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Vapor Recognition with Small Arrays of Polymer-Coated Microsensors. A Comprehensive Analysis

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A comprehensive analysis of vapor recognition as a function of the number of sensors in a vapor−sensor array is presented. Responses to 16 organic vapors collected from six polymer-coated surface acoustic wave (SAW) sensors were used in Monte Carlo simulations coupled with pattern recognition analyses to derive statistical estimates of vapor recognition rates as a function of the number of sensors in the array (≤ 6), the polymer sensor coatings employed, and the number and concentration of vapors being analyzed. Results indicate that as few as two sensors can recognize individual vapors from a set of 16 possibilities with <6% average recognition error, as long as the vapor concentrations are >5 × LOD for the array. At lower concentrations, a minimum of three sensors is required, but arrays of 3−6 sensors provide comparable results. Analyses also revealed that individual-vapor recognition hinges more on the similarity of the vapor response patterns than on the total number of possible vapors considered. Vapor mixtures were also analyzed for specific 2-, 3-, 4-, 5-, and 6-vapor subsets where all possible combinations of vapors within each subset were considered simultaneously. Excellent recognition rates were obtainable for mixtures of up to four vapors using the same number of sensors as vapors in the subset. Lower recognition rates were generally observed for mixtures that included structurally homologous vapors. Acceptable recognition rates could not be obtained for the 5- and 6-vapor subsets examined, due, apparently, to the large number of vapor combinations considered (i.e., 31 and 63, respectively). Importantly, increasing the number of sensors in the array did not improve performance significantly for any of the mixture analyses, suggesting that for SAW sensors and other sensors whose responses rely on equilibrium vapor−polymer partitioning, large arrays are not necessary for accurate vapor recognition and quantification.

An increasing number of reports have appeared in recent years on the analysis of gas-phase species with arrays of partially selective sensors.[1−13] For the analysis of volatile organic compounds, surface acoustic wave (SAW) sensors coated with liquid or rubbery solid polymers have a number of useful attributes. Responses of these sensors vary in direct proportion to the extent of vapor sorption, which is typically rapid, reversible, and a linear function of vapor concentration.[1−6,14−18] In addition, responses to multiple vapors are often additive,[1,3,18] which facilitates modeling and pattern recognition analysis. Response patterns derived from arrays of polymer-coated SAW sensors have been used to recognize, discriminate among, and quantify multiple individual vapors as well as the components of simple multivapor mixtures at low and sub ppm concentrations.[1−5] Other sensor-array technologies employing polymeric interfaces whose responses are similarly affected by differential vapor sorption include optical fiber arrays,[8,9] chemiresistors,[19,20] thickness-shear mode resonators,[13] and flexural plate wave (FPW) sensors.[21]

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A critical question that arises in the development of polymer-coated sensor arrays is how many sensors are necessary for accurate vapor recognition and quantification. The answer depends on the number and nature of vapors to be analyzed, the complexity of possible mixtures, the nature and uniqueness of individual vapor−sensor interactions, the shapes of the response isotherms, absolute and relative concentrations of the vapors, signal-to-noise ratios, environmental factors, etc.[1,2] This dependence on sample- and array-specific variables makes it difficult to develop universal recommendations for minimum array sizes.

Experimental studies on sensor-array vapor analysis reported to date have been limited, in general, by the size of the database generated and/or by the statistical analyses performed. Few reports have considered the analysis of mixtures of vapors in which each component must be recognized and quantified and fewer still have considered mixtures of more than two vapors.[1,3,7,8,13,20,22] The recent increase in commercial sensor-array-based instrumentation, including so-called "electronic nose" technology,[23] has led to speculation over the size of the sensor array required for generalized vapor analysis. Some have argued, on the basis of mammalian olfaction models, that a large number of sensors must be used.[19,20] Others have argued, on the basis of vapor−polymer sorption models, that beyond a few well-chosen sensors little additional information will likely be obtained about vapor identities,[24] at least where sensors whose responses rely on reversible sorption processes are employed. Some evidence to support the latter position can be found.[2,3,19,20,22,25] However, there has yet to be a study that addresses the performance limits of sensor arrays and properly accounts for all relevant variables.

