Anal. Chem. **1995**, *67*, 1092−1106

Optimal Coating Selection for the Analysis of Organic Vapor Mixtures with Polymer-Coated Surface Acoustic Wave Sensor Arrays

Edward T. Zellers,* Stuart A. Batterman, Mingwei Han, and Samuel J. Patrash†

Department of Environmental and Industrial Health, School of Public Health, University of Michigan, Ann Arbor, Michigan 48109-2029

A method for determining the optimal set of polymer sensor coatings to include in a surface acoustic wave (SAW) sensor array for the analysis of organic vapors is described. The method combines an extended disjoint principal components regression (EDPCR) pattern recognition analysis with Monte Carlo simulations of sensor responses to rank the various possible coating selections and to estimate the ability of the sensor array to identify any set of vapor analytes. A data base consisting of the calibrated responses of 10 polymer-coated SAW sensors to each of six organic solvent vapors from three chemical classes was generated to demonstrate the method. Responses to the individual vapors were linear over the concentration ranges examined, and coatings were stable over several months of operation. Responses to binary mixtures were additive functions of the individual component responses, even for vapors capable of strong hydrogen bonding. The EDPCR−Monte Carlo method was used to select the four-sensor array that provided the least error in identifying the six vapors, whether present individually or in binary mixtures. The predicted rate of vapor identification (87%) was experimentally verified, and the vapor concentrations were estimated within 10% of experimental values in most cases. The majority of errors in identification occurred when an individual vapor could not be differentiated from a mixture of the same vapor with a much lower concentration of a second component. The selection of optimal coating sets for several ternary vapor mixtures is also examined. Results demonstrate the capabilities of polymer-coated SAW sensor arrays for analyzing of solvent vapor mixtures and the advantages of the EDPCR−Monte Carlo method for predicting and optimizing performance.

An increasing number of reports have appeared in recent years on the use of polymer-coated surface acoustic wave (SAW) sensors and sensor arrays for direct measurement of organic vapors at low concentrations.[1−6] When configured as the frequency-controlling element in a feedback oscillator circuit, the response of the SAW vapor sensor is based on the reversible, concentration-dependent shift in oscillation frequency caused by changes in the mass and viscoelasticity of the sensor coating accompanying vapor sorption.[7−10] An array of SAW sensors, each coated with a different sorptive polymer, can provide a greater degree of selectivity than an individual sensor. Although each sensor exhibits only partial selectivity, the patterns of responses produced by the array can be correlated with specific vapors using statistical pattern recognition algorithms,[1,11] and the identification and quantification of a wide range of vapors is possible. These capabilities, coupled with the small size and low power requirements of SAW sensors, would be useful attributes in portable instrumentation for many environmental and occupational health monitoring applications.

The ability to discriminate vapors depends on differences in the sorption isotherms among the polymer sensor coatings in the array, which in turn depend on the volatility of each vapor and the strength of the functional group interactions between the vapor and the coatings. Some guidance in coating selection can be obtained by considering the polymer and vapor structures as they affect the relative influences of dispersive, dipolar, and hydrogen-bonding interactions.[5,12,13] Principal components and cluster analyses of sensor calibration data have also been used to identify groups of relatively similar coatings from which subsets can be chosen for inclusion in an array.[14] Our recent study describes several models for estimating sensor responses from physicochemical properties that can also be used to screen coatings.[5] However, none of these approaches provides a general means for determining the best set of sensor array coatings for a specific vapor analysis or for predicting whether an array will reliably discriminate the vapors of concern. In order to realize the

---

[†] Current address: Molecular Science Research Center, Pacific Northwest Laboratory, Richland, WA 99352.

(1) Rose-Pehrrson, S. L.; Grate, J. W.; Ballantine, D. S., Jr.; Jurs, P. *Anal. Chem.* **1988**, *60*, 2801.

(2) Wohltjen, H.; Ballantine, D. S., Jr.; Jarvis, N. L. In *Chemical Sensors and Microinstrumentation*; Murray, R. M., Dessy, R. E., Heineman, W. R., Janata, J., Seitz, W. R., Eds.; ACS Symposium Series 403; ACS: Washington, DC, 1989; pp 157−175.

(3) Ricco, A. J.; Martin, S. J. *Sens. Actuators B* **1993**, *10*, 123.

(4) Grate, J.; Rose-Pehrsson, S. L.; Venezky, D. L.; Klusty, M.; Wohltjen, H. *Anal. Chem.* **1993**, *65*, 1868.

(5) Patrash, S. J.; Zellers, E. T. *Anal. Chem.* **1993**, *65*, 1055.

(6) Frye, G. C.; Martin, S. J.; Cernosek, R. W.; Pfeifer, K. B. *Int. J. Environ. Conscious Manuf.* **1992**, *1*, 37.

(7) Zellers, E. T.; White, R. M.; Wenzel, S. W. *Sens. Actuators* **1988**, *14*, 35−45.

(8) Martin, S. J.; Frye, G. C.; Senturia, S. D. *Anal. Chem.* **1994**, *66*, 2201.

(9) Grate, J. W.; Klusty, M.; McGill, R. A.; Abraham, M. H.; Whiting, G.; Andonian-Haftvan, J. *Anal. Chem.* **1992**, *64*, 610.

(10) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* **1993**, *65*, 940; 987.

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

(12) Ballantine, D. S., Jr.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, *58*, 3058.

(13) Grate, J. W.; Abraham, M. H. *Sens. Actuators B* **1991**, *3*, 85.

(14) Carey, W. P.; Beebe, K. R.; Kowalski, B. R.; Illman, D.; Hirschfeld, T. *Anal. Chem.* **1986**, *58*, 149.

0003-2700/95/0367-1092$9.00/0

potential versatility of this sensor technology, a general method for selecting sensor coatings is needed.

The selection of an optimal set of polymer coatings can be made according to several criteria. First, polymers should be selected that are easily and reproducibly deposited on the surface of the sensor and that do not evaporate or exhibit appreciable flow. They must be resistant to oxidative and hydrolytic decomposition by normal atmospheric constituents and also resistant to irreversible chemical or physical changes from target vapors or potential interferences. Ideally, they should provide rapid responses that are linearly related to the analyte concentration. The effects of temperature and humidity on the polymers and on the polymer–vapor interactions should be small. The affinity for target vapors must be sufficient to achieve adequate sensitivities and limits of detection (LODs), and the response patterns of target and interfering vapors should be different enough to achieve adequate selectivity. At the same time, the smallest number of sensors should be used to reduce the cost and complexity of the array. In the case of polymer coatings, there are diminishing returns on the inclusion of more and more sensors, since the range of solubility interactions which govern the sensor responses is finite.[13] For the general problem of organic vapor monitoring, the range of analytes that can be detected and discriminated should be maximized. Finally, the results obtained from the array should be robust, i.e., not highly sensitive to sensor noise and minor miscalibrations. These multiple criteria for coating selection suggest that trade-offs are necessary because no single set of coatings will provide optimal performance with respect to all specifications. For example, sensitivity may be sacrificed for selectivity, or increased sensitivity to polar organic vapors may be gained at the expense of increased sensitivity to atmospheric humidity.

In this paper, we describe an approach to selecting polymer SAW sensor coatings that will optimize selectivity for a given set of organic vapor analytes. In addition, the approach provides quantitative predictions of array performance. For practical reasons, we limit consideration to a four-sensor array operated at constant temperature and humidity. The effects of changes in temperature and humidity on sensor array performance have been described elsewhere.[15] Calibrated responses to individual vapors are used in an extended disjoint principal components regression (EDPCR) analysis to establish the relationship between the identity of each vapor and the corresponding array response patterns.[11] This procedure is repeated for all vapors of interest using all possible subsets of four coated sensors chosen from a larger set. Assuming that the responses to vapor mixtures are additive, binary and ternary mixtures can also be classified (i.e., identified), and the components of the mixtures can be determined by decomposing the mixture response vectors. The performance of each four-sensor array is then modeled using a Monte Carlo simulation analysis of responses to each vapor and mixture of interest. Error is superimposed upon the modeled responses to represent inherent noise and the effects of environmental variables expected under normal operating conditions. Synthetic response patterns are generated repeatedly and processed using the EDPCR analysis to estimate the rate of correct identification and the accuracy of quantification predictions for each array. Additional analyses are performed to determine which vapors or mixtures of vapors are incorrectly identified. The array providing the lowest error rate is then selected as the optimal array.

Following a more detailed discussion of the classification and error models, the coating selection method is demonstrated using a data base of responses to six organic solvent vapors obtained from 10 different coated SAW sensors. Hexane, isooctane, benzene, xylene, chloroform, and trichloroethylene (TCE) were selected as representatives of three important classes of organic vapors commonly encountered in the industrial environment and in contaminated soil and groundwater. Two members from each class were included to assess capabilities for both within-class and between-class discrimination. Calibrations with each of these vapors are used to establish sensitivities and LODs. Coating stability and response reproducibility are examined by repeated calibrations with benzene. The validity of assuming additivity for binary mixture responses is then tested for a subset of these vapors as well as two additional vapors capable of strong hydrogen-bonding interactions. The coating selection method is then applied to several other multicomponent vapor mixtures.

Sensor Response Equations. The response of a polymer-coated SAW delay line oscillator to a vapor depends on the degree of equilibrium partitioning into the polymer coating, which in turn depends on the amount of polymer deposited on the device. Assuming that a low-modulus, isotropic polymer is used and that the polymer film is thin enough such that cross-film strain gradients are small,[8] the following well-known expression can be used to estimate the mass of deposited polymer, m (μg), from the observed shift in frequency, Δf_c (Hz):[16]

$$\Delta f_c = k f_0^2 m/a \qquad (1)$$

where k (cm^2-s/μg) is a substrate-specific constant, f_0 (MHz) is the oscillator frequency prior to coating, and a (cm^2) is the active area of the device being coated. For the ST-quartz devices used in this study, $k = -1.26$ cm^2-s/μg, $f_0 = 158$ MHz, and $a = 0.08$ cm^2.[2] Thus, a Δf_c value of -200 kHz corresponds to a deposited mass of roughly 0.5 μg, which corresponds to an average coating thickness of 0.06 μm, assuming unit density for the polymer.

Sorption of a vapor will swell and soften the polymer and cause a commensurate shift in the SAW oscillator frequency. The sensitivity, expressed as the change in the sensor frequency, Δf_v, per unit change in vapor concentration, ΔC_v, is given by[17]

$$\Delta f_v/\Delta C_v = \Delta f_c K_e/\varrho_c \qquad (2)$$

where ϱ_c is the coating density and K_e is an effective partition coefficient.[5,9]

Extended Disjoint Principal Components Regression (EDPCR). Pattern recognition analysis of the collective responses from an array of coated SAW sensors affords the possibility of identifying and quantifying a number of different vapors. The problem increases in difficulty as concentration spans increase and as the number of vapors potentially or actually present increases. An array of four SAW sensors, for example, cannot identify more than four vapors simultaneously because the

---

(15) Zellers, E. T.; Han, M.; Batterman, S. A.; Patrash, S. P. 186th Meeting of the Electrochemical Society, Miami Beach, FL, October 1994; Abstract 642. Full manuscript in preparation.

