polymer. The sensors used parallel-plate electrode geometry to measure the dielectric permittivity changes of each polymer when exposed to water and MeS vapor. Of the four polymers tested against MeS, the optimal polymer displayed near or sub-parts-per-million detection limits at 35 °C (0–80%RH).

© 2008 Published by Elsevier B.V.

UNCORRECTED PROOF

1. Introduction

The United States Departments of Homeland Security (DHS) and Defense (DOD) are testing next generation personal protection systems to protect U.S. military personnel from chemical threats. Some of these programs focus on Man-in-Simulant Testing (MIST), where methyl salicylate (MeS) is used to test the effectiveness of chemical suits [1,2]. Currently, the suits are tested with passive absorbent pads to collect samples while soldiers or mannequins wear the suits during MeS exposure [3]. To identify the weaknesses in the system, i.e. chemical break-through sites; small, unobtrusive and light weight sensors are needed to collect real-time data as the suits are used during tests.

A key requirement of this application is that proposed sensors do not interfere with air-flow through the suit or with the wearer's mobility. This significantly restricts the size and power of a viable sensor system. Furthermore, the sensors must operate in high relative humidity and elevated temperature environment proximate to the skin of a warfighter or first responder performing their tasks. Microfabricated sensor arrays have the potential to address this need.

Microsensors using sorbent materials are promising for this niche application since they can operate at ambient temperature and can be miniaturized. Such sensors measure changes in the sorbent material when a vapor or gas is absorbed. Reported technology platforms include: resistive sensors [4,5] and cantilever stress sensors [6] to measure swelling of polymers; resonating cantilevers [7], surface acoustic wave (SAW) devices [8], and flexural plate wave (FPW) devices [9] to measure mass and viscoelasticity changes; and capacitive sensors [10,11] to measure changes in polymer permittivity. Multi-transducer arrays, systems with multiple different technologies, have also been reported for vapor detection [12].

Presented herein are the results from the exposure of four chemicapacitors, each filled with a different semi-selectively MeS absorbing dielectric polymers. As chemicals sorb into the dielectric, they alter its permittivity and thereby raise or lower the capacitance of the sensor. The four polymers have functional groups of varied polarity, acidity, and dielectric constant (~2–10).

2. Experimental

2.1. Sensor structure

The sensor structures used in this study were fabricated using the Multi-User MEMS Process (MUMPs) [13] from MEMSCAP, Inc. (Durham, NC). Fig. 1 shows a top-view photograph and a side-view cross-section diagram of one of these structures. In the present work, two chips were used, each having multiple parallel-plate capacitor structures spaced approximately 300–500 μm apart, on a 2 mm × 5 mm chip [14]. The structures are made from polycrystalline silicon deposited on an insulating silicon nitride layer. Each parallel-plate capacitor is square-shaped, approximately 285 μm on a side, with a 0.75 μm vertical gap between the plates. The top

---

* Corresponding author. Tel.: +1 760 268 0083; fax: +1 760 268 0662.
E-mail address: sanjay@seacoastscience.com (S.V. Patel).

0039-9140/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.talanta.2008.04.035

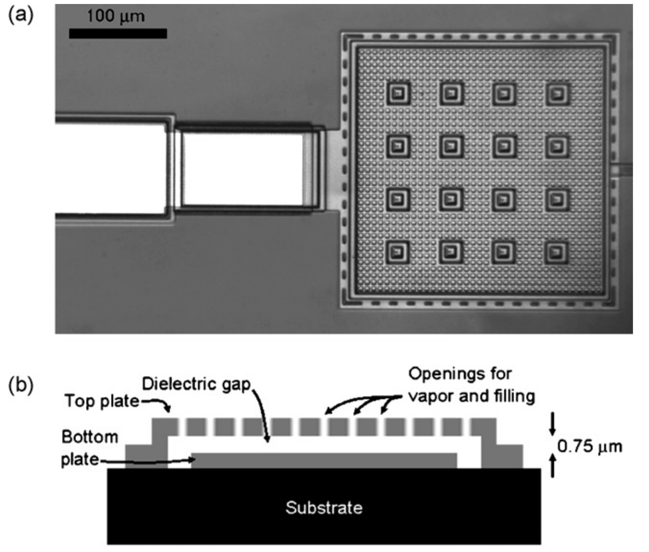

Fig. 1. Seacoast science parallel-plate chemicapacitor element: (a) top-view photograph showing square capacitor and wirebond pad and (b) cross-sectional diagram (not to scale).

plate is perforated forming a waffle pattern, with silicon beams of 2.5 μm and holes of 5 μm. The drive circuit [14,15] applies a square wave to the bottom plate, and the top plate is used to sense the capacitance of the structure. The 16 larger squares are support posts, which together with the outer edge of the square (also perforated) keep the top plate from flexing.