This type of problem lends itself well to Monte Carlo modeling. In a series of recent articles, we have explored the use of Monte Carlo simulation in conjunction with either extended disjoint principal components regression (EDPCR) or neural network analyses for optimizing the selection of polymer coatings and for assessing the accuracy of recognition and quantification of individual vapors and simple vapor mixtures with SAW and FPW sensor arrays.[1−4,21,26] By incorporating the random and systematic variations expected in sensor responses in typical operation, modeling response patterns for vapor mixtures, and providing precise statistical estimates of vapor-specific recognition and quantification error rates, this approach to sensor-array evaluation can provide information on performance that is experimentally inaccessible.

Our previous analyses were limited to testing polymer-coated SAW sensor arrays of fixed size (i.e., three or four SAW sensors) and mixtures of up to only three organic vapors. Refinements have been made to the computer-modeling program to improve the accuracy of the Monte Carlo simulation model, increase the number of sensors considered (up to six), and increase the complexity of the mixtures analyzed (up to six vapors simultaneously). This permits, for the first time, a comprehensive assessment of vapor recognition. In this article, response data from six SAW sensors are analyzed with the Monte Carlo/EDPCR approach to illustrate, in a general way, how the number of sensors and the types of polymer coatings employed in an array affect the nature and number of recognition errors predicted to occur as a function of the nature, number, and concentrations of vapors being analyzed.

EXPERIMENTAL SECTION

Coating Selection. As with all chemometric methods, the Monte Carlo/EDPCR analyses require a database of responses. Establishing such a database, in turn, requires selecting an initial set of sensors, polymer coatings, and vapors for testing, from which various subsets and combinations can be examined. The most rational approach to selecting polymeric coatings for a vapor sensor array entails the use of linear solvation-energy relationships (LSER), which draw upon the analogy between sensor responses to vapors and their retention in the stationary phase of a gas chromatographic (GC) column. Use of LSERs in the context of chemical sensors was first formally described by Grate and Abraham[24] and has been studied extensively in the context of SAW sensors by Grate et al.[27−29] and by others.[18,30] In this approach, vapor−polymer interactions are divided into contributions attributable to dispersion, dipolarity, polarizability, and hydrogen-bond acceptance and donation. An array of sensors, each coated with a polymer whose functionalities give rise to interactions associated predominantly with one of these LSER components, should provide an excellent platform for generalized organic vapor analysis where responses rely on equilibrium sorption into the sensor coating layers.

Limitations on the use of LSER based models for guiding the selection of polymers in an array of SAW sensors must be acknowledged. Many vapors interact by only one or two of the five interactions represented in the LSER models and thus may require more subtle differences in coating structure of a particular type to affect discrimination. In addition, regression models used to predict partitioning with LSERs often have large regression constants indicating residual unexplained components of the overall vapor−polymer interaction. Partition coefficients derived from GC, which form the basis of the LSER coefficient determinations, may not accurately reflect the gravimetric component of SAW sensor response.[31,32] Furthermore, SAW sensor responses are also governed by viscoelastic changes in the polymer,[16,33]

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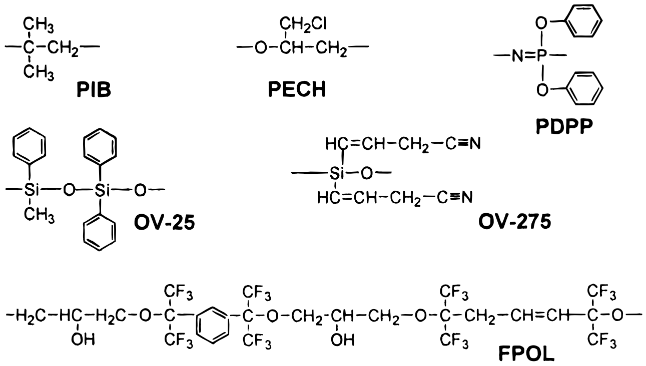

Figure 1. Repeat units of the polymer coatings.

which have eluded modeling thus far. Despite these limitations, accurate estimates of SAW sensor responses are possible using LSER models,[18,29] and they comprise the best approach currently available for selecting polymer coatings in arrays intended for generalized vapor analysis.

