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# Effects of Temperature and Humidity on the Performance of Polymer-Coated Surface Acoustic Wave Vapor Sensor Arrays

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**The influences of temperature and atmospheric humidity on the performance of an array of eight polymer-coated 158-MHz surface acoustic wave vapor sensors were investigated. Sensitivities to the seven organic vapors examined all exhibited negative Arrhenius temperature dependencies, with responses increasing by factors of 1.5−4.4 on going from 38 to 18 °C. The magnitudes of the temperature effects, while generally similar, differed sufficiently among certain sensor−vapor combinations to cause marked changes in vapor response patterns. In addition, it was found that operating identically coated sensors at different temperatures could provide a means for discriminating certain vapors. The changes in sensor responses with temperature agreed reasonably well with those expected assuming ideal vapor sorption behavior and indicated that changes in the moduli of the sensor coatings were not important mediating factors. Responses to relative humidity (RH) from 0 to 85% RH were important even for the nonpolar sensor coatings. Significant changes in the sensitivities to the organic vapors were observed as a function of atmospheric humidity for several sensor−vapor combinations, which, in turn, affected the patterns of responses obtained from the sensor array. Results indicate that small changes in temperature or humidity have a larger effect on baseline stabilities than on the responses to the vapors. Monte Carlo simulations of sensor responses show that the ability to discriminate vapors in binary and ternary mixtures using a four-sensor array remains high regardless of the operating temperature and ambient humidity, provided that temperature- or humidity-induced changes in the response patterns are taken into account.**

The development of coated surface acoustic wave (SAW) and related acoustic wave sensors and sensor arrays for monitoring gases and vapors continues to be an active area of research.[1−3] In these devices, responses depend upon changes in acoustic wave properties (e.g., frequency, attenuation) accompanying the interaction of the target analyte(s) with a chemically sensitive surface coating. For measuring organic solvent vapors, amorphous polymers can be used as effective sensor coating materials, and responses (i.e., changes in output frequencies) are governed by changes in the mass and viscoelasticity of the polymer resulting from reversible vapor sorption.[4,5] For low vapor concentrations, responses are generally linear functions of the vapor concentration, and a given coating−vapor pair can be described by a response isotherm whose slope depends on the mass of the surface coating, the strength of the sorption interactions, and the volatility of the vapor.[6,7] Using an array of differently coated sensors, therefore, can provide a set of responses whose pattern can be decoded statistically to identify and quantify an individual vapor, the composite response of a vapor mixture, or the components of such a mixture.[6−11]

The potential for incorporating SAW sensor arrays into compact portable or personal instrumentation for real-time monitoring of hazardous vapors has motivated much of the work on this sensor technology. It follows that a major focus of research efforts has been the development and characterization of sorptive coating materials that can impart the degree of selectivity necessary to differentiate one hazardous vapor from another.[1,12,13] Initial reports on field testing of prototype instrumentation employing individual SAW sensors and sensor arrays suggest, however, that controlling for environmental variables such as temperature and humidity can be at least as important to the accuracy of measurements as the inherent selectivity and sensitivity for the target vapor(s).[10,14,15] This paper examines the effects of these two important variables on the baseline frequencies and the responses to several organic vapors of a set of eight polymer-coated SAW sensors. The results are assessed in terms of the discrimination and quantification of different vapors based on sensor array response patterns.

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(1) Zellers, E. T.; Batterman, S. A.; Han, M.; Patrash, S. J. *Anal. Chem.* **1995**, *67*, 1092.
(2) Nieuwenhuisen, M. S.; Venema, A. *Sens. Mater.* **1989**, *5*, 261.
(3) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* **1993**, *65*, 987A.
(4) Martin, S. J.; Frye, G. C.; Senturia, S. D. *Anal. Chem.* **1994**, *66*, 2201.
(5) Grate, J.; Klusty, M.; McGill, R. A.; Abraham, M. H.; Whiting, G.; Andonian-Haftvan, J. *Anal. Chem.* **1992**, *64*, 610.
(6) Patrash, S. J.; Zellers, E. T. *Anal. Chem.* **1993**, *65*, 2055.
(7) Grate, J.; Abraham, M. H. *Sens. Actuators* **1991**, *B3*, 85.
(8) Rose-Pehrrson, S. L.; Grate, J. W.; Ballantine, D. S., Jr.; Jurs, P. *Anal. Chem.* **1988**, *60*, 2801.
(9) Carey, W. P.; Beebe, K. R.; Kowalski, B. R. *Anal. Chem.* **1987**, *59*, 1529.
(10) Grate, J. W.; Rose-Pehrsson, S. L.; Venesky, D. L.; Klusty, M.; Wohltjen, H. *Anal. Chem.* **1993**, *65*, 1868.
(11) Wohltjen, H.; Ballantine, D. S., Jr.; Jarvis, N. L. In *Microsensors and Microinstrumentation*; Murray, R. W., Dessy, R. E., Heineman, W. R., Janata, J., Seitz, W. R., Eds.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 157−175.
(12) Grate, J. W.; Patrash, S. J.; Abraham, M. H. *Anal. Chem.* **1995**, *67*, 2162.
(13) McGill, R. A.; Abraham, M. H.; Grate, J. W. *CHEMTECH* **1994**, *24*, 27.
(14) Frye, G. C.; Martin, S. J.; Cernosek, R. W.; Pfeifer, K. B. *Int. J. Environ. Conscious Manuf.* **1992**, *1*, 37.
(15) Frye, G. C.; Pepper, S. H. *AT-OnSite*; InfoSci. Services, Inc.: Northbrook, IL, 1994; p 62.

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**General Considerations.** As with most previous reports on SAW vapor sensors,[2,3] we use a SAW delay line as the frequency controlling element in a feedback oscillator circuit and measure the oscillation frequency, $f$. Deposition of a thin polymer film on the surface of the device results in a decrease in the oscillation frequency that can be related to the mass of the polymer coating.[4,5] Subsequent exposure to a vapor causes the polymer to reversibly swell and soften, leading to a further decrease in $f$.

The sensitivity of a polymer-coated SAW sensor, expressed as the change of frequency per unit change in vapor concentration, can be described by the following equation:[5,16,17]

$$\Delta f_v/\Delta C_v = K_e \Delta f_c/\rho_c \tag{1}$$

where $\Delta f_v$ is the sensor frequency shift caused by the vapor being sorbed by the coating, $\Delta f_c$ is the initial frequency shift from deposition of the coating, $C_v$ is the air concentration of the vapor, $\rho_c$ is the coating density, and $K_e$ is a sensitivity factor that can be thought of as an "effective" partition coefficient. Since SAW sensor responses arise not only from mass increases but also from changes in the viscosity and/or elastic modulus of the polymer upon vapor sorption,[4–6,12] $K_e$ values are generally larger than the corresponding $K$ values derived from gas–liquid chromatography (GLC) or static methods.

GLC studies have shown that the temperature dependence of $K$ at low vapor concentrations and over finite temperature ranges can be described by the Arrhenius-type relationship,[18]

$$K = K_0 e^{-\Delta H_s/RT} = K_0 e^{-(\Delta H_c + \Delta H_m)/RT} \tag{2}$$

where the preexponential term $K_0$ is, to a first approximation, independent of temperature, $\Delta H_s$ is the heat of sorption, $R$ is the gas constant, $T$ is the absolute temperature, $\Delta H_c$ is the molar heat of condensation, which is invariably negative for condensable vapors, and $\Delta H_m$ is the partial molar heat of mixing, which is ideally zero but generally is positive for real solvent–polymer mixtures.[19]

Assuming that $K_e$ is proportional to $K$,[5,6,12] then at a given temperature the proportionality constant can be incorporated into the preexponential term, and eq 2 can be written in terms of $K_e$ rather than $K$. However, to the extent that $K_e$ is affected by modulus changes, eq 2 will underestimate the temperature dependence of the vapor sensitivity because the initial modulus of the polymer decreases with increasing temperature, and the relative contribution of modulus changes to the net response will be reduced. This would lead to a decrease in response with increasing temperature that is greater than that predicted by eq 2. Phase transitions in the polymer coating[20] and/or film resonance effects[4] could also affect the temperature dependence of the vapor sensitivity.