2.2. Sensitive materials

The dielectric gap between the plates of each capacitor was filled with a dilute polymer solution (<1 wt% in chloroform, toluene, or acetone) injected through holes in the top plate using a piezoelectric-driven ink-jet from MicroFab Technologies, Inc. [16]. The residual solvent was allowed to evaporate, leaving the neat polymer in the capacitor.

The same two chips were used for all of the sensor testing. Each chip contained four chemicapacitors, and each chemicapacitor was coated with one of the four polymers listed in Table 1 [17,18]. All data presented are averaged responses from the same polymer on both chips, and all error bars represent ±1 S.D. of the responses for multiple (typically 3–5) chemical exposures. The error bars provide a measure of chip-to-chip repeatability and exposure-to-exposure repeatability.

PEVA and PECH were purchased from Sigma–Aldrich Corp. (St. Louis, MO), PIB from Polysciences, Inc. (Warrington, PA), and ADIOL [19] was received from Dr. McGill at the U.S. Naval Research Laboratories. The values for the dielectric constants were measured on the two chips at 20 °C in dry air, and match well with values found in the literature [14,20,21]. In comparison, MeS has a reported dielectric constant of 9 at 20 °C and 9.41 at 30 °C [22].

2.3. Sensor testing

Sensor chips were wire-bonded in low volume ceramic packages with capacitance measurement circuits [14,23]. The capacitance measurement circuit used in these tests had a range of 0.01–350 pF with a resolution of 0.001 pF. The circuit uses a square wave to charge each capacitor, which is then discharged to a reference capacitor whose potential is measured. A microprocessor and other related circuitry on a printed circuit board are used to control the timing and applied voltages, and to measure the capacitances. Three modifications were made to the previous circuit [23]; (1) the range of measurements was increased to over 350 pF, (2) the measurement circuit operated at 3.3 V, reduced from 5 V, and (3) the applied voltage was centered to prevent charging across the polymer.

Noise in the system ranged from 0.001 pF to 0.7 pF, and was dependant on the capacitance being measured, the resolution of the analog to digital converters, and the applied oscillator voltage (0.012–3.2 V). The highest noise levels occurred at high measured capacitances that were typically encountered at high relative humidity.

A computer controlled gas delivery system, consisting of mass-flow controllers (MKS Instruments, Andover, MA), was used to deliver and dilute the chemical vapors with compressed and dried laboratory air. The sensors were tested under continuous air-flow. The MeS vapors were generated by bubbling air through the liquid in a fritted glass gas-washing bottle (ACE Glass, Inc., Vineland, NJ) that was temperature-controlled in a chilled water bath. Humid air was mixed by adding a stream of air bubbled through deionized water also in a temperature-controlled chilled water bath. Two sensor chips were tested simultaneously in a silcosteel® passivated (Restek, Corp., Bellefonte, PA) stainless steel chamber (approximately 10.8 cm × 2.4 cm × 0.6 cm, internal wetted volume). To keep the exposed volumes low, only the sensor chips and ceramic packages were exposed to chemicals, while the remaining circuit board was connected using a feed-through to outside of the test chamber. The test chamber was temperature controlled to ±0.1 °C.

Vapor pressures were extrapolated from Antoine coefficients in Lange's Handbook of Chemistry [22] and compared to extrapolations from the NIST Webbook [24]. From these data the vapor pressure of MeS was estimated to be 0.1 Torr at 25 °C and 0.35 Torr at 40 °C.

3. Results and discussion

All four polymers responded to MeS vapor in a monotonic fashion, over the range of temperatures and concentrations tested. Fig. 2 shows the raw response of a PECH- and a PIB-filled chemicapacitor to three concentrations of MeS. PECH-filled chemicapacitors pro-

Table 1
Polymers tested and their nominal capacitance measured at 20 °C in dry air with microcapacitors

Polymer	Functionality and properties	Starting capacitance (pF)	Dielectric constant
Polyisobutylene (PIB); MW = 1350	Low-polarity hydrocarbon; viscous liquid	2.4	2.4
Poly(ethylene-*co*-vinyl acetate) (40% acetate content) (PEVA)	Low-polarity, solid, semi-crystalline [17]	4.2	4.0
Bis[(*E*)-1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-ol]siloxane (ADIOL)	Polar; hydrogen-bond acidic; greasy liquid	5.4	5.3
Polyepichlorohydrin (PECH); MW = 700,000	Moderate hydrogen bonding [18]; polar; solid	10.2	9.8

Please cite this article in press as: S.V. Patel, et al., Talanta (2008), doi:10.1016/j.talanta.2008.04.035