Coatings of polyisobutylene (PIB), poly(diphenoxyphosphazine) (PDPP), polyepichlorohydrin (PECH), fluoropolyol (FPOL), triphenylmethyl polysiloxane (OV-25), and bis-cyanoallyl polysiloxane (OV-275) were selected for this study on the basis of LSER considerations, coating stability, and cluster analyses of a previously published data set (Figure 1).[18] PIB is a nonpolar, rubbery, amorphous solid that interacts with vapors almost exclusively through dispersive forces, and as a result, shows progressively greater sensitivity to higher boiling and less polar vapors. PDPP is also a rubbery, amorphous solid. Although the nitrogen−phosphorus backbone is expected to impart strong hydrogen-bond basic character, the phenoxy side chains apparently buffer this property, and it is found that PDPP is relatively more sensitive to moderately polar oxygen-containing vapors such as ethers, ketones, and esters. OV-25 is a slightly polar, highly polarizable, viscous-liquid polymer containing a high percentage of phenyl substituents that interact preferentially with vapors containing aromatic functional groups. OV-275 is a polar, viscous-liquid polymer whose pendant allyl-cyano groups are strongly dipolar and also have significant hydrogen-bond basic character. This coating interacts preferentially with vapors having significant permanent dipoles and/or hydrogen-bond acidic functional groups (e.g., alcohols). PECH is an amorphous rubbery solid whose ether backbone and chloromethyl pendant groups render it moderately dipolar and weakly hydrogen-bond basic. As a result it shows preference for chlorinated hydrocarbons and moderately dipolar oxygenated vapors. FPOL is an oligomeric viscous liquid containing trifluoromethyl and hydroxyl side chains on an aromatic-ether backbone. The combination of these functional groups leads to significant hydrogen-bond acidic character and consequently unusually high sensitivity for alcohols, esters, and organophosphonates.[1,14,16,34]

As noted by Grate et al.,[29] sorption of organic vapors by polymeric coating materials such as these will be governed to a large extent by dispersive interactions, and secondarily by more specific (e.g., dipolar and hydrogen-bonding) interactions. Thus, there is inevitably a nonspecific interaction component shared among any set of such sensor coatings, which correlates inversely with the volatilities of the vapors being measured.[18] This feature is common to most, if not all, vapor sensor arrays employing polymer interfaces. That notwithstanding, the descriptions provided above, coupled with previous results reported by us and others, suggest that the range of structural features and interactions spanned by this set of polymer coatings is reasonably comprehensive and should provide a diverse set of response patterns to the target vapors.

Data Set Description. Response data were collected with two small prototype instruments developed for measuring personal exposures to organic vapors in occupational environments. Details of their design and operation have been published elsewhere.[1] Each instrument contains an array of three polymer-coated SAW resonators operating at 250 MHz, an uncoated reference SAW sensor, a miniature adsorbent preconcentrator, and microprocessor-controlled pneumatic and heating systems for sample capture, sample transport, and thermal desorption.

Each polymer was applied by airbrush in a volatile solvent to give a net frequency shift in the range of 370−470 kHz, corresponding to coating thicknesses of approximately 28−65 nm.[35] Each analysis entailed collection of a 0.24-L sample of air at 25 °C and 50% relative humidity containing a known concentration of an organic vapor or vapor mixture. Vapors are retained on the preconcentrator adsorbent,[36] and then a portion of the coadsorbed water vapor is stripped from the adsorbent with a 30-s backflush of clean, dry air drawn through a cartridge of charcoal and $CaSO_4$ (Drierite). The preconcentrator is then heated to 180 °C to desorb the organic vapor(s) in a dry-air matrix for analysis by the array. The heating rate is about 4 °C/s, and the vapors pass over the sensor array within 15−30 s of the start of heating. An entire sampling and analytical cycle requires 5.5−6.5 min, depending on the length of the heating cycle used.