$\Delta H_c$ is related to the vapor pressure of the solvent via the Clausius–Clapeyron equation, and $\Delta H_m$ is related to the difference in cohesive energies between the vapor and the polymer.[21] The absolute value of $\Delta H_c$ is usually much larger than $\Delta H_m$, consistent with the general observation that vapor sorption into a polymer decreases exponentially with increasing temperature. A negative exponential temperature dependence of polymer-coated SAW sensor responses to vapors has been reported previously by us[22,23] and by others.[5,17,24] The $\Delta H_s$ value estimated from responses to styrene vapor of a PIB-coated SAW sensor between 15 and 40 °C in the former study[23] was within the range of $\Delta H_s$ values reported for other vapors with various GLC stationary phases,[18,21] suggesting that modulus changes do not significantly affect the temperature sensitivity of polymer-coated SAW sensor responses to vapors.

To the extent that $\Delta H_s$ values differ among vapors partitioning into the polymer sensor coatings,[21] the pattern of relative responses obtained from an array of sensors will vary with temperature. This, in turn, should have implications for the ability to discriminate different vapors. One goal of this study was to determine both the temperature dependence of responses for a series of vapors and polymeric sensor coatings that span a range of structures and mutual solubilities and the consequent effects on the performance of an array of such sensors in analyzing one or more vapors.

Baseline frequencies will also be affected by temperature. Although the oscillation frequencies of individual SAW devices fabricated on ST-quartz exhibit relatively small temperature coefficients near room temperature, observed shifts in the frequencies of polymer-coated devices with temperature can be significant.[4,5,20,25,26] Measuring the difference frequency between a coated SAW sensor and an uncoated reference as a means of reducing the inherent temperature sensitivity of the baseline sensor output will not completely compensate for temperature-induced drift because it does not account for the thermal expansion/contraction of the polymer.[5,20] Still, the use of a reference sensor has an important advantage in terms of developing portable instrumentation: the difference frequency obtained by subtracting the reference sensor output from the coated sensor output is typically in the kilohertz range of frequency and can be counted by simple digital frequency counters.

In most practical air monitoring applications, organic vapors must be detected in the presence of relatively high ambient concentrations of water vapor. Sorption of water vapor by the polymer coatings can lead to large shifts in baseline frequencies.[2,15] At high ambient humidity levels, the concentration of sorbed water may be large enough to affect the interaction of the coating with the target vapors. That is, responses to organic vapors and water vapor may not be additive. We reported preliminary results recently suggesting such an effect.[6] Another goal of this study was to characterize the sensitivity to atmospheric humidity of an array of polymer-coated SAW sensors and the effect of changes in humidity on the responses to each of several organic vapors.

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(16) Janghorbani, M.; Freund, H. *Anal. Chem.* **1973**, *45*, 325.

(17) Grate, J. W.; Snow, A.; Ballantine, D. S., Jr.; Wohltjen, H.; Abraham, M. H.; McGill, R. A.; Sasson, P. *Anal. Chem.* **1988**, *60*, 869.

(18) Littlewood, A. B. *Gas Chromatography*; Academic Press: New York, 1970.

(19) Rogers, C. E. In *Polymer Permeability*; Comyn, J., Ed.; Elsevier Applied Science: London, 1985; Chapter 2.

(20) Grate, J. W.; Wenzel, S. W.; White, R. M. *Anal. Chem.* **1992**, *64*, 413.

(21) Laub, R. J.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1978; pp 110–114.

(22) Zellers, E. T. Ph.D. Dissertation, University of California, Berkeley, CA, 1987.

(23) Zellers, E. T.; White, R. M.; Rappaport, S. M. *Anal. Chem.* **1990**, *62*, 1223.

(24) Brace, J. G.; SanFelippo, T. S.; Joshi, S. G. *Sens. Actuators* **1988**, *14*, 47.

(25) Liron, Z. V.; Greenblatt, J.; Frishman, G.; Gratziani, N. *Sens. Actuators B* **1993**, *12*, 115–122.

(26) Ballantine, D. S., Jr.; Wohltjen, H. In *Microsensors and Microinstrumentation*; Murray, R. W., Dessy, R. E., Heineman, W. R., Janata, J., Seitz, W. R., Eds.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 222–236.

## EXPERIMENTAL SECTION

**Materials.** The solvents examined in this study were isooctane, benzene, xylene, trichloroethylene (TCE), tetrahydrofuran (THF), 2-butanone (MEK), and 1-butanol. They were obtained in >99% purity from Aldrich (Milwaukee, WI) and were used as received. The following materials, used as sensor coatings, consisted of rubbery-solid or viscous-liquid polymers or oligomers: polyisobutylene (PIB), acrylonitrile−butadiene copolymer (ABC, 41% acrylonitrile), polychloroprene (PCP), poly(diphenoxyphosphazene) (PDPP), and polyepichlorohydrin (PECH) from Scientific Polymer Products (Ontario, NY); diethylene glycol adipate (DEGA) from Ohio Valley Specialty Chemicals (Marietta, OH); and bis(cyanoallyl)polysiloxane (OV-275) and apiezon-L (APL) from Supelco, Inc. (Bellefonte, PA). These polymers span a fairly broad range of structures and functionalities. They were selected as sensor coatings to provide a range of interaction strengths with the solvent vapors tested and, consequently, to provide sensor response patterns that differ between the different vapors.

**Instrumentation.** SAW devices, sensor array instrumentation, and data acquisition software were obtained from Microsensor Systems, Inc. (Bowling Green, KY). The SAW devices were fabricated on ST-quartz (active area, 8 $mm^2$) and designed to operate at a nominal oscillation frequency of 158 MHz. Details of the transducer configuration and device design have been described elsewhere.[7] Each sensor was anchored with epoxy to a 12-pin, gold-plated TO8 header, and electrical connections were made with ultrasonically bonded gold wires. The headers fit into sockets on a printed circuit board that contained a second (reference) oscillator, rf amplifiers, tuning inductors, mixers, and other signal-conditioning circuitry. A set of four of these printed circuit boards was mounted to the floor of the instrument chassis. The reference sensors were left uncoated and were sealed from the atmosphere with nickel-plated lids soldered to the bases of the TO8 headers. All coated sensors were capped with similar (removable) lids fitted with inlet and outlet tubes to allow exposure to the test atmospheres. The internal volume above the capped sensors was approximately 0.12 $cm^3$. Thin Teflon gaskets were used to seal the lids to the bases of the headers of the coated sensors. The output signal from each sensor in a pair (i.e., one reference and one coated sensor) was mixed and filtered to obtain a difference frequency that was monitored by an on-board four-channel frequency counter and transmitted to a personal computer via an RS-232 buss for display and subsequent data reduction. Signals were sampled and displayed every 2 s. For all of the experiments described here, data were collected from two four-sensor arrays simultaneously, each connected to a separate computer.

**Coating Application.** Solutions of approximately 2 mg/mL of the polymer coatings were prepared in toluene, 2-butanone, or a mixture of toluene and acetone and applied to the sensor with an air brush using $N_2$ as the propellant. Successive passes with the air brush led to a gradual accumulation of the coating on the sensor, which was monitored by the shift in the difference frequency. In certain cases, the frequency declined initially and then increased, indicating that the reference sensor frequency was initially lower than that of the sensor being coated. In all cases, the total shift in frequency was recorded. The values of $\Delta f_c$ (in kHz) for the coatings were as follows: PIB, 185; PDPP, 199; DEGA, 203; PCP, 198; ABC, 202; OV-275, 196; APL, 206; and PECH, 201 (certain coatings were stripped and reapplied during the course of the study, see below). These $\Delta f_c$ values correspond to nominal coating thicknesses of 50−60 nm.[11] Following coating deposition, the sensors were allowed to stand overnight under a constant flow of air or $N_2$ prior to exposure.