(16) Wohltjen, H. *Sens. Actuators* **1984**, *5*, 307.

(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.

problem is underdetermined statistically. Placing restrictions on the pattern recognition problem can improve the ability to identify vapors. Thus, if only individual vapors or binary mixtures are present at any one time, the four-sensor array may be able to correctly identify more than four vapors. In many practical applications, the number of vapors that might be present is limited. In contaminated soil and groundwater, for example, it is frequently observed that as few as one or two contaminants predominate.[18] This is also the case in many industrial settings.[19] Furthermore, the identities of potential air contaminants typically can be determined from bulk analyses of processing chemicals and waste streams.

Several methods are available for classifying or identifying an analyte on the basis of the pattern of responses obtained from an array of acoustic wave chemical sensors.[1,20-23] In most reports, a principal component analysis (PCA) and cluster analysis (CA) are performed on the concentration-normalized set of sensor responses. The vector sum of the responses to each vapor is calculated and plotted in *n*-dimensional space, where *n* is the number of sensors used. The degree to which response vectors for different analytes cluster in different spatial regions essentially determines the selectivity of the array. An unknown vapor can be identified from its response vector using one of several classification methods (e.g., the *K*-nearest-neighbor method), and its concentration can be determined by multiple linear regression, partial least squares, or principal component regression (PCR).[22,23]

EDPCR represents an alternative method for analyzing and modeling polymer-coated SAW vapor sensor array responses.[11] It is similar, in many respects, to SIMCA (soft independent modeling of class analogy)[20,21,24] in that principal components models are developed for individual groups within a data set, and classification of an unknown is based on the goodness-of-fit of its response vector to each of the models. It differs from conventional PCR, where principal components are derived from the data matrix as a whole. For the application considered here, a group is defined as the set of response vectors derived from one set of coated sensors for an individual vapor or vapor mixture over a range of concentrations. The matrix of sensor−vapor response data can be summarized by a set of equations—one for each group.

The first step in EDPCR entails a PCA of each group of sensor responses (i.e., the collection of sensor responses to all concentrations of a single vapor). The response vectors for that vapor are then modeled using the most significant principal component(s) after mean-centering (i.e., subtracting the mean response vector from the individual response vectors for a group).

The model used to classify vapor *i* is given by

$$\mathbf{r}_i = \mathbf{m}_i + \sum_{n=1}^{N} a_{i,n}\boldsymbol{\mu}_{i,n} + \mathbf{e}_i \qquad (3)$$

where $\mathbf{r}_i$ is the response vector for the vapor at a given concentration, $\mathbf{m}_i$ is the mean response vector determined from all of the calibration concentrations measured for that vapor, $a_{i,n}$ is the projection coefficient which determines the location of each response vector along the *n*th principal component represented by the unit vector $\boldsymbol{\mu}_{i,n}$, $\mathbf{e}_i$ is the residual error vector of the model for the vapor at the measured concentration, and N is the number of principal components. For all of the data considered in this study, the first principal component accounted for nearly all of the variance, and a one-principal-component model was used.

Provided that the collective responses of the sensors differ among the different vapors, each vapor will be represented by a unique response model. The response vector from a given concentration of an unknown vapor ($\mathbf{r}_\mathrm{u}$) can be tested for its goodness-of-fit to each of the models established during calibration by replacing $\mathbf{r}_i$ by $\mathbf{r}_\mathrm{u}$ in eq 3 and solving for a_u so that the residual error is minimized. The identity of the unknown is determined from the model for which the smallest error is obtained. Once the identity of the vapor has been established, its concentration can be determined by linear regression of a_i versus concentration.

The composite response vector for a mixture of two components whose responses are additive can be projected onto the plane defined by the two individual vapor response vectors. Each binary mixture can then be thought of as an additional group consisting of two vapors, *i* and *j*, in some combination of concentrations. The classification model for such a binary mixture is represented by the following equation:

$$\mathbf{r}_{i,j} = \mathbf{m}_i + \mathbf{m}_j + a_i\boldsymbol{\mu}_i + a_j\boldsymbol{\mu}_j + \mathbf{e}_{i,j} \qquad (4)$$

where $\mathbf{r}_{i,j}$ is the response vector for the $i + j$ mixture and the other variables have the same definitions as in eq 3 for the individual vapor case. Each combination of vapor concentrations will have corresponding specific values of a_i and a_j. The response vector for an unknown is again compared to all possible models of the binary vapor mixtures and classified on the basis of the smallest residual error. Models analogous to eq 4 can be used for ternary or more complex mixtures.

The vector for a mixture can be projected onto the principal component of each component vapor, and the concentrations can be obtained from the calibration data for the individual vapors. Note that the principal component for one vapor may not be orthogonal to that of the other vapor(s), and this must be taken into account in determining the vapor concentrations.[11]

Monte Carlo Simulation Analysis. Once the EDPCR classification models are established, the performance of various coated sensor subsets can be analyzed and optimal subsets can be determined via Monte Carlo simulation. The approach taken here involves generating a synthetic response, $\langle\Delta f_{ij}\rangle$, to vapor *i* for each coated sensor, *j*, using the following equation:

$$\langle\Delta f_{ij}\rangle = (C_{\mathrm{m}i} + \alpha_i\Delta C_i)S_{ij}(1 + k_1\beta_{ij}) + k_2\gamma_j \qquad (5)$$

where $C_{\mathrm{m}i}$ is the mean calibration concentration of vapor *i* (μg/L),

---

[18] U.S. Department of Energy. *Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Surface Science*; Report No. DOE/ER-0547T; U.S. Department of Energy: Washington, DC, 1992.

[19] Cralley, L. V.; Cralley, L. J. *In-Plant Practices for Job Related Health Hazards Control*; Wiley: New York, 1989; Vol. 2.

[20] Sharaf, M. A.; Illman, D. L.; Kowalski, B. R. *Chemometrics*; Wiley-Interscience: New York, 1986.

[21] Massart, D. L.; VanDeginste, B. G. M.; Demming, S. N.; Michotte, Y.; Kaufman, L. *Chemometrics*; Elsevier Science: Amsterdam, 1988; pp 403−407.

[22] Carey, W. P.; Beebe, K. R.; Sanchez, E.; Geladi, P.; Kowalski, B. R. *Sens. Actuators* **1986**, *9*, 223.

[23] Carey, W. P.; Beebe, K. R.; Kowalski, B. R. *Anal. Chem.* **1987**, *59*, 1529.

[24] Albano, C.; Dunn, W., III; Endlund, U.; Johansson, E.; Norden, B.; Sjostrom, M.; Wold, S. *Anal. Chim. Acta* **1978**, *103*, 429.

Table 1. Polymer Coatings and Δf_c Values Used To Generate the Data in Table 2

abbrev	coating material[a]	ϱ (g/cm^3)	Δf_c (kHz)	thickness[b] (nm)
PIB	polyisobutylene (S)	0.918	195	67.5
PDPP	polydiphenoxyphosphazene (S)	1.20	202	53.5
DEGA	diethylene glycol adipate (L)	1.16	298	81.7
PCP	polychloroprene (S)	1.23	179	46.3
ABC	acrylonitrile/butadiene copolymer (41/59) (S)	1.00	199	63.3
APL	apiezon L (S)	0.892	206	73.4
OV-275	biscyanoallyl polysiloxane (L)	1.00	196	62.3
PECH	polyepichlorohydrin (S)	1.36	201	47.0
OV-25	phenylmethyldiphenylsilicone (75% phenyl) (L)	1.15	220	60.8
OV-215	vinyl-modified trifluoropropylmethylsilicone (L)	1.00	228	72.5
TBEP	tributoxyethyl phosphate (L)	1.19	222	59.3
PHA	poly(hexyl acrylate) (S)	1.02	162	50.5
PHOEA	poly(2-hydroxyethyl acrylate) (S)	1.15	193	53.4
ETSA	*N*-ethyl *o*,*p*-toluenesulfonamide (L)	1.19	193	51.6
PMMA	poly(methyl methacrylate) (S)	1.20	227	60.1
PPE	poly(phenyl ether) 6-rings (L)	1.22	192	50.0

[a] S, solid; L, liquid. [b] From eq 1.

α_i is a uniformly distributed random variable ($-0.5 \le \alpha_i \le 0.5$), C_i is the concentration range over which vapor i was calibrated (μg/L), S_{ij} is the sensitivity of sensor j to vapor i as determined from the slope of the calibration curve (Hz/(μg/L)), k_1 is a constant that specifies the relative standard deviation (RSD) of the slope, β and γ are independent normally distributed variables with zero mean and unit standard deviation, and k_2 is a constant that specifies the root-mean-square (rms) error in the sensor baseline frequency.

The $(C_{mi} + \alpha_i \Delta C_i) S_{ij}$ term in eq 5 generates a sensor response to vapor i at a concentration selected randomly from within the range of calibration. This response is altered by some fractional amount through the $1 + k_1\beta_{ij}$ term to reflect potential errors in S_{ij}. The $k_2\gamma_j$ term alters the response further to reflect the inherent oscillator noise that is independent of the magnitude of the response. For mixtures, responses are generated for the individual vapors separately and then summed.

A value of $k_1 = 0.025$ was used in the initial cases considered below. It reflects the magnitude of error that might be expected from either slight miscalibration or temperature fluctuations during operation. A value of $k_2 = 15$ Hz was used since this is the typical short-term rms noise level associated with the SAW oscillators employed in the study. A uniform distribution was used for α so that concentrations within the calibration range would be chosen with equal likelihood. Normal distributions were used for β and γ because slope and random errors should be approximately Gaussian.

Synthetic responses to a given concentration of each vapor are generated for each sensor in the subset of four under consideration. The response vector from this collection of responses is then processed as an unknown using EDPCR to determine its assigned identity. By performing this procedure repeatedly (e.g., 100 times for each possible vapor or vapor mixture), the percentage of correct identifications expected for each coating subset is determined. After all coating subsets are simulated, they are ranked accordingly. The optimal set can be analyzed further to determine which vapors are more likely to be misidentified and at what rate.

EXPERIMENTAL SECTION

Materials. The sensor coatings examined are listed in Table 1 with their corresponding abbreviations. Some of the coating materials were chosen on the basis of a pattern recognition analysis of McReynold's gas chromatographic retention data reported by Huber and Reich.[25] Several of the materials identified in that analysis were not commercially available, so additional coatings were selected on the basis of general considerations of structure and anticipated affinities for the test vapors. Recommendations by Grate and Abraham[13] were also considered. Collectively, the coating materials selected span a wide range of polarities and structural features. PIB was obtained from the Aldrich Chemical Co. (Milwaukee, WI); PDPP, PCP, ABC, and PECH were obtained from Scientific Polymer Products (Ontario, NY); and the remaining coating materials, comprising various standard gas chromatography (GC) stationary phases, were obtained from Anspec (Ann Arbor, MI). The solvents were all >98% pure (Aldrich) and were used without further purification (see Table 2).