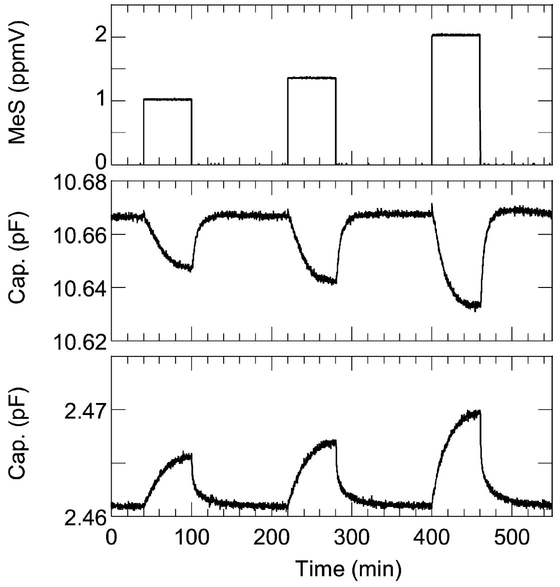

Fig. 2. Sensor responses to MeS in 50% relative humidity at 25 °C. MeS concentrations (top), PECH chemicapacitor (middle), PIB chemicapacitor (bottom).

Table 2
Average capacitance change (ΔC) for a 0–20% relative humidity step at each temperature

	At 35 °C (pF)	At 25 °C (pF)	At 15 °C (pF)
PIB	0.002	0.002	0.002
PEVA	0.024	0.022	0.022
PECH	0.110	0.089	0.076
ADIOL	0.665	0.463	0.338

duced negative capacitance shifts when exposed to MeS, whereas the other polymer-filled chemicapacitors produced positive capacitance changes upon MeS exposure. This discrepancy has been discussed in the literature and is associated with the balance between swelling effects versus the increase in number and density of dipoles in the bulk polymer [10]. If swelling dominates and the analyte has a lower dielectric constant than the polymer, as with PECH, the MeS causes the bulk permittivity to decrease. Other work on parallel-plate chemicapacitors showed that both PIB and PEVA provided decreasing permittivity upon sorption of analytes with low dielectric constants, including some aromatic compounds and alkanes [10,14].

The capacitance and dielectric permittivity of all four polymers increase when exposed to water vapor, but to varying degrees (Table 2). PIB- and PEVA-filled chemicapacitors were the least sensitive, followed by PECH and ADIOL, which was the most sensitive to water vapor. Note that water vapor equilibrated faster than MeS in the test system. These devices have previously demonstrated response times in the order of 200 ms to 1 s [23]. The measured capacitance of the PECH, PIB and PEVA chemicapacitors all decreased upon heating in both dry air and 50% relative humidity. In contrast, the capacitance of the ADIOL-filled sensors increased in both environments.

Fig. 3 contains graphs of the response of the PECH chemicapacitors at temperatures ranging from 15 °C to 50 °C. At lower temperatures (<30 °C), sub-ppmV (parts-per-million by volume) concentrations of MeS were detectable in both dry and 50% relative humidity. The dashed horizontal line denotes the "noise" floor for the measurements. The lowest detectable concentration increases drastically at higher temperatures consistent with the proposed physisorption-based sensing mechanism [25]. In addition, the slope of the response curves becomes shallower, i.e. the sensitivity decreases as temperature increases. This is primarily due to the vapor–liquid equilibrium favoring the vapor phase at the higher temperatures.

Similarly, PIB- and PEVA-filled chemicapacitors provide sensitivity profiles (Figs. 4 and 5) that exhibit decreased sensitivity at higher temperature; however, their lowest detectable concentrations are better than PECH. ADIOL-filled chemicapacitors were most sensitive to MeS at all temperatures (Fig. 6), although their response speed was significantly slower at 15 °C. Due to the slow equilibration 15 °C ADIOL response data is presented in the inset graphs. This extremely slow equilibration causes the measured response at 15 °C to be much smaller than at 20 °C, behavior that is not observed on the other polymers at 15 °C. PECH and PEVA are solids at this temperature and PEVA is semi-crystalline [17], although PECH is well above its glass transition temperature (−22.5 °C). One possible explanation for this response speed is that ADIOL is approaching its glass transition temperature (T_g), drastically slowing the diffu-