**Test-Atmosphere Generation System.** Machined aluminum blocks were clamped over each coated sensor/reference sensor pair using bolts secured to the floor of the chassis. Stainless steel tubing fitted through grooves in the aluminum blocks was used to circulate thermostated water through the blocks to maintain constant temperature throughout both arrays. Thermistors soldered between two of the unused posts of one sensor in each array were calibrated against an NBS traceable thermometer and used to monitor temperature.

The sensor arrays were incorporated into a dynamic test-atmosphere generation system. All tubing was constructed of either stainless steel or Teflon. Dry $N_2$ was used as the diluent for the vapors in experiments designed to examine temperature effects. For studies of humidity effects, air was used as the diluent, and the relative humidity (RH), flow rate, and temperature of the dilution stream were controlled with a Miller-Nelson Research Model HCS-302 controller equipped with an in-line temperature/RH sensor (Model 411E, General Eastern, Watertown, MA) which was previously calibrated above saturated salt solutions ranging from 11 to 90% RH. Vapors were generated by passing a low flow (∼0.1−1 L/min) of $N_2$ (or humidified air) through a fritted bubbler containing the liquid solvent to be tested and then into the dilution stream maintained at ∼10 L/min. For tests where humidified air was passed through the solvent bubbler, it was allowed sufficient time to equilibrate with the RH of the dilution stream prior to exposure to the sensor array to avoid changes in the overall RH of the test atmosphere. The majority of the diluted vapor stream was vented from the system after mixing. A three-way Teflon solenoid valve was used to pass 1 L/min of either clean or contaminated air (or $N_2$) to the sensor arrays. A coil of tubing just upstream of the first array was immersed in the constant temperature bath to aid in thermally equilibrating the flow stream with the sensors. The flow stream was then split into four parallel branches, with each branch directing flow over one sensor in the first array and then another sensor in the second array. Four rotameters downstream of the second array were used to balance and monitor the flow rates through the lines. The flow rate through each path was maintained at approximately 250 mL/min.

The concentrations of the vapors were adjusted by varying the flow through the bubbler while passing clean air (or $N_2$) over the sensors. Vapor concentrations were verified before and after exposure to the sensor array by taking duplicate aliquots of the test atmosphere with a gas-tight syringe from a septum port upstream from the sensor arrays and analyzing the samples with a gas chromatograph (Model 2860, Varian, Mountain View, CA) equipped with a packed column (2-ft., $^1/_8$-in. o.d., Chromosorb + 1% SP-1000, Supelco) and a flame ionization detector. Peak areas were quantified with an electronic integrator (Model 3390A, Hewlett Packard, Palo Alto, CA). Calibrations were performed using solutions of the pure solvents in carbon disulfide.

**Data Collection and Analysis.** Baseline difference frequencies were determined after the thermostated bath temperature was adjusted to the desired setting and the outputs from the thermistors stabilized. At each temperature, sensor responses were collected for each vapor at four to six concentrations covering

Table 1. Temperature Coefficients (d*f*/d*T*) of Baseline Difference Frequencies Determined from 18 to 30 °C[a]

| PIB | PDPP | DEGA | PCP | ABC | APL | OV-275 | PECH |
|---|---|---|---|---|---|---|---|
| 860 (30) | 160 (30) | 660 (20) | 170 (2) | 280 (30) | 170 (10) | 810 (40) | 140 (10) |

[a] Units of d*f*/d*T* are Hz/°C. Values in parentheses are standard deviations ($n = 2-5$).

at least a 10-fold range of concentration. The minimum exposure concentration used was that producing a response of at least 45 Hz for the least sensitive sensor. This response level corresponds to 3 times the typical short-term RMS noise level of 15 Hz. Limits of detection were calculated using this criterion as well. Each measurement consisted of an initial exposure to clean humidified air (or dry $N_2$), followed by duplicate 60-s exposures to the vapor at the preestablished concentration. The exposures were separated by a 60-s exposure to clean air ($N_2$). Responses and recoveries reached full equilibrium values within 10−20 s of introduction or removal of the vapor stream. (Note: response times generally decreased with increasing temperature, although a detailed study of this issue was not performed.) Measurements from the last 30 s of each exposure period were subtracted from the pre- and postexposure baseline readings and then averaged to yield the net response at a given vapor concentration. By collecting vapor exposure measurements over relatively short times (i.e., <5 min) and performing pre- and postexposure baseline subtractions, any short-term baseline drifts were effectively removed from the signals measured for vapor sorption. Vapor concentrations were corrected for temperature using the ideal gas law, where necessary.

Response patterns obtained at different conditions of temperature and RH were analyzed using a method called extended disjoint principal components regression (EDPCR), which has been described previously.[1,27] Similar to other pattern recognition methods, EDPCR permits assignment of vapor identities to sensor array response patterns. Used in conjunction with a Monte Carlo simulation analysis, EDPCR can determine the likelihood of identification errors under different operating conditions.[1] This EDPCR−Monte Carlo method was used with the data presented here to determine whether temperature or ambient humidity changes would affect the ability of a given four-sensor array to discriminate vapors present in binary or ternary mixtures. All EDPCR−Monte Carlo analyses were performed in Matlab (Mathworks, Inc., Natick, MA) using a personal computer.

## RESULTS AND DISCUSSION

**Shifts in Baseline with Temperature.** The baseline difference frequencies for each sensor were determined from the averages of measurements collected over several minutes following equilibration at the desired temperature. At a specific temperature, the net baseline drift measured every 5 min over 4 h was typically less than 150 Hz, indicating good overall temperature control. The short-term drift measured between successive 5-min periods was typically less than 10 Hz but would occasionally reach values as high as 50 Hz. Drift was comparable at all temperatures.

Shifts in baseline frequency as a function of temperature were positive in all cases, consistent with the expectation that the coated sensor frequency would decrease at a higher rate than that of the uncoated reference sensor due to polymer thermal expansion.[5,20] However, shifts observed with uncoated working sensors were of the same order as those for the coated working sensors, indicating that factors other than polymer expansion are involved. Baseline shifts were linear or approximately linear over the entire temperature range studied for the uncoated sensors and for sensors coated with PIB, OV-275, ABC, and PECH. For the remaining sensors, the rate of change with temperature was nearly constant up to 30 °C and then either decreased (DEGA, APL) or increased (PDPP, PCP) slightly between 30 and 38 °C. As a means of roughly comparing baseline shifts among the different sensors, the frequencies were regressed against temperature over the range of 18−30 °C ($r^2 > 0.9$). The temperature coefficients obtained from the slopes of the resulting lines ranged from 140 to 860 Hz/°C, as shown in Table 1. Values presented in Table 1 are averages of 3−5 separate determinations. Relative standard deviations (RSDs) were typically less than 10%. Temperature coefficients for the two uncoated sensors were 650 and −660 Hz/°C. (Note: the negative shift observed with the latter uncoated sensor is probably not significant since it could arise merely from the reference sensor frequency being initially lower than that of the uncoated working sensor.)

The temperature coefficients for the coated sensors are similar to those reported by Grate et al.[5] and Ballantine and Wohltjen[26] for polymer-coated SAW sensors operating at the same nominal frequency. However, the data are not directly comparable. In the former study, coefficients were determined by subtracting the uncoated-sensor frequency shifts from those of the *same* sensor which was subsequently coated with a polymer. In the latter study, coated and (uncoated) reference SAW devices were on the same substrate. No attempt was made here to use reference and coated sensors with perfectly matched frequencies. This factor, along with possible differences in thermally induced stresses in the epoxy-mounted device substrates, may have contributed to the observed baseline shifts. Small differences in temperature between the sealed reference devices and the coated devices, which were operated under a stream of $N_2$, may also have contributed to the shifts observed here. The values reported in Table 1, therefore, should be viewed as typical of the baseline shifts to be expected in practical systems configured with sealed, uncoated reference sensors and a common heat sink.