Equipment. An ac-powered instrument from Microsensor Systems Inc. (Bowling Green, KY) was used for testing the sensors. The instrument housed four 158-MHz SAW oscillators, four sealed reference oscillators, radio frequency electronics modules, frequency counters, and signal-conditioning circuitry. Difference frequency measurements between the coated and reference sensors were collected every 2 s and transferred to a personal computer via an RS-232 buss for display, storage, and subsequent manipulation.

The instrument was incorporated into the exposure system shown in Figure 1. Test atmospheres of the vapors were generated by passing air or N_2 gas through a fritted bubbler containing the liquid solvent and then into a metered dilution air stream maintained at 25 °C and 50% relative humidity (RH). The dilution air was prefiltered to remove any particulate or vapor contamination. After allowing for proper mixing of the vapors in the dilution stream, a portion of the stream was passed through a calibrated infrared gas analyzer (MIRAN 1A, Foxboro, Bridgewood, MA), and the remainder was diverted to a solenoid valve used to direct the flow of the test atmosphere either to the sensor array or to an exhaust vent. A separate humidified clean air line could also be directed to the array for the purpose of measuring baseline frequencies before and after vapor exposures.

---

(25) Huber, J. F. K.; Reich, G. *J. Chromatogr.* **1984**, *294*, 15.

Table 2. Calibration Data for 10 Vapors Using the Initial Set of SAW Sensor Coatings

	PIB	PDPP	DEGA	PCP	ABC	APL	OV-275	PECH	OV-25	OV-215	TBEP	PHA
chloroform												
sensitivity (Hz/(μg/L))	0.068	0.055	0.121	0.064	0.194	0.054	0.088	0.088	0.106	0.023	0.199	0.177
LOD (μg/L)[a]	658	821	371	705	232	823	513	510	425	1930	226	255
concn range (μg/L)	5700–30 000	5700–30 000	5700–30 000	5700–30 000	5700–30 000	1760–7050	5700–30 000	5700–30 000	5700–30 000	5700–30 000	2600–26 600	2600–26 600
hexane												
sensitivity (Hz/(μg/L))	0.078	0.014	0.0036	0.011	0.016	0.062	0.007	0.012	0.040	0.005	0.049	0.047
LOD (μg/L)	576	3230	12600	4180	2760	719	6680	3890	1130	9990	909	959
concn range (μg/L)	3400–41 500	3402–41 500	3404–41 500	3400–41 500	3400–41 500	3880–10 300	6800–23 700	3401–41 500	6800–23 700	3403–41 500	1400–18 200	1400–18 200
benzene												
sensitivity (Hz/(μg/L))	0.131	0.095	0.100	0.080	0.205	0.103	0.109	0.147	0.213	0.039	0.201	0.176
LOD (μg/L)	343	476	451	564	219	436	413	306	211	1150	224	256
concn range (μg/L)	2100–22 700	2100–22 700	2100–22 700	2100–22 700	2100–22 700	910–5440	1800–6800	2100–22 700	1800–6800	2100–22 700	1500–8100	1500–8100
trichloroethylene												
sensitivity (Hz/(μg/L))	0.186	0.101	0.114	0.085	0.206	0.172	0.090	0.123	0.231	0.039	0.300	0.261
LOD (μg/L)	242	447	394	530	219	262	498	365	195	1170	150	172
concn range (μg/L)	1400–22 300	1400–22 300	1400–22 300	1400–22 300	1400–22 300	690–3630	3400–12 400	1400–22 300	3400–12 400	1400–22 300	1500–18 300	1500–18 300
isooctane												
sensitivity (Hz/(μg/L))	0.193	0.023	0.013	0.031	0.037	0.150	0.012	0.027	0.082	0.021	0.100	0.092
LOD (μg/L)	233	2000	3440	1440	1220	298	3750	1680	549	2100	449	488
concn range (μg/L)	2700–20 200	2700–20 200	2700–20 200	2700–20 200	2700–20 200	770–4650	2000–14 400	2700–20 200	2000–14 400	2700–20 200	2600–10 100	2600 –10 100
xylene												
sensitivity (Hz/(μg/L))	1.35	0.595	0.576	0.827	1.42	1.11	0.396	1.01	1.01	0.283	1.52	1.31
LOD (μg/L)	33	76	78	54	32	40	114	45	45	159	30	34
concn range (μg/L)	1600–8400	1600–8400	1600–8400	1600–8400	1600–8400	204–5740	400 –3300	1600–8400	401–3300	1600–8400	400–1700	400–1700
styrene												
sensitivity (Hz/(μg/L))	1.74	1.69	1.13	1.10	2.61	1.30	0.790	2.22	1.95			
LOD (μg/L)	26	27	40	41	17	35	57	20	23			
concn range (μg/L)	60–1080	60–1080	60–1080	60–1080	60–1080	50–815	280–1460	60–1080	280–1460			
2-butanone												
sensitivity (Hz/(μg/L))	0.062	0.068	0.063	0.103	0.147	0.044	0.189	0.159	0.169			
LOD (μg/L)	716	653	713	437	305	1020	238	282	266			
concn range (μg/L)	2180–35 700	2180–35 700	2180–35 700	2180–35 700	2180–35 700	1400–9270	2830–9500	2180–35 700	2830–9500			
dichloromethane												
sensitivity (Hz/(μg/L))	0.024	0.023	0.030	0.020	0.035	0.020	0.057	0.029	0.054			
LOD (μg/L)	1810	1930	1500	2220	1290	2220	787	1550	825			
concn range (μg/L)	11500–19 2000	11500–19 2000	11500–19 2000	11500–19 2000	11500–19 2000	2700–9960	6510–39 000	11500–19 2000	6510–39 000			
methanol												
sensitivity (Hz/(μg/L))	0.013	0.017	0.099	0.106	0.124	0.004	0.155	0.056	0.015			
LOD (μg/L)	3370	2560	451	424	363	9120	290	797	2820			
concn range (μg/L)	2780–16 600	2780–16 600	2780–16 600	2780–16 600	2780–16 600	9600–23 600	6270–18 900	2780–16 600	6270–18 900			

[a] To convert vapor LODs to parts per million (ppm, v/v), multiply by (MW)/24.45.

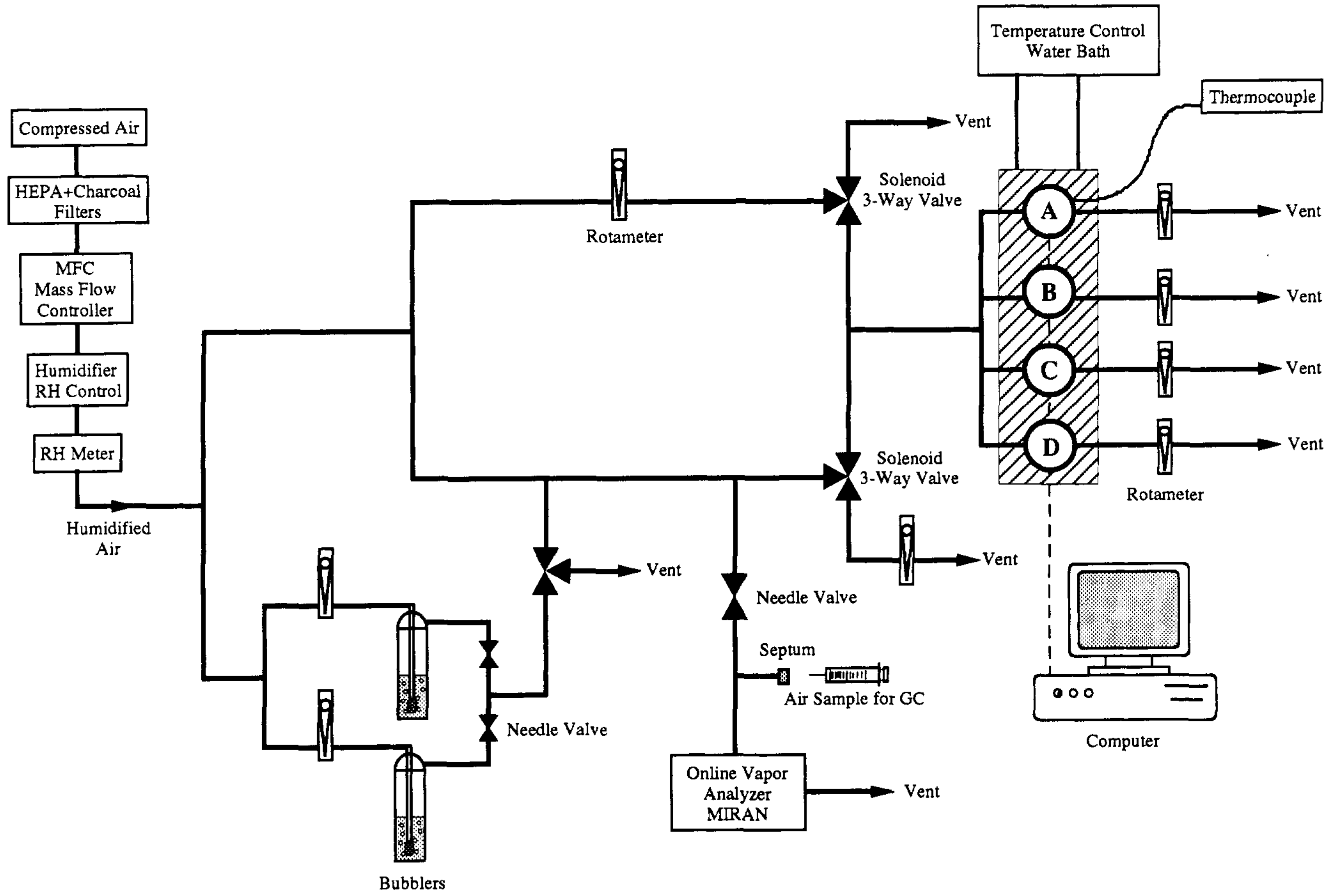

Figure 1. Dynamic test atmosphere generation system.

For mixture exposures, an additional bubbler was incorporated into the system, and vapor concentrations were verified by taking aliquots with a gas-tight syringe and injecting them into a gas chromatograph (Model 2860, Varian, Mountain View, CA) equipped with a packed column (2 ft, $^1/_8$-in. o.d., 1% SP-1000 on acid-washed Chromosorb P, Supelco, Inc., Eighty Four, PA) and an FID. Peak areas were quantified using an electronic integrator (Model 3390A, Hewlett-Packard, Palo Alto, CA). The gas chromatograph was calibrated before each experiment using solutions of the analytes in CS_2.