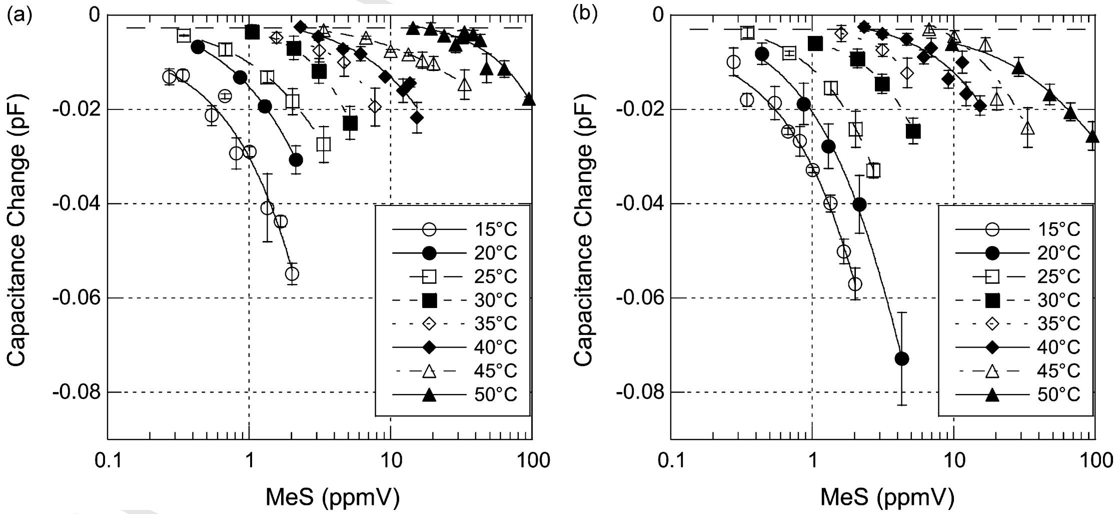

Fig. 3. Isotherms for the PECH-filled chemicapacitors, (a) under 50% relative humidity and (b) in dry air, for MeS concentrations between 300 ppbV and 100 ppmV. The lines are only meant to guide the eye. The dashed horizontal line in each figure represents the peak-to-peak noise. Each point represents the average response and the error bars are ±1 S.D. of the responses for multiple (typically 3–5) chemical exposures.

Please cite this article in press as: S.V. Patel, et al., Talanta (2008), doi:10.1016/j.talanta.2008.04.035

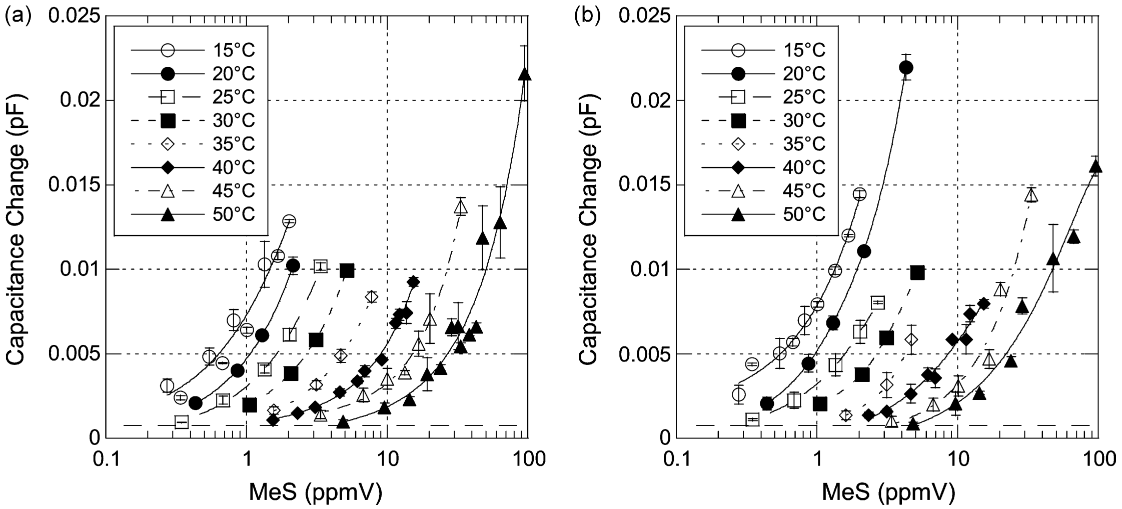

Fig. 4. Isotherms for the PIB-filled chemicapacitors: (a) under 50% relative humidity and (b) in dry air, for MeS concentrations between 300 ppbV and 100 ppmV.