To provide some perspective for the data in Table 1, the temperature coefficients can be compared to vapor sensitivities. For example, responses to 100 ppm (380 $\mu$g/L) xylene at 25 °C ranged from 110 to 530 Hz for the sensors in the array. Sensitivities to the other vapors are generally lower. This confirms that the magnitudes of the frequency changes per °C for this dual-sensor array are similar to typical vapor responses in the concentration ranges of interest.

**Effect of Temperature on Vapor Responses.** Response isotherms were linear, and vapor sensitivities were determined

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(27) Zellers, E. T.; Pan, T.-S.; Patrash, S. P.; Han, M.; Batterman, S. A. *Sens. Actuators B* **1993**, *12*, 123.

Table 2. Effect of Temperature on Sensor Responses to Organic Vapors

| | PIB | PDPP | DEGA | PCP | ABC | APL | OV-275 | PECH |
|---|---|---|---|---|---|---|---|---|
| Isooctane (1250−29 000 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 2590 | 3200 | 3670 | 2800 | 2830 | 3970 | 3690 | 2460 |
| $r^2$ | 0.990 | 0.998 | 0.994 | 0.996 | 0.999 | 1.000 | 0.998 | 0.992 |
| temp coeff (25 °C)[a] | −2.9 | −3.6 | −4.1 | −3.1 | −3.1 | −4.5 | −.41 | −2.7 |
| LOD (18 °C)[b] | 164 | 716 | 1950 | 520 | 771 | 283 | 2420 | 1190 |
| sensitivity (18 °C)[c] | 0.275 | 0.063 | 0.023 | 0.087 | 0.058 | 0.159 | 0.019 | 0.038 |
| sensitivity (38 °C) | 0.155 | 0.031 | 0.010 | 0.047 | 0.031 | 0.066 | 0.008 | 0.022 |
| ratio (18/38 °C) (2.4)[d] | 1.8 | 2.0 | 2.2 | 1.8 | 1.9 | 2.4 | 2.3 | 1.7 |
| THF (2500−23 000 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 3390 | 3350 | 3980 | 2340 | 3180 | 2100 | 3040 | 3280 |
| $r^2$ | 0.990 | 0.997 | 0.996 | 0.968 | 0.996 | 0.991 | 0.987 | 0.993 |
| temp coeff (25 °C) | −3.8 | −3.8 | −4.4 | −2.6 | −3.6 | −2.4 | −3.4 | −3.7 |
| LOD (18 °C) | 380 | 376 | 352 | 486 | 286 | 807 | 523 | 271 |
| sensitivity (18 °C) | 0.118 | 0.120 | 0.128 | 0.093 | 0.157 | 0.056 | 0.086 | 0.166 |
| sensitivity (38 °C) | 0.056 | 0.057 | 0.053 | 0.055 | 0.079 | 0.036 | 0.044 | 0.082 |
| ratio (18/38 °C) (2.2) | 2.1 | 2.1 | 2.4 | 1.7 | 2.0 | 1.6 | 1.9 | 2.0 |
| Butanol (210−3700 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 4560 | 3890 | 6840 | 3760 | 3310 | 4930 | 4050 | 3960 |
| $r^2$ | 0.989 | 0.998 | 0.995 | 0.999 | 1.000 | 0.968 | 0.991 | 0.996 |
| temp coeff (25 °C) | −5.1 | −4.3 | −7.6 | −4.2 | −3.7 | −5.5 | −4.6 | −4.4 |
| LOD (18 °C) | 209 | 112 | 138 | 69 | 31 | 279 | 50 | 52 |
| sensitivity (18 °C) | 0.215 | 0.403 | 0.327 | 0.651 | 1.429 | 0.161 | 0.898 | 0.864 |
| sensitivity (38 °C) | 0.080 | 0.156 | 0.075 | 0.289 | 0.561 | 0.048 | 0.334 | 0.326 |
| ratio (18/38 °C) (3.7) | 2.7 | 2.6 | 4.4 | 2.2 | 2.6 | 3.4 | 2.7 | 2.6 |
| TCE (1500−21 000 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 3380 | 3790 | 4110 | 2030 | 3300 | 3490 | 3120 | 3240 |
| $r^2$ | 0.991 | 0.986 | 0.995 | 0.910 | 0.989 | 0.995 | 0.992 | 0.966 |
| temp coeff (25 °C) | −3.8 | −4.2 | −4.6 | −2.3 | −3.7 | −3.9 | −3.5 | −3.6 |
| LOD (18 °C) | 137 | 215 | 178 | 385 | 130 | 215 | 421 | 223 |
| sensitivity (18 °C) | 0.329 | 0.209 | 0.253 | 0.117 | 0.347 | 0.209 | 0.107 | 0.202 |
| sensitivity (38 °C) | 0.157 | 0.091 | 0.102 | 0.076 | 0.170 | 0.097 | 0.054 | 0.100 |
| ratio (18/38 °C) (2.3) | 2.1 | 2.3 | 2.5 | 1.5 | 2.0 | 2.2 | 2.0 | 2.0 |
| Benzene (1400−29 000 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 3140 | 3690 | 3890 | 2000 | 3460 | 3100 | 3180 | 3300 |
| $r^2$ | 0.998 | 0.995 | 0.994 | 0.926 | 0.961 | 0.989 | 0.995 | 0.990 |
| temp coeff (25 °C) | −3.5 | −4.1 | −4.3 | −2.3 | −3.9 | −3.5 | −3.6 | −3.7 |
| LOD (18 °C) | 206 | 282 | 291 | 579 | 176 | 381 | 423 | 224 |
| sensitivity (18 °C) | 0.219 | 0l160 | 0.155 | 0.078 | 0.256 | 0.118 | 0.106 | 0.201 |
| sensitivity (38 °C) | 0.109 | 0.072 | 0.065 | 0.050 | 0.122 | 0.061 | 0.053 | 0.098 |
| ratio (18/38 °C) (2.3) | 2.0 | 2.2 | 2.4 | 1.6 | 2.1 | 1.9 | 2.0 | 2.0 |
| *m*-Xylene (150−4600 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 4190 | 4520 | 505 | 3430 | 4350 | 3300 | 4030 | 4170 |
| $r^2$ | 0.994 | 0.997 | 0.997 | 0.949 | 0.985 | 0.996 | 0.999 | 0.995 |
| temp coeff (25 °C) | −4.6 | −5.0 | −5.6 | −3.8 | −4.8 | −3.7 | −4.5 | −4.6 |
| LOD (18 °C) | 23 | 43 | 42 | 93 | 25 | 37 | 98 | 35 |
| sensitivity (18 °C) | 1.943 | 1.050 | 1.074 | 0.482 | 1.769 | 1.231 | 0.459 | 1.278 |
| sensitivity (38 °C) | 0.787 | 0.397 | 0.353 | 0.225 | 0.707 | 0.614 | 0.197 | 0.531 |
| ratio (18/38 °C) (2.9) | 2.5 | 2.6 | 3.0 | 2.1 | 2.5 | 2.0 | 2.3 | 2.4 |
| MEK (730−27 000 $\mu$g/L) | | | | | | | | |
| Arrhenius slope | 2170 | 3390 | 4110 | 1920 | 3180 | 3770 | 3160 | 3560 |
| $r^2$ | 0.991 | 0.997 | 1.000 | 0.984 | 0.998 | 0.981 | 0.990 | 0.995 |
| temp coeff (25 °C) | −2.4 | −3.8 | −4.6 | −2.2 | −3.6 | −4.2 | −3.5 | −4.0 |
| LOD (18 °C) | 545 | 382 | 249 | 326 | 185 | 1120 | 250 | 184 |
| sensitivity (18 °C) | 0.083 | 0.118 | 0.180 | 0.138 | 0.243 | 0.040 | 0.180 | 0.245 |
| sensitivity (38 °C) | 0.051 | 0.056 | 0.073 | 0.091 | 0.120 | 0.018 | 0.090 | 0.112 |
| ratio (18/38 °C) (2.3) | 1.6 | 2.1 | 2.5 | 1.5 | 2.0 | 2.3 | 2.0 | 2.2 |