Each sensor was capped with a nickel-plated lid sealed with a Teflon (DuPont) gasket to the 12-pin TO-8 header on which each sensor was mounted. Reference sensors were sealed. Inlet and outlet tubes soldered to the coated sensor lids provided access to the test atmospheres. The sensor lids were held in place with machined aluminum blocks (one for each coated sensor/reference sensor pair) clamped on top of the lids with bolts that were anchored to the floor of the instrument chassis. The sensor array was maintained to within 0.2 °C of a preset value by circulating thermostated water through the aluminum blocks. A 3-mm-diameter type-K thermocouple was fed through the seal of one of the sensor lids, and the temperature just above the sensor was monitored with a digital temperature meter (Model HH-71 K1, Omega Engineering, Stamford, CT). All system connections were made using either Teflon or stainless steel tubing and fittings to minimize adsorptive vapor losses.

Flow rates over the sensors were maintained at 0.250 L/min and monitored continuously with four downstream rotameters. The internal volume of each capped sensor was about 0.1 cm^3, and thus the theoretical mixing time is about 25 ms. With humidified, contaminant-free air passing continuously over the sensors, the 2-s rms noise level of the baseline was 11−15 Hz.

Coating Deposition and Vapor Exposure. Solutions of approximately 0.2% by weight of the coatings in toluene or a mixture of toluene and acetone were applied by airbrush to the sensors. The amount of coating deposited was inferred from the net frequency shift, Δf_c, observed shortly after evaporation of the carrier solvent, via eq 1. Values of Δf_c were all in the range of 160−300 kHz (Table 1).

For each vapor concentration tested, the array was exposed in duplicate for 60 s, with each exposure separated by a 60-s purge with clean, humidified air or N_2. The last 15 frequency measurements (30 s) in each exposure period were averaged, and the net response was determined after subtracting the average of the pre- and postexposure baseline frequencies. This procedure was repeated for at least four different concentrations of each test vapor, covering a 4−10-fold concentration range, depending on the vapor. Calibrations performed subsequent to initial screening experiments entailed measurements of five or six concentrations covering a 12−30-fold range. For binary mixture exposures, N_2 was used as the diluent, and the concentration of each component was varied to examine whether the relative concentration of the vapors affected their combined response or the ability to discriminate each component using pattern recognition.

Calibrations were performed for 15 of the 16 coatings listed in Table 1 (APL was not included in initial tests), typically in sets of four, for each of the six vapors. Following exposure of a given set of coatings to each vapor, the coatings were removed and new coatings were applied and tested. Of the 15 coating materials initially examined, several were eliminated from further analyses

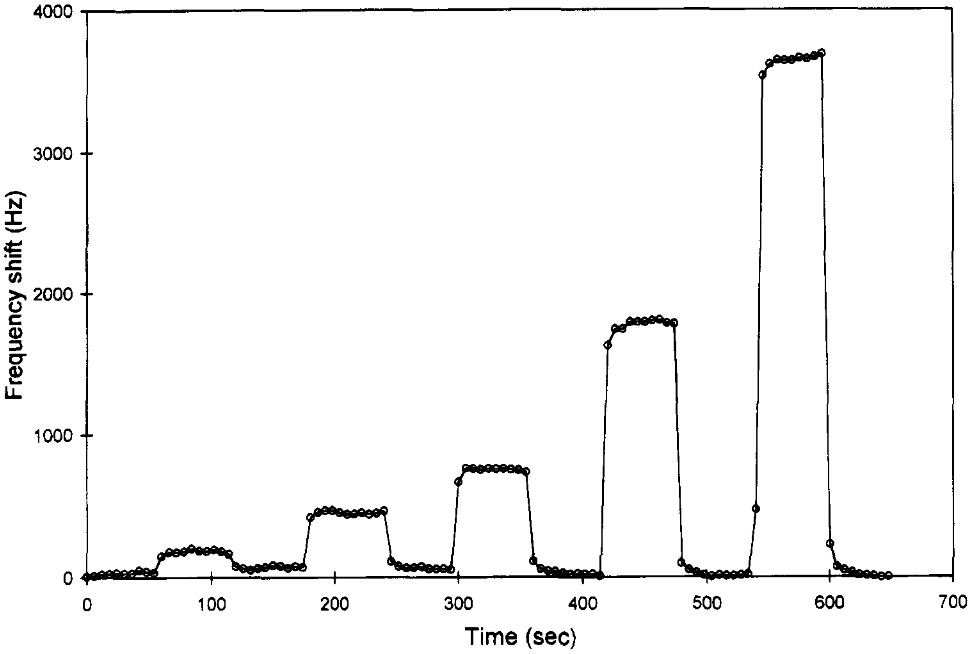

Figure 2. Reconstructed response profile for PIB-coated SAW sensor exposed to TCE vapors at concentrations ranging from 300 to 13 000 μg/L.

for reasons described below. Analyses of the calibration curves from the remaining coatings were performed to select the optimal subset of four coating materials. Subsequent tests were performed on freshly deposited coatings of the optimal four polymers to assess the additivity of binary mixture responses.

APL was then added to the list of sensor coatings and tested. Additional vapors for which calibration curves were generated for nine of the coatings included styrene, 2-butanone, dichloromethane, and methanol. These data were used in modeling the performance of different four-sensor arrays for measuring several ternary mixtures. A study of additivity for two hydrogen-bonding vapors, 1-butanol and 2-methoxyethanol, was also performed with a subset of four sensors.

Data Analysis. Statistical analyses of response data were performed using commercial spreadsheet packages. EDPCR analyses were performed in MATLAB (Mathworks, Inc., Natick, MA). The averages of the duplicate sensor responses at each vapor concentration were regressed against concentration to obtain the sensitivity for each vapor–coating combination. LODs were determined by extrapolating the response curves to a frequency shift of 45 Hz, representing 3–4 times the rms noise observed.

EDPCR analyses performed to establish the classification models for the six initial vapors employed a one-principal-component model because >95% of the variance in responses was accounted for using the first principal component. Binary mixtures were also classified this way under the assumption that the composite response was equal to the sum of the responses from the vapors constituting each mixture (see below). To rank all 210 possible combinations of four coatings (out of 10) according to the percentage of correctly identified vapors, the individual vapor–coating sensitivities were used in a Monte Carlo simulation of responses to each vapor and binary vapor mixture. This analysis considered the general case where any of the six vapors might be present, but where only one or two might be present at any one time. The synthetic responses were generated using eq 5, and the performance of each subset of four coatings was assessed using EDPCR. For each coating subset, 2100 simulations were performed: 100 for each of the 6 individual vapors and 15 binary mixtures. The rates of correct identification determined for the 21 vapors and mixtures were averaged, and the standard deviation and 95% confidence interval were determined. When only one component of a binary mixture was correctly identified, or when an individual vapor was identified as a mixture, a score of 0.5 was assigned.

RESULTS AND DISCUSSION

Sensor Responses to Individual Vapors. Figure 2 shows a set of reconstructed response profiles obtained by exposing the PIB-coated sensor alternately to TCE and then clean, humidified air over a TCE concentration range of 300–13 000 μg/L. These profiles are typical of those obtained for all of the vapors and vapor mixtures tested. Responses and recoveries reached >90% of their equilibrium values within 6–10 s of introduction and removal of the vapor, respectively.

Plots of vapor concentration versus Δf_v were linear, and regression correlation coefficients (r^2) typically exceeded 0.99. Representative results for four of the coatings are shown in Figure 3 for exposure to TCE over the same concentration range as in Figure 2. The PIB-coated sensor showed the highest sensitivity to TCE, and the DEGA-coated sensor showed the lowest. The ratio of TCE sensitivities for these coatings was about 2:1. Table 2 provides statistics for all coatings and vapors derived from the initial series of calibrations. Calibration concentration ranges, sensitivities, and calculated LODs are given for each coating–vapor pair based on a single exposure test. In general, the linearity and precision were excellent. The relative standard errors of the sensitivities were typically <3%, although somewhat higher values were observed for vapors giving low responses (e.g., hexane and DEGA). This can be attributed to the greater influence of random oscillator noise and errors in concentration measurements. Small differences in relative humidity between the clean and contaminant flow streams may also have contributed to variability in the DEGA and OV-275 sensor responses since

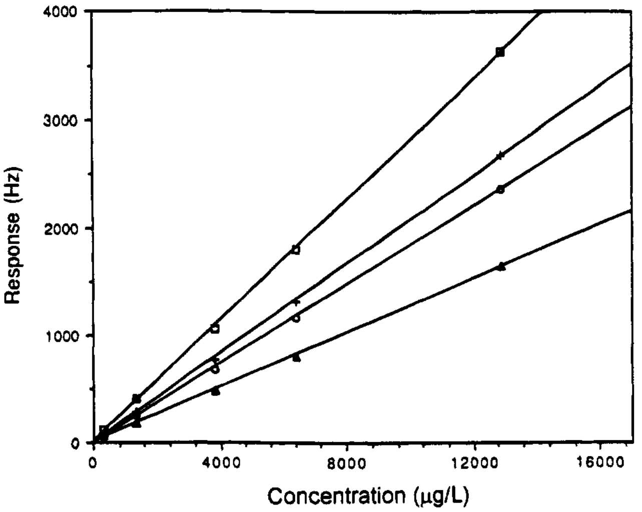

Figure 3. Calibration curves for sensors coated with PIB (□), PDPP (○), DEGA (△), and PCP (+) exposed to TCE.

Table 3. Reproducibility of Sensor Responses over Time Based on Sensitivities to Benzene Vapor

	individual coating films				replicate coating films		
coating	*n*	time span (months)	mean sensitivity (Hz/(µg/L))	RSD (%)	*n*	mean sensitivity (Hz/(µg/L))[a]	RSD[b] (%)
PIB	7	8	0.151	5.6	3	0.144	8.0
PDPP	21	16	0.121	6.4	2	0.108	17.3
DEGA	7	8	0.072	14.5	2	0.059	16.8
PCP	18	12	0.086	9.8	2	0.087	2.8
ABC	12	8	0.202	6.5	3	0.192	9.2
APL	13	5	0.074	10.4	2	0.089	24.5
OV-275	18	9	0.080	14.2	2	0.087	14.3
PECH	22	12	0.157	7.0	2	0.156	0.4
OV-25[c]	9	1	1.490	7.4			

[a] These sensitivities are normalized to a value of Δf_c = 200 kHz. [b] Between-coating RSD. [c] Sensitivity value is for *m*-xylene rather than benzene for this coating.

these highly polar coatings show the greatest sensitivity to RH fluctuations.