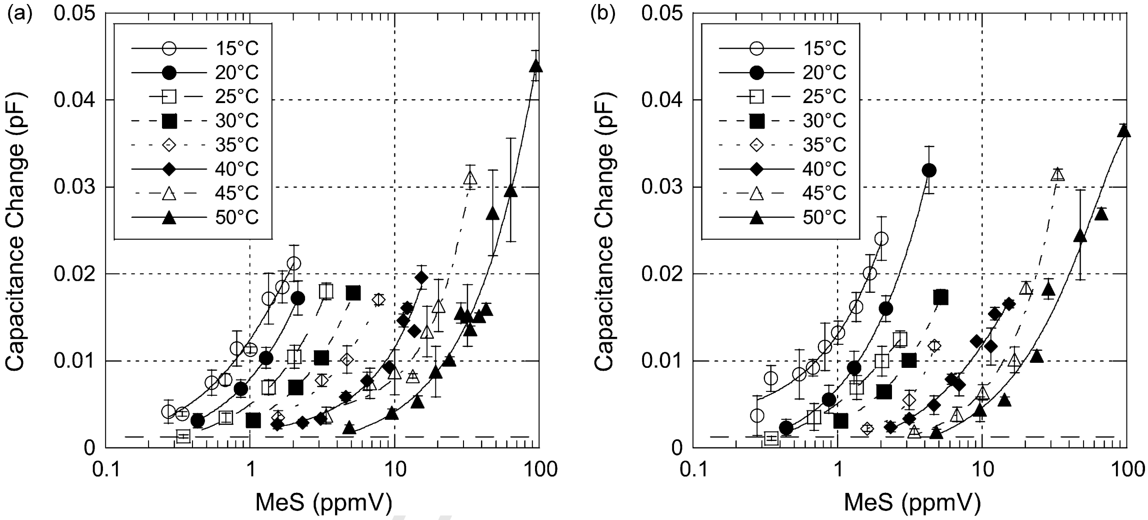

Fig. 5. Isotherms for the PEVA-filled chemicapacitors: (a) under 50% relative humidity and (b) in dry air, for MeS concentrations between 300 ppbV and 100 ppmV.

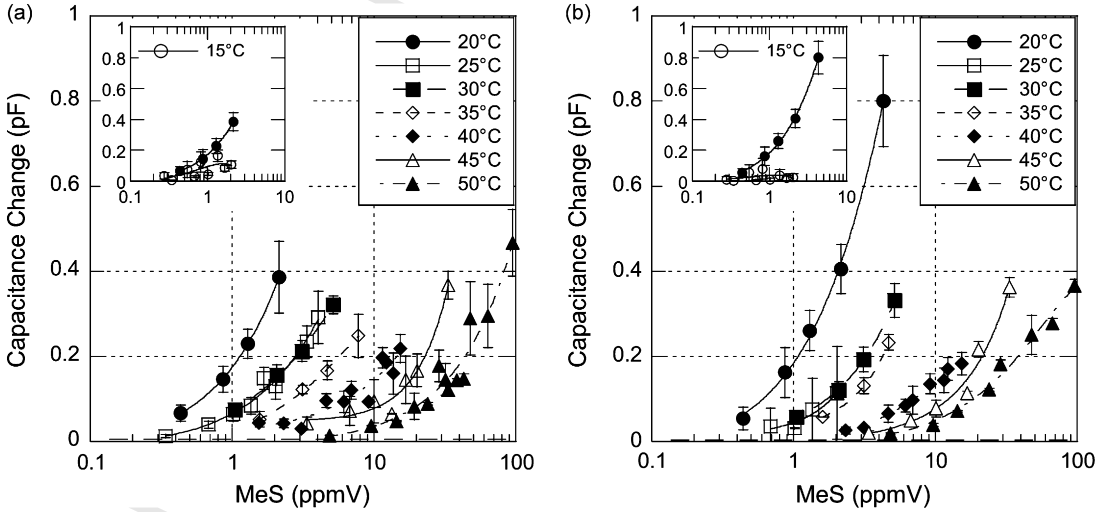

Fig. 6. Isotherms for the ADIOL-filled chemicapacitors: (a) under 50% relative humidity and (b) in dry air, for MeS concentrations between 300 ppbV and 100 ppmV. Inset graphs show the 15 °C and 20 °C isotherms with the same *y*-axis scale.

Please cite this article in press as: S.V. Patel, et al., Talanta (2008), doi:10.1016/j.talanta.2008.04.035

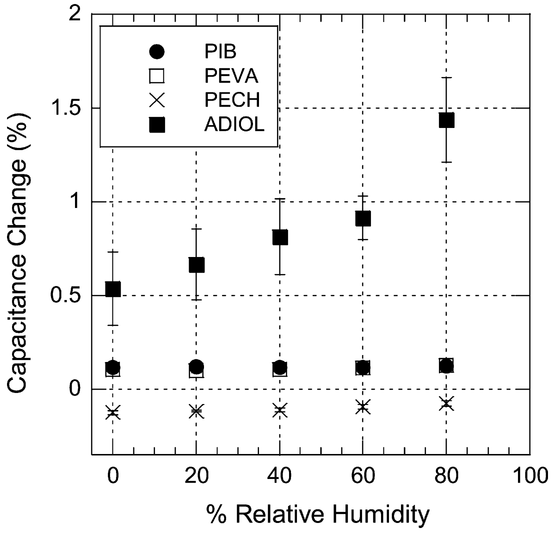

Fig. 7. Affect of humidity on response of all four polymer-filled chemicapacitors to 1 ppmV MeS, exposures at 25 °C. *Note*: PIB and PEVA responses overlap on all exposures.