[a] Change in vapor sensitivity (°C$^{-1}$) × 100. [b] Units, $\mu$g/L. [c] Units, Hz $\mu$g$^{-1}$ L$^{-1}$. [d] Theoretical sensitivity ratio (see text).

from the slopes of the calibration curves by regression. Regression $r^2$ values were >0.99, with the exceptions of those sensors providing very low responses to a specific vapor (e.g., DEGA and OV-275 with isooctane). Table 2 summarizes the effect of temperature on the responses to the vapors. In all cases, the sensitivities decrease exponentially with increasing temperature. The differences in the temperature dependence of the sensitivities among the vapor−polymer pairs are reflected in the slopes of the Arrhenius plots and in the sensitivity ratios, which were determined by dividing the sensitivity at 18 °C by that at 38 °C. Butanol stands out as having larger Arrhenius slopes than the other vapors for all sensor coatings, which is consistent with its larger heat of condensation.[20]

The sensitivity ratios in Table 2 can be compared to those expected under the assumption of ideal sorption behavior. Ideally, $\Delta H_s = \Delta H_c$, and the vapor sensitivity should vary in proportion to $T/p_{v(T)}$ where $p_{v(T)}$ is the saturation vapor pressure at a given temperature.[18,21] Responses at 18 and 38 °C should thus differ by $(291/311)(p_{v(311)}/p_{v(291)})$, which corresponds to factors of 2.4, 2.2, 3.7, 2.3, 2.3, 2.9, and 2.3 for isooctane, THF, butanol, TCE, benzene, xylene, and MEK, respectively.[28–30] Most of the observed ratios shown in Table 2 are less than these ideal values, consistent with expectation of a positive heat of mixing contribution (see eq 2). The data indicate that, with the possible exception of DEGA, changes in the moduli of the sensor coatings accompanying the changes in temperature are of no apparent consequence in terms of sensor responses. In addition, there is no indication of any polymer phase transitions or film resonance effects over this temperature range. Thus, the maximum change in sensor responses with temperature can be predicted reasonably well from the ratio of the vapor pressures of the analyte vapor.

Tests with benzene and xylene were repeated several times to assess the reproducibility of the temperature effects. For a given deposited polymer coating film, the RSD around the mean Arrhenius slope was less than 9% ($n = 2-5$) in all cases for both benzene and xylene.

Between-film variations were also examined for a subset of coating materials. Arrhenius slopes determined for benzene from two films of PIB and PDPP differed by only 7 and 14%, respectively. Films of PCP and APL gave more variable results, with differences of 28 and 33%, respectively, in the slopes for benzene with successive films. Four different coating films of DEGA were tested. Three of the films gave very similar results (RSD < 7%) for both benzene and xylene. The fourth film, however, gave an Arrhenius slope that was nearly twice that of the average of the other three films for benzene and about 1.5 times that of the others for xylene. Similarly, a third film of APL gave a xylene Arrhenius slope that was 2.3 times the average of the other two films. Tests were repeated for these latter DEGA and APL films, and the higher Arrhenius slopes were reproducible. The magnitudes of the responses to benzene at 25 °C for these coating films were determined prior to the temperature studies and were similar to those of the other films of these materials. (Note: benzene responses at 25 °C were monitored periodically for all coatings as a quality control measure throughout the study.) In the case of the APL film, the benzene sensitivity was found to have increased by about 40% after the temperature study, indicating that the film properties had changed. This was not observed with the DEGA film. These anomalously large Arrhenius slopes probably arise from differences in mechanical properties (e.g., adhesion strength) between the former and latter DEGA and APL films. Unfortunately, it is not possible to provide a more detailed explanation of these phenomena from the data collected. No further testing with these films was performed. All other results for DEGA and APL described in this paper were obtained from films showing the more typical behavior.

It was of interest to determine the magnitude of error in the responses to be expected from small changes in the operating temperature of the sensors. Using the Arrhenius slope for a given vapor–coating pair, the change in sensitivity resulting from an incremental change in temperature can be derived at any temperature. The temperature coefficients provided in Table 2 were determined by evaluating the sensitivity change near 25 °C. Values range from about −2 to −8%/°C among the different vapors. Although the coefficient decreases with increasing temperature, over the range of 18–38 °C, none of the coefficients changed by more than 15%.

Comparing these temperature coefficient values with those given in Table 1 shows that the influence of temperature on the sensor baselines is significantly larger than that on the vapor sensitivities over the range of concentrations and sensor response values considered. The data indicate that, while the temperature must be controlled precisely at a given value, a slight error in the set point could be tolerated without incurring a large error in the individual responses or the response patterns to the vapors. Such errors could be compensated for via the temperature coefficients, provided that an accurate measure of the sensor temperature could be obtained.

It was also of interest to consider the effect of a large change in the operating temperature on the sensitivity and selectivity of an array of sensors. As shown in Table 2, sensitivities decreased (LODs increased) by factors ranging from 1.5 to 4.4 between 18 and 38 °C, with most of the sensitivity ratios falling between 1.9 and 2.4. For a specific vapor, the change in sensitivity was quite similar for most of the coatings, although the sensitivity ratios and Arrhenius slopes for DEGA tend to be higher and those for PCP tend to be lower than for the other coatings. It should be noted that differences of less than 10% between sensitivity ratios are not considered significant because variations in the individual sensitivity values of 5% are often observed. Thus, moderate changes in operating temperature could be tolerated without seriously compromising the ability to detect the vapors.

The differences in the temperature coefficients of sensitivity among the different vapor–coating pairs, while generally small, are large enough in certain cases to cause changes in the vapor response pattern obtained from an array of sensors when operated at different temperatures. The magnitude of the effect depends on the coatings included in the array. Figure 1 illustrates this point for THF and xylene by presenting the relative response patterns for two different four-sensor arrays at 18 and 38 °C. In Figure 1a and c, coatings with similar temperature coefficients of sensitivity were chosen, and it is seen that the response patterns do not change significantly with temperature. In Figure 1b and d, coatings having quite different temperature coefficients were chosen, and the response patterns change markedly between the two operating temperatures.

To explore the effect of such changes on the ability to discriminate vapors, the data at 18 and 38 °C were analyzed separately with the EDPCR–Monte Carlo model described above, which simulates the performance of the array under the expected operating conditions. The sensitivity values for each vapor at a given temperature were entered into the model, and the responses for the vapor mixtures were constructed assuming additivity. (Note: the additivity assumption has been verified in a separate study, see ref 1.) EDPCR was used to correlate the identities of the vapors or vapor mixtures with the corresponding response vectors obtained. A Monte Carlo analysis was then employed to superimpose Gaussian error due to inherent sensor noise (assumed to have a standard deviation of 15 Hz) and slope variability (assumed to have an RSD of 5% of the response value) on the responses and to generate a simulated response vector. Each simulated vector was analyzed via EDPCR to identify it as a specific vapor or vapor mixture. By running the Monte Carlo analysis iteratively (e.g., $n = 100$), a statistical estimate of the percentage of correct vapor identifications was obtained for each set of coated

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(28) Dreisbach, R. R. *Physical Properties of Chemical Compounds*; American Chemical Society: Washington, DC, 1955.

(29) Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds, Part A: Hydrocarbons and Ketones*; Elsevier: New York, 1986.

(30) Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds, Part B: Halogenated Hydrocarbons and Alcohols*; Elsevier: New York, 1986.