The trends in detection limits are similar to those found in our previous investigations,[5] with higher LODs being associated with the more volatile vapors and with coating–vapor combinations where the solubility interactions are expected to be weak. It should be mentioned that the LOD needed to *quantify* vapor concentrations will differ from the LOD needed to *identify* vapors. For quantification, the LOD for the most sensitive sensor in the array will apply, assuming that a single vapor is present and that the vapor is known. If the vapor must be identified or if multiple vapors are present, then signals from several sensors would generally be required. The number of signals required will depend on the complexity of the mixture and the similarity in responses between target vapors and potentially interfering vapors. Such conditions are not unusual, as many instruments have LODs and other performance characteristics that depend on the complexity of the sampled matrix.

Coating Stability and Response Reproducibility. Six coatings were eliminated from consideration after initial screening experiments due to problems with baseline and/or response stability (PPE, TBEP, OV-215), negative responses to vapors and difficulty in determining the amount of coating deposited (ETSA), low responses to most vapors (PMMA), or extreme water sensitivity (PHOEA). The sensitivity of OV-25 to xylene increased over the first 2 weeks of exposure and then remained relatively stable. The data from this coating were not included in the initial coating selection procedure but were considered in subsequent selection procedures for selected binary and ternary vapor mixtures. Initial measurements with TBEP and OV-215 indicated that these coatings were quite stable and that responses were reproducible. However, subsequent testing with different coating films of these materials showed a steady and significant decline in sensitivity over time. The same sort of sensitivity decline was observed with PPE, as described previously.[5] For ETSA, the Δf_c value obtained directly after coating was 200 kHz, but after the sample was allowed to stand for a few hours it drifted toward zero. Thus, it was not possible to obtain an accurate measure of the amount of coating deposited. In addition, although the magnitudes of the responses to several vapors increased with concentration, the responses were all negative (difference frequencies should be positive if mass loading and reductions in stiffness dictate the sensor responses). Given this unusual behavior, ETSA was eliminated from further analyses. The coating PHA was tested with a number of vapors and was found to give stable and reproducible responses. Although it was included in our initial analyses of optimal coating sets, for logistical reasons (i.e., the limited number of sensors that could be tested at any one time) and because it did not appear to provide particularly unique responses relative to other moderately polar coatings, it was not included in subsequent analyses.

The remaining nine coatings were well-behaved. APL, which was subsequently added to the list of tested coatings, also performed well. Repeated exposures to benzene over the course of several months indicated that the sensitivities remained stable. The RSDs around the mean sensitivities determined from replicate calibrations were generally below 10%, and no systematic drifts were observed. Table 3 provides summary data on response reproducibility determined from repeated calibrations with benzene for representative coating films of each material. The length of time over which these tests were performed differs for each coating because certain coatings have been included in ongoing studies of sensor performance while others have not. The higher RSDs around the mean sensitivities for OV-275 and DEGA, again, can be attributed to their relatively low responses and the increased influence of sensor noise and RH fluctuations. Thus, with a few possible exceptions, the response variations of the coated sensors are similar to typical errors in GC and IR calibration procedures (~5%).

A limited study of intercoating reproducibility was performed for several of the coatings. This entailed calibrations with benzene for two or three separate coating films of the same polymer. In the case of OV-275, an additional investigation was performed by coating all four sensors in the array simultaneously with this material and collecting repeated measurements of xylene responses over several days. Since there were slight differences in the amount of coating deposited each time, comparisons for all polymers were based on sensitivities normalized to a common value of Δf_c = 200 kHz using eq 2.

For most of the polymer coatings, there was excellent agreement between average sensitivities to benzene determined for successive coating films. As expected, coatings with lower benzene sensitivity (i.e., DEGA, OV-275, and APL) showed greater

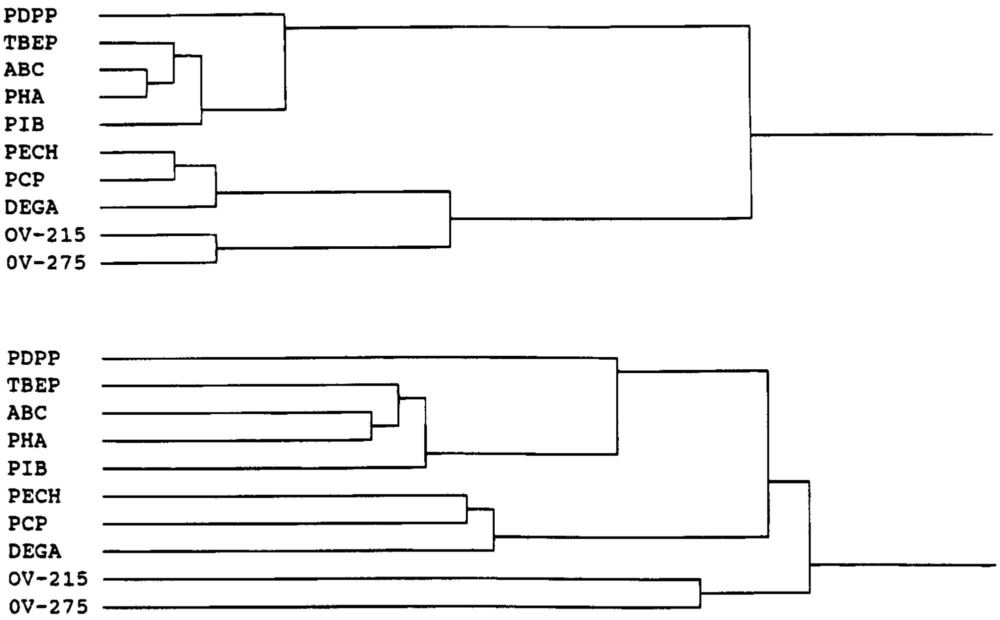

Figure 4. Dendrograms derived from hierarchical clustering analysis of sensor response data for the six vapors employing (a, top) Euclidean distance metric with complete linkage method and (b, bottom) Euclidean distance metric with single linkage method.

variability. The higher variability for PDPP is most likely due to an error in estimating Δf_c for the first coating deposition. The uncertainty in Δf_c values used to determine the normalized sensitivities in Table 3 should be recognized. The degree of drift in the sensor output after coating deposition varied: the larger drift associated with solvent evaporation (minutes) was sometimes followed by a more gradual drift (hours, days), apparently associated with structural relaxations of the polymer chains. Thus, the point in time at which Δf_c values are measured can affect the determination of the normalized sensitivities. Differences in wetting and adhesion of the coating film to the substrate may also be important in this regard.[26,27] The *m*-xylene sensitivity for each of the OV-275-coated sensors tested was stable over time, with average values ranging from 0.293 to 0.401 Hz/(μg/L). The average for all four coatings was 0.340 Hz/(μg/L), and the between-coating RSD was 13%. Overall, the degree of intercoating variation in sensitivity observed here is somewhat less than that reported by other researchers.[9]

Coating Selection by Cluster and K-Means Analyses. To provide some context for assessing the EDPCR–Monte Carlo coating selection method, two hierarchical cluster analyses and a K-means analysis were performed on the data set. These analyses, which used a 10 × 6 matrix comprising the sensitivity of each coated sensor to each of the six vapors, are similar to those reported in previous studies of SAW chemical sensor arrays.[1,12]

Figure 4 presents the results from the cluster analyses which used different protocols to assign clusters. The dendrograms group the sensors according to their similarities in response patterns to the six vapors. Those sensors connected at a lower point are more similar. The selection of four coated sensors to include in an array would be based on the dissimilarity among the sensors. From Figure 4a, coatings would be chosen from the following groups: (1) PIB, ABC, TBEP, PHA; (2) PECH, DEGA, PCP; (3) OV-215, OV-275; (4) PDPP. This provides 24 different choices. Groupings in Figure 4b are slightly different and would provide more choices.

The K-means analysis is an alternative to cluster analysis that also provides groupings of similar coatings. Used iteratively, it can provide groups that satisfy a criterion such as minimum within-group variance. This procedure was performed for the same data set using a large iteration limit (i.e., $n = 100$). The results yielded groupings similar to those obtained from the dendrogram shown in Figure 4b.

Implicit in the selection of coatings using the cluster and K-means analyses is the assumption that all coatings within an identified group are interchangeable with respect to their contribution to the performance of the array. However, further analyses would be required to confirm this, particularly where vapor mixtures are involved. More importantly, there is no means by which the performance of a given set of coatings can be assessed. That is, while four "dissimilar" coatings can be selected, it is not clear whether the chosen coatings can provide the desired discrimination between the vapors to be encountered. These analyses also do not provide any information on the expected rates of error in identifying vapors, which vapors will be incorrectly identified, how the array would perform when mixtures are present, or how random or systematic variations in sensor output would affect performance. Some additional insight could be obtained from PCA plots or eigenvector analyses, but most of these issues would remain unresolved.

Coating Selection by EDPCR and Monte Carlo Simulation Analysis. An EDPCR analysis was performed on the same data set followed by a Monte Carlo simulation analysis under the condition that any of the six vapors might be present but that only one or two could be present any one time. Table 4 shows the results of the analysis for the 16 top-ranked coating sets. Not surprisingly, many different coating combinations provide similar performances. There are 26 coatings sets with average correct identification rates within the range of 93–95%, and the difference in performance of the top 15 coating sets is not statistically significant at the 95% confidence level. Coating sets near the middle and bottom of the rankings had significantly lower rates, with the lowest ranked coatings (rankings 200–210) providing correct identification rates ranging from 67 to 75%. These analyses

---

[26] Grate, J. W.; Wenzel, S. W.; White, R. M. *Anal. Chem.* **1992**, *64*, 413.

[27] Grate, J. W.; McGill, A. R. *Anal. Chem.*, submitted for publication.

Table 4. 16 Top Ranked Coating Sets and Correct Identification Rates from EDPCR and Monte Carlo Analyses[a]

rank	coating set				corr ident rate (%)	95% confidence interval (%)
1	PDPP	DEGA	PIB	PCP	95.2	94.5−95.9
2	PECH	PDPP	DEGA	PIB	94.9	94.1−95.7
3	PDPP	DEGA	PIB	OV-275	94.7	94.0−95.4
4	PECH	OV-215	DEGA	PIB	94.7	93.9−95.5
5	PDPP	PIB	PHA	OV-275	94.6	93.8−95.4
6	OV-215	DEGA	PIB	OV-275	94.5	93.7−95.3
7	PDPP	PIB	TBEP	OV-275	94.5	93.7−95.3
8	OV-215	DEGA	PIB	PCP	94.5	93.7−95.3
9	PDPP	DEGA	TBEP	OV-275	94.2	93.3−95.1
10	PDPP	DEGA	PHA	OV-275	94.2	93.4−95.0
11	PECH	OV-215	DEGA	OV-275	94.0	93.1−94.9
12	PECH	PDPP	TBEP	OV-275	94.0	93.1−94.9
13	PDPP	DEGA	PCP	TBEP	93.9	93.1−94.7
14	PECH	PDPP	DEGA	OV-275	93.8	93.0−94.6
15	PIB	PCP	PHA	OV-275	93.6	92.7−94.5
16	PECH	PDPP	PHA	OV-275	93.6	93.8−94.4

[a] $k_1 = 0.025$; $k_2 = 15$ Hz.

were repeated using a higher slope error ($k_1 = 0.05$) and then a higher baseline noise level ($k_2 = 22$ Hz), which did not change the rankings significantly. Table 4 illustrates the improvement over hierarchical clustering and K-means analyses in terms of the amount of information obtained on the performance of the various coating sets. In addition, several of the coating sets that might have been selected on the basis of these other analyses do not rank among the top sets shown in Table 4.