sion of MeS into the polymer. Another possibility is that at lower temperatures, the ADIOL response is able to accumulate significant amounts of MeS by very strong hydrogen-bonding interactions [26]. Whereas the other polymers equilibrated with MeS in 1 h at 15 °C, ADIOL did not equilibrate even after 3 h except at the highest concentrations. Albeit faster, the ADIOL response was still slow at 20 °C and 25 °C, therefore the equilibrated response after 1 h of exposure is presented in all graphs.

To compare the sensors' sensitivity to MeS under various conditions, sensor responses to 1 ppmV MeS exposures at 15 °C, 25 °C, and 35 °C were measured. 1 ppmV exposures at 25 °C show that PECH, PIB and PEVA are unaffected by the background humidity (Fig. 7). This is true for PIB and PEVA at 15 °C and 35 °C also. In contrast ADIOL's sensitivity to MeS improves at higher relative humidity levels at 25 °C, but does not continue this trend at 35 °C (Fig. 8a). As seen in Fig. 6 at 15 °C the ADIOL response is significantly increased at higher humidity levels when compared to dry conditions. Comparing the behavior of PECH (Fig. 8b) at 15 °C, 25 °C, and 35 °C, one sees a very mild decrease in sensitivity at highest humidity levels, although not nearly as pronounced as the influence of water on the ADIOL response.

One explanation for the observed sensor behavior is that the PECH/water bulk matrix has a higher overall polarity at high humidity, leading to a less soluble matrix than when dry. That is, the water-laden matrix rejects or lessens the amount of MeS absorbed. Furthermore, for PECH the dominant mechanism is swelling, for which the incremental change in dielectric constant is less when preloaded with water vapor and a lower permittivity analyte is added. In either case, the effect is not significant. For ADIOL, the water vapor helps to sorb more MeS, likely because the hydrated polymer chains have an apparent higher polarity increasing the MeS/ADIOL interaction. At higher temperatures the humidity-enhanced sensitivity diminishes for the ADIOL sensors, where less water is sorbed.

Theoretical limits of detection (LOD) are estimated from the lowest concentration exposures (Figs. 3–6) at dry and 50% relative humidity conditions. These values are conservatively estimated using three times the peak-to-peak noise as the figure of merit. Fig. 9 shows the dry and wet LODs estimated at various temperatures for the four polymer-filled chemicapacitors. For ADIOL, in humid conditions, the LOD was ~300 ppbV at 25 °C and ~1 ppmV at 40 °C. This provides a basis for development of a system to be used by chemical suit manufacturers for product testing or potentially even warfighters for real-time use. The trade-off will be size (few cm^3) versus ppb-level sensitivity that has been achieved with mass spectrometry [27].

4. Summary and conclusions

The capacitive sensing method provides near or sub-ppmV level limits of detection for MeS over the temperature range tested. Of the four polymers tested, ADIOL was most sensitive to MeS; however, the current formulation's response speed decreases at lower temperatures, which may limit its effectiveness. At elevated humidity, the ADIOL coated sensors' response to MeS improved, possibly due to a cosolvency effect [28]. PECH provided some basis for selectivity as its response to MeS was negative; however its response diminishes at higher temperatures. Although their chemical structure is quite different, PIB and PEVA provided little discernable difference in response. Since sensitivity of all of the polymers was