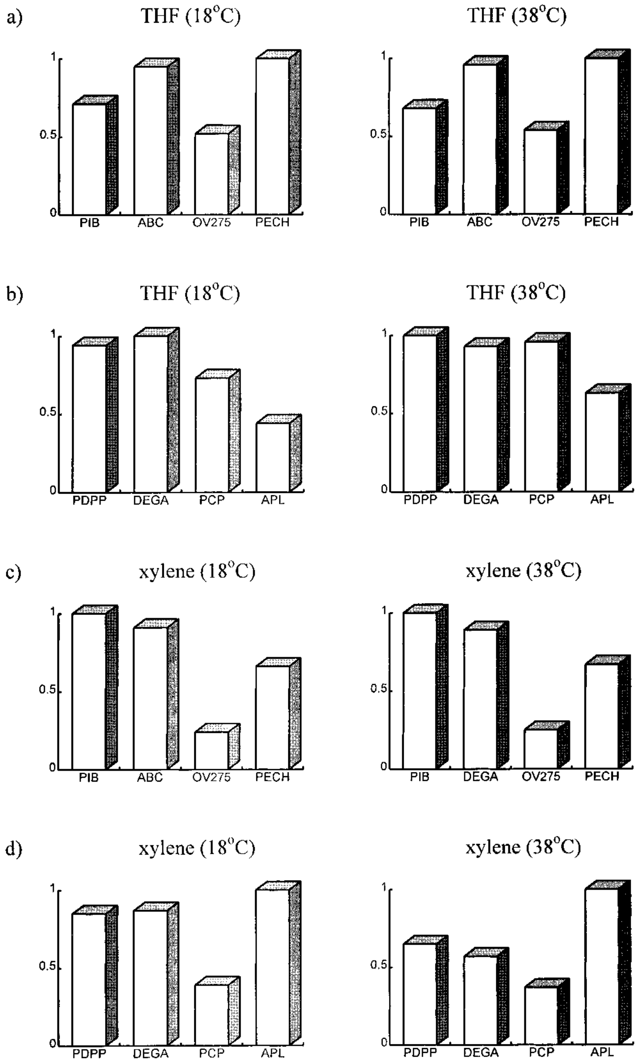

Figure 1. Relative response patterns for THF and xylene as a function of temperature for sensor arrays coated with (a, c) PIB, ABC, OV-275, and PECH and (b, d) PDPP, DEGA, PCP, and APL.

sensors. For this study, we restricted consideration to arrays of four sensors. Performing the EDPCR−Monte Carlo analysis on all possible combinations of four sensors provides the means to rank the various possible arrays in terms of the overall rate of correct identification.

This type of analysis was performed for the binary and ternary vapor mixtures presented in Table 3. Each binary mixture analysis considered the case where the two vapors could be present either individually or as a mixture in any combination of concentrations within the calibrated ranges. For the ternary mixture analyses, the vapors could be present individually, as a binary mixture, or as a ternary mixture. For each set of vapors, the rates of error in identifying the vapors were assessed at both 18 and 38 °C for all possible combinations of coatings.

For consistency, the coating sets considered in the first part of Table 3 are the same as those shown in Figure 1, even though these were not necessarily the coatings that would provide optimal selectivity. The first entry in Table 3 for each vapor mixture represents a set of coatings with similar temperature coefficients (coating set A), and the second entry represents a set with a wide range of temperature sensitivities (coating set B). As shown, there is no significant change in performance at the higher operating temperature for the coatings with similar temperature coefficients. Even for the set of coatings with a range of temperature coefficients, changes in performance are very small. Thus, for the relatively simple mixtures considered, array performance is not seriously affected by changes in operating temperature. As the complexity of the analysis or the similarity in response patterns for the mixture components increases, the importance of small changes in response patterns will become more important.

Table 3. Effect of Operating Temperature and RH on the Expected Rates of Correct Identification of Vapor Mixture Components As Determined from EDPCR−Monte Carlo Analysis for Different Four-Sensor Arrays

| vapor mixture | temp (°C) or RH (%)[a] | coating set[b] | rate of correct ident (%) |
|---|---|---|---|
| xylene + benzene | 18/38 | A | 94/95 |
| | 18/38 | B | 95/96 |
| TCE + benzene | 18/38 | A | 92/91 |
| | 18/38 | B | 89/86 |
| MEK + butanol | 18/38 | A | 96/97 |
| | 18/38 | B | 99/100 |
| THF + butanol | 18/38 | A | 99/99 |
| | 18/38 | B | 98/99 |
| xylene + benzene + TCE | 18/38 | A | 87/86 |
| | 18/38 | B | 84/86 |
| THF + MEK + butanol | 18/38 | A | 94/92 |
| | 18/38 | B | 96/98 |
| TCE + benzene | 0/85 | C | 95/94 |
| MEK + butanol | 0/85 | C | 98/98 |
| TCE + benzene + MEK | 0/85 | C | 88/87 |
| benzene + MEK + butanol | 0/85 | C | 97/97 |

[a] Analyses at 18 and 38 °C were at 0% RH; analyses at 0 and 85% RH were at 25 °C. [b] A, PIB, ABC, OV-275, PECH; B, PDPP, DEGA, PCP, APL; C, PIB, DEGA, PCP, OV-275.

The data in Table 2 reveal an alternative approach to achieving selectivity that entails operating pairs of identically coated sensors at different temperatures. This issue has been considered in the context of reagent-coated SAW sensors[31] but not with polymer-coated SAW sensor arrays. As an example, consider the responses to benzene and xylene from the sensors coated with PIB, ABC, OV-275, or PECH. The data in Table 2 and Figure 1 show that the temperature coefficients among these coatings are nearly the same for a specific vapor but that they differ between the two vapors: for benzene, the temperature coefficients are about −3.7%/°C, while for xylene they are about −4.7%/°C. If a subset of two sensors were coated with the same polymer but operated at different temperatures, the ratio of responses could be used to discriminate between these two vapors in a manner similar to using two separate coating materials at the same temperature. To illustrate, note that the responses of the PECH-coated sensor to benzene and xylene at 38 °C are similar to those for the OV-275 coating at 18 °C. The lower RH sensitivity of the PECH coating might argue for its use at the elevated temperature in place of the more RH-sensitive OV-275 coating in certain monitoring situations (see next section). For discriminating benzene from xylene, the two arrays would be equivalent. This approach will not work for all vapors because many have the same, or similar, temperature coefficients for all coatings (e.g., TCE and benzene).

**Responses to Atmospheric Humidity.** The response of each sensor to atmospheric humidity was determined by exposure

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[31] Zellers, E. T.; Zhang, G. Z. *Anal. Chem.* **1992**, *64*, 1277−1284.

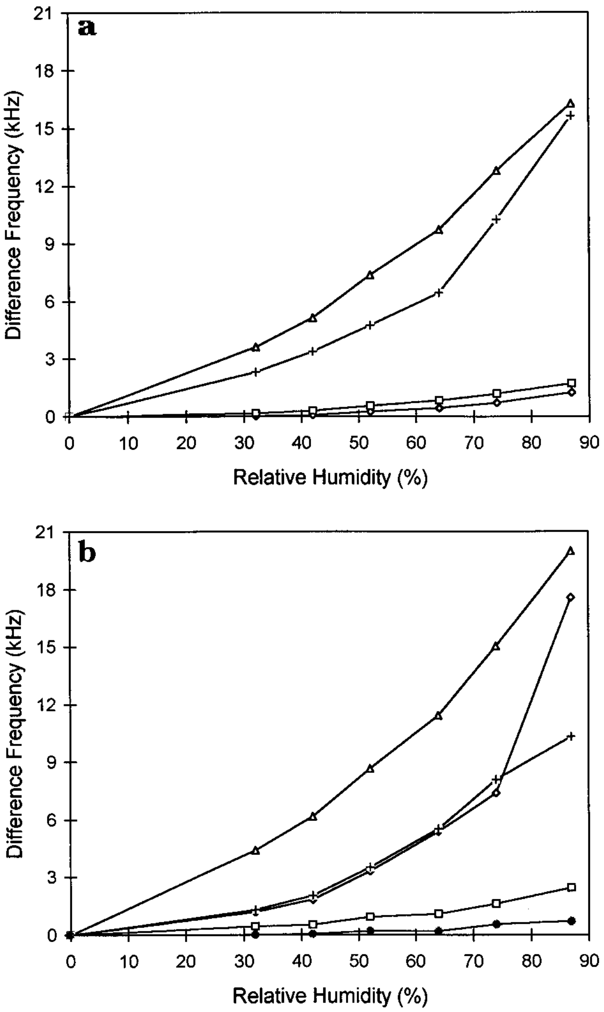

Figure 2. Baseline difference frequencies as a function of atmospheric humidity at 25 °C for sensor arrays coated with (a) PIB (◇), PDPP (□), DEGA (△), and PCP (+) and (b) ABC (◇), APL (□), OV-275 (△), PECH (+), and uncoated (●).