The set consisting of PIB, PDPP, DEGA, and PCP ranked first in the initial analysis and remained in the top five coating sets in the subsequent analyses. Overall, its modeled performance was better than that of any other coating set, so it was chosen as the optimal coating set for the array.

A new set of coating films of these polymers was then deposited on the sensors, and calibrations were repeated. Figure 5 shows the response pattern for each vapor using this array. As expected, the aliphatic vapors have very similar patterns. In addition, the sensitivity to hexane is low for all four sensors, thus its pattern is likely to be affected more by baseline noise. These two factors would be expected to make discrimination of isooctane and hexane more problematic. The patterns for xylene and benzene are qualitatively similar but differentiable even by visual inspection. The two chlorinated vapor patterns are quite distinct, perhaps as a consequence of the double bond in TCE. These vapors should be easily distinguishable. Note that the patterns for TCE and benzene are very similar. Although this result was not anticipated, it is not too surprising since it is known that TCE and benzene can be difficult to separate by GC.

This coating set was then tested again with the EDPCR−Monte Carlo method with $n = 1000$. Identification rates of 94.6 and 86.7% were predicted with $k_1 = 0.025$ and 0.05, respectively ($k_2 = 15$ Hz in both cases). Additional analyses were performed to determine the error rates associated with identifying each vapor and vapor mixture. As shown in Table 5, the highest error rates are associated with mixtures of hexane and isooctane, regardless of the assumed slope error. For $k_1 = 0.025$, all the individual vapors are predicted to be correctly identified at rates exceeding 92%. The rates are somewhat lower for $k_1 = 0.05$. It is interesting to note that the change in predicted identification rates with the assumed slope error is relatively large (i.e., >10%) in certain cases while quite moderate (i.e., <5%) in others, apparently due to differences in the uniqueness of the response patterns. Such information is important to consider since the error sensitivity provides a measure of robustness toward slight miscalibration or changes in operating temperature.

Additivity of Sensor Responses for Binary Mixtures. An important assumption in EDPCR and other pattern recognition methods is the additivity of sensor responses. Experiments were performed to evaluate the assumption of additivity using six binary mixtures of four vapors: benzene + isooctane; benzene + xylene; benzene + chloroform; chloroform + TCE; TCE + isooctane; and isooctane + hexane. Thus, both within- and between-class combinations were tested. For each mixture, the optimal sensor array was exposed to between 7 and 18 different test atmospheres spanning a range of different absolute and relative concentrations. A total of 33 individual vapor and 62 mixture exposures were performed. The data were analyzed by several methods, as described below.

First, sensor responses predicted from the sums of the individual vapor calibrations were compared to responses measured during mixture exposures. Differences between measured and predicted responses were typically below 10%, as shown in Table 6. Occasionally, larger errors occurred at low concentrations or where sensor responses were small, owing largely to signal-to-noise problems. This was particularly evident in the case of DEGA.

Second, multiple linear regressions of sensor response versus vapor concentration were performed using the experimental binary mixture response data to obtain the sensitivity for each vapor−coating combination. These sensitivities were compared to those obtained from the individual vapor calibrations (Table 7). The r^2 values for the binary mixture regressions typically exceeded 0.98, and the sensitivities derived from the coefficients of the regression were very similar to those obtained from the individual vapor regressions.

Third, multiple linear regressions were performed using a global data base consisting of responses from all mixture exposures involving a given vapor. That is, sensor responses were regressed against the vapor concentrations as just described, but in this case, all binary mixture data were used. This method is similar to training procedures used in partial least-squares fitting and estimation.[28] It has the advantage of providing the sensitivities of a given sensor to all vapors in a single regression, and it increases the degrees of freedom available, thereby decreasing uncertainties associated with estimated sensitivities. Table 7 shows the results from this multiple regression analysis under the heading of "all mixtures". Again, r^2 values generally exceeded 0.98, and the sensitivities closely match those determined using individual calibrations.

The RSD values among the sensitivities determined by the regressions just described are generally below 5% (Table 7), which is comparable to the precision of the sensitivity estimates for the individual vapors. Results for the DEGA coating with isooctane and hexane show greater variability, largely due to the relative insensitivity of this coating to these vapors. By any measure, these data support the assumptions of linearity and additivity of responses.

---

(28) Macland, D. M.; Thomas, E. V. *Anal. Chem.* **1988**, *60*, 1193.

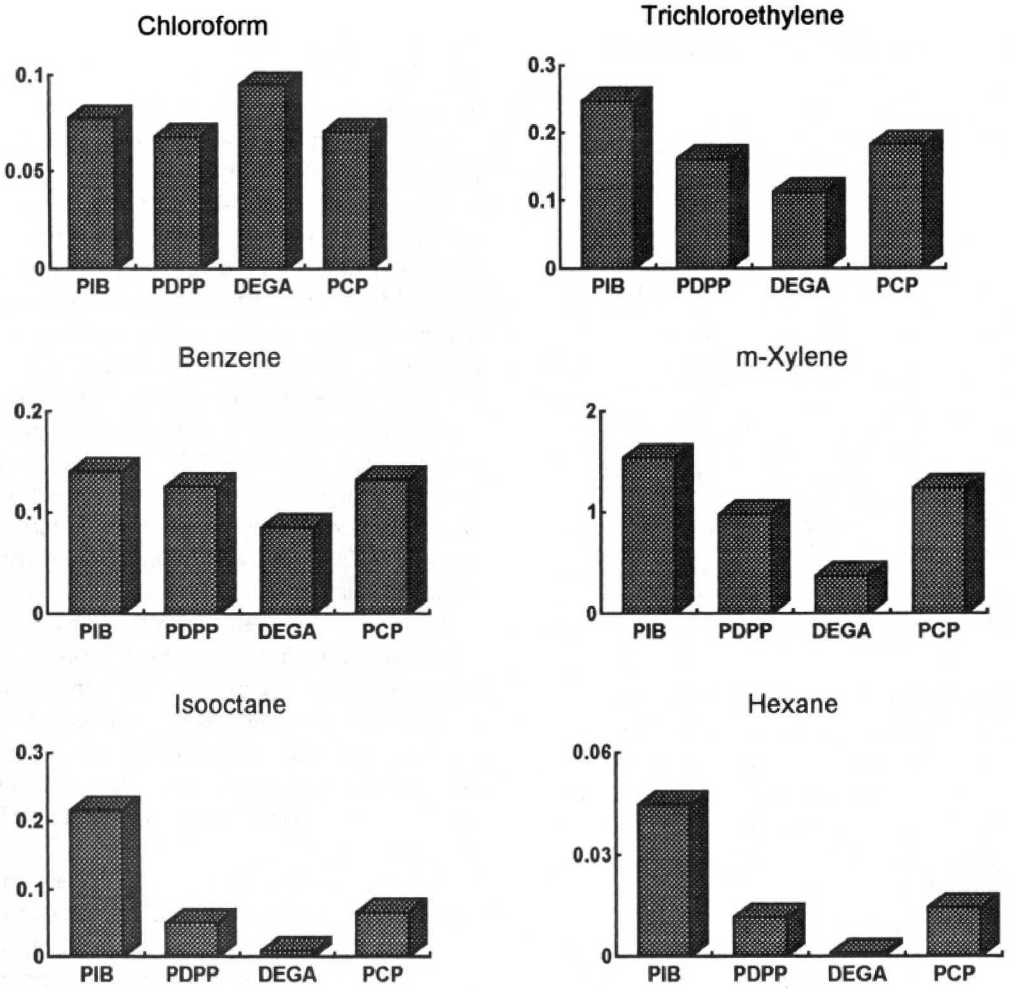

Figure 5. Response patterns for six vapors using the optimal four-sensor array. The *y*-axes represent sensitivities in Hz/(μg/L).

Table 5. Matrix of Correct Identification Rates for Individual Vapors and Binary Mixtures Predicted Using the EDPCR–Monte Carlo Method[a]

	BEN	CHL	TCE	ISO	XYL	HEX
			$k_1 = 0.025$			
BEN	92.1	97.9	91.8	97.2	97.2	94.6
CHL		98.8	93.9	99.0	94.0	97.2
TCE			91.5	95.8	93.3	92.3
ISO				100	96.2	73.5
XYL					96.2	92.0
HEX						96.4
			$k_1 = 0.05$			
BEN	82.7	94.1	84.4	91.8	92.6	85.8
CHL		94.5	85.7	96.1	82.4	93.6
TCE			74.6	85.8	87.2	83.7
ISO				98.3	81.8	65.1
XYL					87.4	86.8
HEX						85.8

[a] $n = 1000$; $k_2 = 15$ Hz. BEN, benzene; CHL, chloroform; ISO, isooctane; XYL, *m*-xylene; HEX, hexane.

Table 6. Percentage of Experimental Mixture Responses within Specified Ranges of Responses Expected under the Assumption of Additivity

vapor mixture	range (%)	PIB	PDPP	DEGA	PCP
BEN + ISO	±10	71	100	86	100
	±25	100	100	100	100
BEN + XYL	±10	100	100	80	100
	±25	100	100	90	100
BEN + CHL	±10	100	100	88	100
	±25	100	100	100	100
TCE + CHL	±10	82	91	82	55
	±25	100	100	100	100
HEX + ISO	±10	100	100	44	100
	±25	100	100	78	100
TCE + ISO	±10	100	94	59	88
	±25	100	100	100	100
all mixtures	±10	94	97	71	89
	±25	100	100	95	100

Experimental Verification of the EDPCR–Monte Carlo Method. The capabilities for EDPCR and the optimal array to identify and quantify the vapors were assessed using the experimental responses obtained from the 95 individual vapor and binary mixture exposures. Overall, the correct identification rate was 86%, which is similar to the 87% predicted for all possible mixtures assuming $k_1 = 0.05$. If the predicted rate is adjusted to account for the fact that only a subset of vapors was tested experimentally (i.e., by weighting the predicted rate for each vapor or vapor mixture by the number of exposures actually performed), then the predicted rate is exactly 86%. Thus, the overall agreement between experimental and predicted results is extremely good.