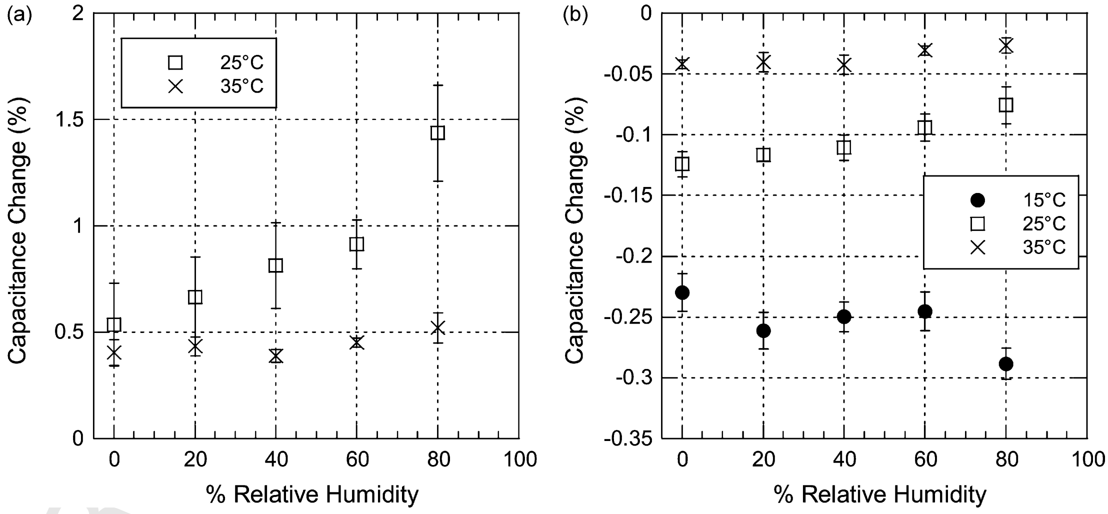

Fig. 8. Responses to 1 ppmV MeS exposures from (a) ADIOL chemicapacitors at 25 °C and 35 °C, and (b) PECH chemicapacitors at 15 °C, 25 °C and 35 °C. 15 °C data for ADIOL are not presented in due to slow equilibration.

PROOF

Please cite this article in press as: S.V. Patel, et al., Talanta (2008), doi:10.1016/j.talanta.2008.04.035

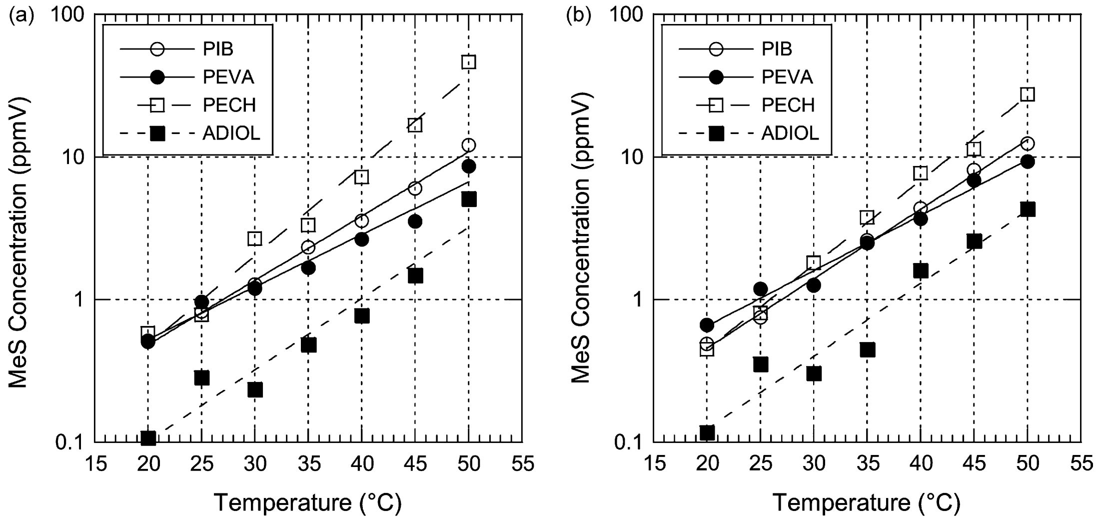

Fig. 9. Calculated limits of detection (LOD) in ppmV at various temperatures in (a) 50% relative humidity and (b) dry air. The lines are only intended to guide the eye.

temperature-dependent, the sensors must be temperature controlled or the data processed using artificial intelligence algorithms to take into account temperature related changes.

Acknowledgements

The authors acknowledge the funding support from the US Army Research Office Program # W911NF-06-C-0009, and the US Department of Homeland Security Program # NBCHC050063. In addition the authors acknowledge the many useful discussions with Dr. Michael von Fahnestock and Dr. Fredrick Cox at Battelle Memorial Laboratories, and Ms. Leticia Mota at TNO Defence, Security and Safety. The authors would also like to thank Dr. R. Andrew McGill and Dr. Eric Houser for the ADIOL sample.