at 25 °C to dry $N_2$ and to air at RH values ranging up to 85%. The resulting response isotherms (Figure 2) are nonlinear, invariably becoming steeper at higher RH levels. Responses for PIB, APL, PDPP, and the uncoated sensor are quite small and nearly linear over the entire RH range, while those for DEGA and OV-275 are significantly larger, consistent with their polar structures. PECH shows moderate water sensitivity, and ABC and PCP show moderate water vapor sensitivities at low RH, followed by a sharp increase in sensitivity at the higher RH levels. The increase in sensitivity with concentration seen with these latter coatings is a general characteristic of sorption isotherms of water vapor with certain (hydrophobic) organic polymers that can be attributed to the clustering of water molecules within the polymer matrix at higher vapor concentrations.[18] The ABC and PCP isotherms were reproducible at low RH but somewhat more variable at higher RH (i.e., >65% RH).

In general, the order of sensitivities is as expected on the basis of the relative polarities of the polymer coatings. Despite the fact that PIB and APL are nonpolar aliphatic hydrocarbons, they still sorb water vapor from the atmosphere to some extent. On the other hand, PDPP is rather insensitive to humidity even though it contains polar functional groups. As shown in Figure 2b, adsorption of water vapor at the surface of the quartz substrate may contribute significantly to the total RH sensitivity of these less-polar coatings, as suggested by McGill et al.[32] and in earlier studies.[5,6] However, it is clearly a minor effect for the remaining sensor coatings.

The sensitivities to water vapor are summarized in Table 4 as humidity coefficients in units of Hz/(%RH). For convenience, the data above and below 65% RH were treated separately, since the isotherms in each of these ranges were approximately linear for all coatings and data were collected at too few RH levels to accurately define a continuous function. The responses to xylene at 25 °C presented above can, again, be used to place these results in perspective. While the sensitivities to atmospheric humidity for the PIB, APL, and PDPP coatings are quite low over the entire RH range, they are still significant. That is, a step change of 1% RH would cause shifts of 40−60 Hz in these sensors, or 8−16% of the responses to 100 ppm of xylene. The effects would be even greater for those vapors giving smaller responses (see Table 2). For the remaining coatings, in particular for DEGA and OV-275, a change of 1% RH would lead to baseline shifts greater than the responses to many of the organic vapors at the concentrations of interest. Thus, small, abrupt shifts in humidity will cause large errors in organic vapor analysis.

**Effect of Ambient Humidity on Vapor Responses.** The effect of the atmospheric humidity level on the responses to several of the organic vapors at 25 °C was then examined by comparing responses in a dry $N_2$ atmosphere to those in atmospheres of approximately 30, 50, and 85% RH. Response curves were linear over the concentration ranges examined, regardless of the RH level. Results are summarized in Table 5, where the sensitivity at each RH level has been normalized by the sensitivity at 0% RH for each coating−vapor pair. For the PIB-, PDPP-, and APL-coated sensors, responses were unaffected by the RH level in all cases, consistent with the low level of sorbed water in the coatings and at the substrate surface. Although PECH sorbs more water than these coatings, there is still little or no effect on its responses to the organic vapors. We can conclude that there is no significant plasticization or solvation by water for these polymers. With ABC, a higher response is observed for MEK at the higher humidity levels, while a lower response is observed for butanol at high RH. The increase for MEK can be explained as due to an increase in MEK solubility as the moderately polar ABC polymer sorbs more and more water. But the decreased response to butanol suggests a net decrease in coating polarity, perhaps through an increased occupation by sorbed water of the dipolar cyano groups in this polymer.

With PCP, an increase in response at higher RH levels is observed for benzene, MEK, and butanol, with the effect becoming more important with increasing vapor polarity. In this case, the presence of water vapor apparently leads to a steady increase in vapor solubility. The effect is particularly strong for the more polar vapors MEK and butanol. However, it was found that the responses to both MEK and butanol with this PCP film were much lower than those measured previously with this coating material. (Note: a fresh film was deposited just prior to the MEK and butanol exposure tests in this series.) Although responses to benzene measured directly after deposition of this PCP film were satisfactory, the benzene responses following the humidity tests with MEK and butanol were also reduced. The observed behavior

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(32) McGill, R. A.; Grate, J. W.; Anderson, M. R. In *Interfacial Design and Chemical Sensing*; Mallouk, T. E., Harrison, J. D., Eds.; ACS Symposium Series 561; American Chemical Society: Washington, DC, 1994; pp 280−294.

Table 4. RH Coefficients ($df/dH$) of Baseline Difference Frequencies Determined from 0 to 85% RH[a]

| | PIB | PDPP | DEGA | PCP | ABC | APL | OV-275 | PECH |
|---|---|---|---|---|---|---|---|---|
| <65% RH | 13 (4) | 17 (7) | 190 (3) | 120 (16) | 120 (14) | 21 (5) | 210 (27) | 120 (13) |
| >65% RH | 42 (6) | 42 (4) | 290 (24) | 410 (55) | 700 (170) | 58 (5) | 400 (42) | 200 (23) |

[a] Units of $df/dH$ are Hz/(%RH). Values in parentheses are standard deviations ($n = 2-3$).

Table 5. Effect of RH (25 °C) on Sensitivities to Organic Vapors[a]

| RH (%) | PIB | PDPP | DEGA | PCP | ABC | APL | OV-275 | PECH |
|---|---|---|---|---|---|---|---|---|
| | | | | Isooctane | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 30 | 1.00 | 1.00 | 0.87 | 1.15 | 0.97 | 0.98 | 0.87 | 0.98 |
| 50 | 1.00 | 1.00 | 0.77 | 1.32 | 0.98 | 0.99 | 0.75 | 0.93 |
| 85 | 1.01 | 0.98 | 0.86 | 1.23 | 1.00 | 1.00 | 0.93 | 0.97 |
| | | | | TCE | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 30 | 0.99 | 0.98 | 0.87 | 0.97 | 0.97 | 0.95 | 0.91 | 0.97 |
| 50 | 0.99 | 0.98 | 0.82 | 1.09 | 0.95 | 0.94 | 0.90 | 0.93 |
| 85 | 1.02 | 1.02 | 0.71 | 1.14 | 1.00 | 0.97 | 0.82 | 0.91 |
| | | | | Benzene | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 30 | 1.05 | 1.02 | 0.99 | 1.14 | 0.90 | 1.05 | 0.97 | 1.02 |
| 50 | 1.06 | 1.02 | 0.88 | 1.23 | 0.90 | 1.05 | 0.95 | 1.01 |
| 85 | 1.07 | 1.02 | 0.70 | 1.30 | 0.89 | 1.02 | 0.77 | 0.94 |
| | | | | MEK[b] | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 40 | 0.99 | 0.99 | 0.89 | 1.32 | 1.04 | 0.97 | 0.98 | 1.01 |
| 50 | 0.99 | 1.00 | 0.81 | 1.47 | 1.15 | 1.00 | 1.00 | 1.01 |
| 85 | 0.99 | 1.01 | 0.74 | 1.81 | 1.16 | 1.02 | 1.07 | 0.97 |
| | | | | Butanol[b] (Trial 1) | | | | |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 40 | 0.91 | 0.95 | 0.97 | 1.50 | 1.02 | 0.95 | 1.02 | 1.10 |
| 50 | 0.92 | 0.99 | 0.93 | 1.80 | 1.04 | 0.94 | 0.93 | 1.09 |
| 85 | 0.96 | 1.01 | 0.89 | 3.40 | 0.81 | 0.94 | 1.11 | 1.00 |
| | | | | Butanol[c] (Trial 2) | | | | |
| 0 | | | | 1.00 | | | | |
| 30 | | | | 1.30 | | | | |
| 50 | | | | 1.39 | | | | |

[a] Sensitivity values for each coating–vapor pair are normalized by that obtained at 0% RH. [b] Responses with the PCP coating for these vapors were lower than normal (see text). [c] No data collected at 85% RH.