Table 8 provides the classification and quantification results for each test atmosphere where an EDPCR analysis was used to identify and predict the concentration of each vapor. For the mixtures, at least one of the components was correctly identified in all but one test involving TCE + isooctane. For the individual

Table 7. Regression Analyses of Individual Vapors and Binary Mixtures Demonstrating Additivity of Responses

vapor (test conditions)	sensitivity (Hz/(μg/L))[a,b] PIB	PDPP	DEGA	PCP
BEN (alone)	0.140	0.125	0.061	0.132
BEN (+ ISO)	0.151	0.128	0.062	0.134
BEN (+ XYL)	0.139	0.125	0.059	0.132
BEN (+ CHL)	0.152	0.135	0.070	0.143
BEN (all exposures)	0.147	0.130	0.066	0.138
av	0.146	0.129	0.065	0.136
RSD (%)	4	3	6	3
CHL (alone)	0.078	0.068	0.095	0.071
CHL (+ BEN)	0.080	0.070	0.103	0.075
CHL (+ TCE)	0.082	0.072	0.101	0.075
CHL (all exposures)	0.081	0.071	0.102	0.074
av	0.080	0.070	0.100	0.074
RSD (%)	2	2	3	3
TCE (alone)	0.248	0.161	0.112	0.182
TCE (+ CHL)	0.229	0.147	0.097	0.165
TCE (+ ISO)	0.248	0.161	0.112	0.182
TCE (all exposures)	0.237	0.155	0.103	0.173
av	0.240	0.156	0.106	0.176
RSD (%)	3	4	6	4
ISO (alone)	0.214	0.050	0.009	0.066
ISO (+ BEN)	0.210	0.051	0.010	0.065
ISO (+ HEX)	0.201	0.046	0.007	0.059
ISO (+ TCE)	0.206	0.048	0.008	0.061
ISO (all exposures)	0.214	0.050	0.009	0.066
av	0.209	0.049	0.009	0.063
RSD (%)	3	3	13	5
XYL (alone)	1.53	0.979	0.374	1.23
XYL (+ BEN)	1.69	1.10	0.436	1.39
XYL (all exposures)	1.62	1.04	0.381	1.33
av	1.61	1.04	0.397	1.32
RSD (%)	4	5	7	5
HEX (alone)	0.045	0.012	0.0004	0.015
HEX (+ ISO)	0.045	0.012	0.0005	0.015
HEX (all exposures)	0.044	0.012	0.0004	0.014
av	0.045	0.012	0.0004	0.015
RSD (%)	0.3	0	14	0.6

[a] Δf_c = 185, 199, 275, and 268 kHz for PIB, PDPP, DEGA, and PCP, respectively. [b] Relative standard errors of the sensitivities were <5% in all cases except DEGA with HEX and ISO (~14%).

vapor exposures, there were only three cases of complete misidentification. Hexane and isooctane were difficult to discriminate in several cases. Mixture identification errors were most often associated with cases where one component was present at a relatively low concentration and the mixture was identified as the higher concentration component alone. Similarly, errors in identifying individual vapors were most often found when the vapor was identified as a mixture with a low concentration of the second component. Table 8 also lists the rates of correct identification obtained experimentally for each exposure series. Although the number of test data is small compared to the number of simulations used to generate the predicted rates presented in Table 5, the agreement is very good: in 9 out of 12 cases, the correct identification rates obtained experimentally are within 8% of those predicted for $k_1 = 0.05$, and in most cases the experimental rate exceeds the predicted rate.

Concentration predictions via EDPCR for the correctly classified vapors were generally very accurate. For the 140 concentrations predicted, the median ratio of predicted to actual concentrations is 1.04, indicating a slight tendency toward overestimation. While ratios range from 0.5 to 4.2, the majority of predicted concentrations are within 10% of the experimental values. This is reflected in the geometric standard deviation of the ratios, which is a very low 1.27, and in the 95% confidence interval around the median ratio, which is 0.99−1.08. As with the classification errors, larger errors usually occurred at low vapor concentrations.

The accuracy of concentration predictions is still somewhat lower than expected on the basis of the results presented in Table 6. This can be explained by the fact that the data in Table 6 are based on the combined responses of the mixture components, where relatively large errors in the minor component of the mixture have a small effect on the overall response. In contrast, the ratios listed in Table 8 treat each vapor individually. Considering the similarity in structure of several of the test vapors and the fact that the ratio of concentrations of mixture components was as high as 320 (benzene + xylene), this series of exposures represents a stringent test of performance.

Additivity of Responses to Hydrogen-Bonding Vapor Mixtures. The preceding results demonstrate the additivity of responses for mixtures of the six vapors examined. However, none of these vapors are capable of strong hydrogen-bonding interactions either with the coatings or with other vapors. The report of Rose-Pehrsson et al.[1] suggests that deviations from additivity might be expected in cases where hydrogen-bonding interactions are prevalent. Therefore, a series of experiments was performed to examine whether hydrogen-bonding vapors would also exhibit response additivity with the four-sensor array. Vapors of 1-butanol and 2-methoxyethanol (2-ME) were generated individually and as mixtures in various relative concentrations using dry N_2 as the diluent. Representative results are given in Table 9. As shown, the responses to mixtures of these vapors were within 10% of predictions based on the sums of the component vapor responses. Individual concentration predictions were also accurate (data not shown). Responses for the PIB-coated sensor were consistently overestimated, while those for the other sensors were generally underestimated. Although these trends may indicate some systematic differences in vapor−coating interactions, they could be easily explained by calibration error. The small differences between experimental and expected results effectively confirm the additivity of responses and indicate no significant vapor−vapor interactions within the coating films at these concentrations. A similar experiment was performed by exposing the array to nearly equivalent concentrations of these vapors using air at 50% RH as the diluent. The mixture response was only 4−8% higher than expected on the four sensors, indicating that sorbed water vapor does not affect response additivity.

EDPCR was used to model the responses to the two vapors and their mixtures. Of the responses to five 1-butanol concentrations, six 2-ME concentrations, and 10 binary mixtures, only two incorrect identifications occurred: a mixture containing a low concentration of 1-butanol was identified as 2-ME alone, and an intermediate concentration of 2-ME was identified as a mixture containing a low concentration of 1-butanol. All the remaining cases were correctly identified. These results are consistent with those described above for the other six vapors.

Optimal Coating Selections for Specific Binary Mixtures. The preceding analyses considered the case where any of six vapors might be present in the environment either individually or in binary mixtures. Also of interest were situations where fewer vapors might be present. EDPCR−Monte Carlo analyses of the

Table 8. Comparison of Predicted and Experimental Results of Identification and Quantification of Individual Vapors and Binary Vapor Mixtures[a]

exptl concn (μg/L)		pred:exptl concn ratio	
BEN	ISO	BEN	ISO
940	386	0.99	1.43
4900	426	0.99	1.62
9760	351	1.01	1.59
7410	9860	0.96	1.02
1090	4200	(XYL, 157 μg/L)	0.78
834	10400	0.89	0.93
4620	4240	1.03	0.94
		corr ident rate, 93%	
BEN	XYL	BEN	XYL
1080	59	1.02	0.81
881	59	0.81	1.07
6110	63	0.90	1.43
20000	62	0.92	2.69
905	399	(TCE, 573 μg/L)	1.07
5810	433	0.87	1.25
16900	409	0.98	1.20
825	1440	0.94	1.09
5780	1500	0.95	1.09
16200	1550	1.09	1.02
		corr ident rate, 95%	
CHL	BEN	CHL	BEN
2200	20500	1.10	1.07
6960	632	1.10	0.99
9420	5290	1.11	1.02
1980	5690	1.23	1.00
8580	20400	1.15	1.05
38300	5300	1.09	0.81
33500	626	1.07	(0)
33000	22600	1.18	0.99
		corr ident rate, 94%	
CHL	TCE	CHL	TCE
1120	1280	1.06	0.85
1040	3980	0.59	0.94
1180	8570	(0)	0.96
15800	8510	0.98	0.91
31400	8780	1.06	0.93
33100	4000	1.07	0.85
31200	1330	1.06	0.81
12200	1420	0.99	0.82
13800	3920	0.98	0.87
641	1090	1.42	0.71
734	148	1.36	(0)
		corr ident rate, 91%	
TCE	ISO	TCE	ISO
788	1630	1.21	0.95
804	2400	1.10	1.03
784	2400	(BEN, 1430 μg/L)	(HEX, 14600 μg/L)
725	4770	1.26	0.97
687	4760	1.47	0.95
813	7480	1.26	0.97
822	7400	1.22	1.01
812	10400	1.36	1.05
778	10300	1.17	1.08
1810	1740	1.08	(HEX, 7990 μg/L)
1790	1780	1.14	(HEX, 7600 μg/L)
2940	1730	1.11	(HEX, 7640 μg/L)
3000	1720	1.10	(HEX, 7610 μg/L)
5410	1700	1.07	0.89
5180	1700	1.07	(HEX, 8320 μg/L)
9290	1640	1.07	0.83
9200	1640	1.06	0.86
		corr ident rate, 79%	

exptl concn (μg/L)		pred:exptl concn ratio	
HEX	ISO	HEX	ISO
4100	1240	0.86	1.12
1800	3520	2.43	0.80
1920	7620	1.69	0.91
2100	13200	4.27	0.84
47900	1000	1.13	(0)
21400	5130	0.85	1.09
41100	5680	0.98	0.88
45300	13100	1.10	0.90
17800	13100	0.50	1.14
		corr ident rate, 91%	
BEN		BEN	
496		(TCE, 340 μg/L)	
2060		1.00	
3930		1.00	
11800		0.92	(CHL, 521 μg/L)
11800		0.95	
19800		1.02	(XYL, 34 μg/L)
		corr ident rate, 67%	
CHL		CHL	
291		1.62	
3090		1.02	
6750		1.01	
20700		1.00	
		corr ident rate, 100%	
TCE		TCE	
283		(CHL, 553 μg/L)	(HEX, 1480 μg/L)
1290		1.10	
1320		1.07	
2400		1.03	
3790		0.98	
6410		0.99	
7670		0.97	(BEN, 350 μg/L)
12900		1.00	
		corr ident rate, 81%	
ISO		ISO	
1280		0.99	
2540		0.98	
4640		0.99	
6810		0.98	
14700		0.99	(HEX, 1380 μg/L)
		corr ident rate, 90%	
XYL		XYL	
37		1.68	
167		1.07	
486		1.00	
964		0.97	(TCE, 210 μg/L)
1720		1.00	
		corr ident rate, 90%	
HEX		HEX	
3770		1.02	
11200		0.57	(ISO, 1040 μg/L)
24400		0.67	(ISO, 1860 μg/L)
53600		0.99	
3880			(ISO, 730 μg/L)
		corr ident rate, 60%	

[a] Incorrectly identified vapors are given in parentheses along with their apparent concentrations; a zero in parentheses is used to designate a mixture component that was not detected.