References

[1] National Research Council: Assessment of the U.S. Army Chemical and Biological Defense Command, Report 1, Technical Assessment of the Man-In-Simulant Test (MIST) Program, National Academy Press, Washington, DC, 1997, pp. 30–36.
[2] R. L. Barker, A review of gaps and limitations in test methods for first responder protective clothing and equipment, final report presented to the National Personal Protection Technology Laboratory at the National Institute for Occupational Safety and Health, January 31, 2005, p. 37.
[3] P. Gao, W.P. King, R. Shaffer, J. Occup. Environ. Hyg. 4 (2007) 562.
[4] M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs, N.S. Lewis, Chem. Mater. 8 (1996) 2298.
[5] M.P. Eastman, R.C. Hughes, G. Yelton, A.J. Ricco, S.V. Patel, M.W. Jenkins, J. Electrochem. Soc. 146 (1999) 3907.
[6] C.L. Britton, R.L. Jones, P.I. Oden, Z. Hu, R.J. Warmack, S.F. Smith, W.L. Bryan, J.M. Rochelle, Ultramicroscopy 82 (2000) 17.
[7] M. Maute, S. Raible, F.E. Prins, D.P. Kern, U. Weimar, W. Gopel, Microelectron. Eng. 46 (1999) 439.
[8] J.W. Grate, B.M. Wise, M.H. Abraham, Anal. Chem. 71 (1999) 4544.
[9] Q. Cai, J. Park, D. Heldsinger, M.-D. Hsieh, E.T. Zellers, Sens. Actuators B 62 (2000) 121.
[10] A. Hierlemann, D. Lange, C. Hagleitner, N. Kerness, A. Koll, O. Brand, H. Baltes, Sens. Actuators B 70 (2000) 2.
[11] M. Kitsara, D. Goustouridis, S. Chatzandroulis, M. Chatzichristidi, I. Raptis, T. Ganetsos, R. Igreja, C.J. Dias, Sens. Actuators B 127 (2007) 186.
[12] C. Jin, P. Kurzawski, A. Hierlemann, E.T. Zellers, Anal. Chem. 80 (2008) 227.
[13] J. Carter, A. Cowen, B. Hardy, R. Mahadevan, M. Stonefield, S. Wilcenski, PolyMUMPs Design Handbook, Rev. 11.0, MEMSCAP, Inc. 2005.
[14] S.V. Patel, T.E. Mlsna, B. Fruhberger, E. Klaassen, S. Cemalovic, D.R. Baselt, Sens. Actuators B 96 (2003) 541.
[15] D.R. Baselt, B. Fruhberger, E. Klaassen, S. Cemalovic, C.L. Britton Jr., S.V. Patel, T.E. Mlsna, D. McCorkle, B. Warmack, Sens. Actuators B 88 (2003) 120.
[16] MJ-AB01-030 30 μm dispenser and CT-M3-01 inkjet controller from MicroFab Technologies, Inc., Plano, TX. A 30 or 60 μm diameter nozzle was used to deposit polymer solutions.
[17] R. Hiss, S. Hobeika, C. Lynn, G. Strobl, Macromolecules 32 (1999) 4390.
[18] R.A. McGill, M.H. Abraham, J.W. Grate, Chem. Tech. 24 (1994) 27.
[19] R.A. McGill, E.J. Houser, T.E. Mlsna. Linear and branched chemoselective siloxane polymers and methods for use in analytical and purification applications, U.S. Patent #6,630,560, October 7, 2003.
[20] F. Rodriguez, Principles of Polymer Systems, 3rd ed., Hemisphere, New York, 1989, pp. 589–603.
[21] D. McCorkle, R.J. Warmack, S.V. Patel, T. Mlsna, S.R. Hunter, T.L. Ferrell, Sens. Actuators B 107 (2005) 892.
[22] Lange's Handbook of Chemistry, 14th ed., ed. John A. Dean, McGraw-Hill, New York, 1992, pp. 5–50 and 5–116.
[23] T.E. Mlsna, S. Cemalovic, M. Warburton, S.T. Hobson, D.A. Mlsna, S.V. Patel, Sens. Actuators B 116 (2006) 192.
[24] http://webbook.nist.gov/cgi/cbook.cgi?Name=methyl+salicylate&Units=SI.
[25] D.S. Ballantine, R.M. White, S.J. Martin, A.J. Ricco, G.C. Frye, E.T. Zellers, H. Wohltjen, Acoustic Wave Sensors: Theory, Design and Physicochemical Applications, Academic Press, Boston, MA, 1997.
[26] K. Neimann, R. Neumann, Org. Lett. 2 (2000) 2861.
[27] I. Cotte-Rodriguez, D.R. Justes, S.C. Nanita, R.J. Noll, C.C. Mulligan, N.L. Sanders, R.G. Cooks, Analyst 131 (2006) 579.
[28] A.F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd ed., CRC Press, Boca Raton, FL, 1983, pp. 390–392.

ORRECTED PROOF

Please cite this article in press as: S.V. Patel, et al., Talanta (2008), doi:10.1016/j.talanta.2008.04.035