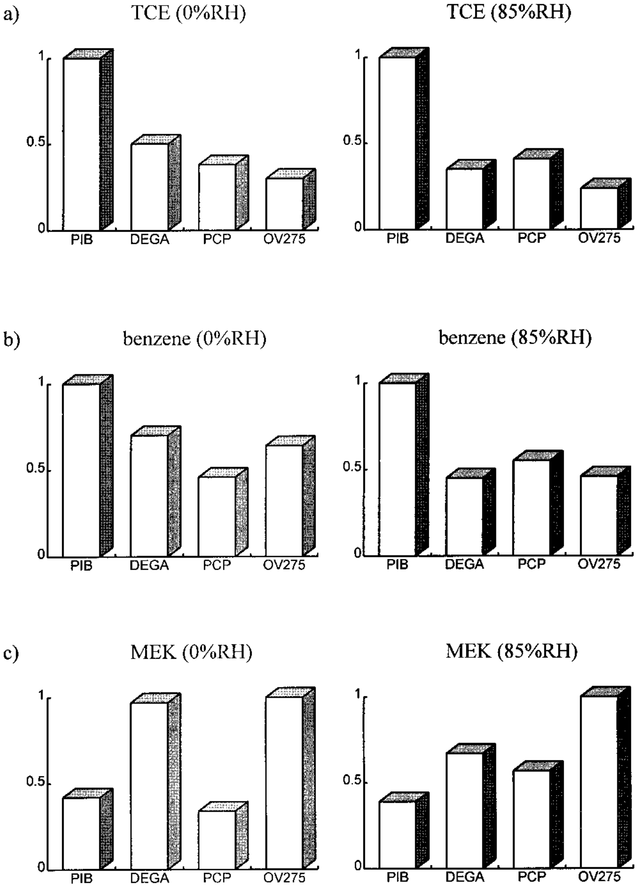

Figure 3. Relative response patterns for TCE, benzene, and MEK at 0 and 85% RH (25 °C) for a four-sensor array with coatings of PIB, DEGA, PCP, and OV-275.

is consistent with dewetting of the PCP film from the substrate surface—a phenomenon described recently by Grate et al. in the context of polymer-coated SAW sensors.[33] We speculate that the strength of the humidity dependence is at least partly attributable to the interactions of water vapor and butanol with the surface of the substrate. Data from another butanol trial performed with a PCP film that was well-behaved are presented in Table 5 to show that there is still a significant humidity effect for butanol.

In contrast to the behavior observed with the aforementioned coatings, relatively large decreases in sensitivity with increasing RH level were observed with the DEGA coating for all of the vapors except butanol. Similarly, the OV-275 coating showed decreased sensitivity with increasing RH for the moderately polar benzene and TCE vapors. These coatings sorbed larger amounts of water vapor than the other coatings (see Figure 1). The decrease in response at high RH for the less polar vapors follows from the expected increase in overall coating polarity. The lack of a significant effect for butanol is also consistent with this interpretation. The data for isooctane for all of the coatings are more variable due, in part, to the low responses obtained (see Table 2). Thus, the relatively large changes in response for DEGA, OV-275, and PCP may be artifacts.

In comparing the effect of RH changes on baseline shifts to those on the responses to the organic vapors, in general the former are more important. A small change in RH leads to a large shift in baseline, but only a marginal change in the sensitivity to the organic vapors, with the possible exceptions of butanol and MEK with PCP.

For large differences in RH level, the effect on the response patterns obtained for different vapors can be significant. As with temperature, the magnitude of the effect varies with the vapor and the coatings included in the array. Figure 3 illustrates the extent to which patterns can change between 0 and 85% RH for TCE, benzene, and MEK using an array with the coatings PIB, DEGA, PCP, and OV-275. The extent to which such changes affect the ability to discriminate between vapors was assessed using the EDPCR–Monte Carlo method described above for two binary mixtures and two ternary mixtures. The results are presented in Table 3 in terms of the expected rates of correct

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[33] Grate, J. W.; McGill, A. R. *Anal. Chem.* **1995**, *67*, 4015.

identification of the vapors present individually or as the components of the mixtures. The noise and sensitivity errors assumed in the Monte Carlo analyses were the same as those used to generate the other data in Table 3. As shown, there is little or no effect on the ability to identify the vapors with the array, provided that the changes in response patterns as a function of ambient humidity are taken into account. If calibrations performed at 0% RH are used to analyze vapors on the basis of response patterns obtained at 85% RH, then significant errors in analysis can be expected.

**Implications for Instrument Design.** Although there are certain monitoring environments where the ambient temperature and humidity may not change appreciably, in many situations this cannot be assumed. Even in well-controlled environments, it would generally be necessary to periodically reestablish a baseline or instrument "zero" by drawing a filtered air sample past the sensor(s). The data in Table 1 show that a step change in temperature of as little as 0.1 °C is sufficient to cause significant error due to baseline shifts, which is consistent with other reports.[15,20] Thus, careful balancing of the flow rates is important to account for differences in pressure drops between sample and reference streams. If sealed reference sensors are employed, then the reference devices could be coated with the same polymers as used on the corresponding working sensors as a means of reducing baseline shifts arising from polymer thermal expansion/contraction.[15] However, the large baseline shifts observed here with uncoated sensors confirm that other factors such as stresses in the sensor substrates must also be addressed to minimize such errors.

The effect of humidity differences between baseline and sample streams must also be addressed, particularly for the more polar coatings. As shown in Table 4, a step change of $<0.1\%$ RH would be sufficient to cause significant error in the responses for these coatings. Granular adsorbents such as Tenax GC have been used successfully to scrub organic vapors from baseline streams while allowing water vapor to pass through.[15] Alternatively, Nafion tubing can be used at the inlets to the baseline and sample streams to balance the RH levels, provided that polar organic vapors are not being monitored.[15]

The data in Table 2 indicate that small changes in operating temperature will not affect the sensitivities to the organic vapors significantly. That is, a change of 5 °C will result in changes in vapor sensitivity and LOD of only about 15−20% in most cases. Responses for all vapor−sensor combinations exhibited negative temperature dependencies, and most sensors had similar temperature coefficients of sensitivity. Furthermore, it was shown that the maximum changes in response with temperature were predicted reasonably well by the change in vapor pressure of the analyte. Since the changes in sensitivities and LODs are small and predictable, it should be possible to compensate for them using correction factors. Thus, with adequate heat sinking or insulation to buffer any abrupt changes in temperature, the baseline subtraction to account for any inherent sensor drift, it is feasible to consider operating without active temperature control. This would have the advantages of greater simplicity and lower power, which are important considerations for portable instruments. If active temperature control were employed, it might be possible to take advantage of differences in the temperature dependence of vapor responses to achieve vapor discrimination.

The effects of incremental ambient humidity changes on sensor responses to the organic vapors studied here were small in most cases. However, large humidity differences between calibration and sampling conditions will lead to errors in identification and quantification of the vapors. While the direction and magnitude of most of the humidity-induced sensitivity changes could be explained in terms of the solvation effects of sorbed water, exceptional behavior was observed, and additional study of this issue seems warranted. In monitoring settings where wide variations in the RH level are possible, a measure of RH, perhaps via the sensor array itself, and application of correction factors to the responses for the affected vapors would be required.

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