response data for the six vapors were therefore repeated where only a given pair of vapors was allowed to be present either individually or in binary mixtures of various concentrations. Each of the 15 possible binary vapor combinations was considered for

Table 9. Experimental:Predicted Response Ratios for Mixtures of 1-Butanol and 2-ME Assuming Additivity of Responses

concentration (μg/L)		exptl:pred concn ratio			
1-butanol	2-ME	PIB	PDPP	DEGA	PCP
511	532	0.90	1.12	1.14	1.05
484	2450	0.92	1.04	1.05	1.04
1210	943	0.91	1.02	1.03	1.05
2360	515	0.94	1.01	1.06	1.05
2240	2210	0.95	1.04	1.07	1.08

Table 10. Top-Ranked Coating Selections and Identification Rates for Simulated Binary Mixtures[a]

vapor mixture	highest-ranked coating sets				corr ident rate (%)	corr ident rate with PIB, PDPP, DEGA, and PCP (%)
CHL + XYL	9 sets				>99.0	97.8
TCE + ISO	98 sets				>99.0	99.7
ISO + BEN	106 sets				>99.0	100
CHL + TCE	PIB	PDPP	DEGA	OV-275	97.7	95.3
	PIB	OV-25	DEGA	OV-275	97.7	
	PIB	PCP	ABC	OV-275	97.2	
BEN + XYL	PIB	APL	DEGA	OV-275	97.5	90.7
	PIB	PCP	DEGA	OV-275	97.3	
	PIB	APL	PECH	OV-275	97.2	
TCE + XYL	PIB	PCP	DEGA	OV-275	96.0	94.7
	PCP	DEGA	ABC	OV-275	95.5	
	PIB	PCP	DEGA	PECH	95.3	

[a] $n = 100$, $k_1 = 0.025$, $k_2 = 15$ Hz. Where many sets gave rates >99%, they are not listed individually.

Table 11. Top-Ranked Coating Selections and Identification Rates for Simulated Ternary Mixtures as a Function of Relative Slope Error (k_1)

vapor mixture[a]	k_1	highest ranked coating sets				corr ident rate (%)
STY + MEK + DCM	0.025	ABC	PECH	OV-275	APL	95.7
	0.025	DEGA	PCP	ABC	OV-275	95.6
	0.025	PIB	PECH	OV-275	APL	95.4
	0.05	DEGA	PECH	OV-275	APL	90.7
	0.05	PIB	PECH	OV-275	APL	90.4
	0.05	PCP	PECH	OV-275	APL	90.2
MOH + ISO + XYL	0.025	PIB	PDPP	OV-275	APL	100
	0.025	PDPP	PECH	OV-275	APL	99.9
	0.025	PIB	PDPP	DEGA	PCP	99.9
	0.05	PDPP	PECH	OV-275	APL	98.8
	0.05	PIB	DEGA	PECH	OV-275	98.6
	0.05	PIB	PCP	PECH	OV-275	98.6
CHL + DCM + TCE	0.025	PIB	ABC	OV-275	APL	93.6
	0.025	PIB	DEGA	ABC	OV-275	93.0
	0.025	PIB	DEGA	OV-275	APL	92.8
	0.05	PIB	PCP	ABC	OV-275	89.1
	0.05	PIB	ABC	PECH	OV-275	88.3
	0.05	PIB	ABC	OV-275	APL	88.2
STY + XYL + BEN	0.025	PIB	DEGA	ABC	OV-275	92.8
	0.025	PIB	ABC	OV-275	APL	92.2
	0.025	PIB	ABC	PECH	OV-275	92.2
	0.05	DEGA	ABC	OV-275	APL	86.8
	0.05	PIB	ABC	OV-275	APL	86.6
	0.05	PIB	DEGA	ABC	OV-275	85.6

[a] STY, styrene; MEK, 2-butanone; DCM, dichloromethane; MOH, methanol.

all 126 possible combinations of four coatings from a total of nine (PHA was excluded). Table 10 provides the top-ranked coating sets and the expected performance for a representative subset of the mixtures tested. In general, high rates of correct identification are predicted, which is not surprising when four sensors are used to determine only one or two vapors. For the first three mixtures listed in Table 10, many different coating sets are predicted to perform equally well and to provide a very high rate of correct identification. This was also the case for six of the other mixtures tested. For the remaining mixtures, the rates are expected to be lower and the selection of coatings is more critical. The optimal coating set selected on the basis of all possible vapor combinations (i.e., PIB, PDPP, DEGA, and PCP) was also among the top-ranked coating sets for most of the specific mixtures. In all cases this set ranked highly. However, in several cases (e.g., chloroform + TCE, benzene + xylene) it did not rank among the top 10 coating sets. This highlights the trade-offs that must be made in some situations between selectivity and the range of detectable vapors.

Coating Selections for Ternary Mixtures. The use of the EDPCR–Monte Carlo method for selecting coatings for several ternary mixture determinations was also explored. Calibrations for the individual vapors were used to simulate individual vapor, binary mixture, and ternary mixture responses at various randomly chosen concentrations using the procedures described previously. Table 11 presents results for the top three ranked coating sets for set of vapors. Again, the optimal coating set and identification rate vary with the situation. The level of slope error affects the rate and the coating selection, although only marginally in most cases. That is, the optimal coatings chosen assuming $k_1 = 0.025$ are also among the top five or 10 ranked coatings assuming $k_1 = 0.05$, and the rates of correct identification decrease by less than 5%. In addition, certain coating sets rank highly for several mixtures. While the highest identification rates are obtained for mixtures containing vapors with the largest differences in structure (e.g., methanol, isooctane and xylene), high rates are predicted in all cases for the optimal coatings.

For the mixture of styrene, dichloromethane, and 2-butanone, which are solvents commonly encountered together in the reinforced plastics industry, errors with the top-ranked coatings were found to be primarily associated with 2-butanone being misidentified as dichloromethane. The response patterns for these vapors are rather similar. An important point to recognize, however, is that the sensitivity to dichloromethane is quite low. Simulations used dichloromethane concentrations high enough to give measurable signals in at least one of the sensors. Since this vapor may not be easily detected in practice, it follows that identification of styrene and 2-butanone would be increased. In any case, these results indicate that successful identification of vapors that may be present individually or in mixtures comprising up to three components is possible with a four-sensor array.

CONCLUSIONS

The EDPCR–Monte Carlo method presented here provides a general means for accurately predicting and optimizing the performance of polymer-coated SAW sensor arrays. Its primary advantages over previously reported approaches to sensor coating selection are that quantitative measures of performance are obtained and that it accounts for the number and nature of vapors analyzed, sensor noise, and environmental factors. EDPCR is wellsuited for polymer-coated SAW sensor arrays where responses to individual vapors are linear and additive, and it is computationally efficient in the sense that qualitative and quantitative analyses are combined in the procedure. The agreement between experimental and predicted results indicates that the model used in the Monte Carlo simulation analysis (eq 5, with $k_1 = 0.05$) adequately represents sensor responses obtained under experimental conditions.

Sensor responses to individual vapors were shown to be linear, and mixture responses were additive functions of the component vapor responses over the range of vapor concentrations examined, even for vapors capable of strong hydrogen-bonding interactions. Additivity for the latter vapors was not affected by atmospheric humidity up to 50% RH. Thus, the assumption of additivity, which is critical for the simulation of mixture responses with the EDPCR analysis, should be valid for many practical monitoring situations. It should be noted, however, that in a separate study the ambient humidity level was found to affect the responses to several vapors with certain polymer sensor coatings.[15] The lack of any significant aging effects over several months of operation with the 10 coatings used in this study indicates that sensor recalibration needs should be minimal. Intercoating response reproducibility was good in most cases, although uncertainties in the amount of polymer deposited limited the accuracy of such tests for a few of the coatings.

The capability of an array containing only four polymer-coated SAW sensors to provide within- and between-class discrimination of organic solvent vapors in binary and ternary mixtures has not been previously demonstrated. Although a high degree of selectivity was obtained for most vapors, certain vapors were difficult to resolve due to similarities in structure and/or sorption properties, indicating the need for continued research on new coating materials. Sorptive materials that exhibit size or shape selectivity, such as liquid crystals, have been shown to enhance the selectivity of a SAW sensor array in the analysis of isomeric or structurally similar organic vapors.[29] Increasing the number of sensors employed in the array would increase selectivity and might allow for more complex mixture analyses. However, there are diminishing returns accompanying an increase in polymer-coated sensors because there is a finite range of solubility interactions involved in the sorption of vapors into polymers. Other reported approaches to improving selectivity include measuring SAW frequency and attenuation simultaneously[8] and using an array of sensors operating at different frequencies[3] or at different temperatures.[15]

Limits of detection, while sufficiently low for many potential applications, could be improved. Among the factors affecting the LOD is the complexity of the analytical sample. That is, the LOD is determined not only by the ability to detect a measurable signal for a vapor but also by the ability to discriminate one vapor from another. This work showed that certain vapors present at low concentrations in mixtures are misclassified or undetected. While further work is needed to define the LOD in this context, it is clear that improvements in design that would lower LODs would be desirable. The use of thicker coating layers or lower operating temperatures would lead to higher sensitivities and improved LODs. SAW resonators, which have less inherent baseline noise than SAW oscillators, can provide higher signal-to-noise ratios and lower LODs.[30] Grate et al.[4] have shown the feasibility of using an adsorbent preconcentrator with thermal desorption to enhance further the sensitivity in SAW resonator-based instrumentation, albeit at the cost of instrument complexity and analysis time. Of course, the EDPCR–Monte Carlo method presented here would also be applicable to preconcentrated pulses of vapor presented to a polymer-coated SAW resonator array from a preconcentrator.

The analyses considered in this study were restricted to cases where the range of possible vapors present was finite and known. While this often occurs, there are situations where unknown, and previously uncalibrated, interferences may be encountered. Under the current EDPCR classification scheme, such vapors would be misidentified. By modifying the classification rules used in the analysis, for example, by placing constraints on the allowable residual error for classification, this problem could be addressed. The related problem of identifying previously uncalibrated vapors with a SAW sensor array is more challenging, though certainly not unique to this sensor technology.

ACKNOWLEDGMENT

Funding for this research by the Whitaker Foundation Biomedical Engineering Research Program, the National Institute for Occupational Safety and Health of the Centers for Disease Control (Grant K01-OH00077), and the U.S. Department of Energy (Contract 02112408) is gratefully acknowledged. The authors are also indebted to Dr. Tin-Su Pan for developing the initial version of the EDPCR software.

Received for review September 1, 1994. Accepted December 16, 1994.[⊗]

AC940881Q

---

(29) Patrash, S. J.; Zellers, E. T. *Anal. Chim. Acta* **1994**, *288*, 167.

(30) Bowers, W. D.; Chuan, R. L.; Duong, T. M. *Rev. Sci. Instrum.* **1991**, *62*, 1624.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1995.