Net responses are determined from the shift in frequency (Hz) between the pre-desorption reference point and the point at which the response maximum is observed for each vapor. Responses were measured over a 20- to 80-fold range of concentrations for each of 16 vapors using test atmospheres, generated in air at 50% relative humidity (RH) in a series of Tedlar bags, whose concentrations were verified by GC. Binary mixture responses were collected for a subset of vapors over a wide range of relative concentrations. Quality-control samples of toluene at 100 ppm collected periodically over the course of the six-month study indicated that sensor responses were extremely stable. Net response maxima were determined after subtraction of blanks containing only background humidity, and sensitivities were determined by linear regression with forced zero.

EDPCR/Monte Carlo Model. The modeling approach used here is similar to the approaches we have reported elsewhere,[1−4,21] except that the Monte Carlo error model has been refined to describe the specific sources of response variation associated with the instruments used in this study, and the program has been revised to permit consideration of up to six sensors and of vapor mixtures of up to six components. A limited validation study of the revised error model showed good agreement between experimental and modeled vapor-recognition rates.[1]

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Table 1. Calibration Data for the 16 Test Vapors and Six Polymer-Coated SAW Sensors

vapor	(abbr)	calibration range (ppm)	sensitivity, Hz/ppm (LOD, ppm)					
			PIB	PECH	FPOL	PDPP	OV-25	OV-275
dichloromethane	(DCL)	20−400	2.68 (6.54)	4.73 (8.97)	0.89 (46.8)	2.85 (3.97)	4.70 (6.18)	3.81 (9.99)
trichloroethylene	(TCE)	10−250	31.2 (0.52)	18.1 (2.21)	4.88 (5.98)	13.0 (0.84)	22.0 (2.71)	9.11 (5.42)
perchloroethylene	(PCE)	2.5−125	95.2 (0.24)	32.4 (1.41)	9.37 (3.89)	27.2 (0.46)	43.3 (1.22)	14.7 (4.12)
acetone	(ACE)	50−2500	1.19 (11.7)	4.64 (8.27)	9.80 (3.52)	1.52 (7.44)	3.01 (14.3)	3.06 (11.3)
2-butanone	(MEK)	20−1000	4.70 (2.95)	14.1 (2.76)	25.6 (1.03)	5.07 (1.97)	9.18 (4.89)	7.34 (5.89)
2-methoxyethanol	(2ME)	2−50	14.3 (1.18)	60.1 (0.70)	206 (0.15)	20.1 (0.61)	29.5 (1.46)	57.1 (0.91)
isopropanol	(IPA)	40−2000	2.75 (5.04)	7.09 (5.42)	25.7 (1.35)	2.93 (3.86)	3.73 (11.5)	7.67 (4.53)
1,4-dioxane	(DOX)	2.5−125	15.0 (1.32)	41.4 (1.04)	66.2 (0.52)	15.0 (0.89)	23.0 (1.88)	19.7 (2.88)
tetrahydrofuran	(THF)	20−1000	6.86 (2.12)	10.1 (3.97)	26.3 (1.01)	4.79 (2.18)	8.93 (5.90)	4.41 (10.7)
n-hexane	(HEX)	5−400	10.3 (1.21)	1.63 (22.7)	0.87 (30.7)	1.63 (6.23)	2.69 (18.6)	1.31 (30.2)
isooctane	(IOC)	30−1500	23.5 (0.79)	2.72 (15.9)	1.48 (21.4)	2.97 (4.16)	6.35 (7.53)	2.80 (19.5)
isoamyl acetate	(IAA)	10−500	104 (0.27)	114 (0.47)	241 (0.17)	48.8 (0.45)	97.4 (0.50)	33.2 (2.03)
n-butyl acetate	(BAC)	15−750	58.5 (0.48)	78.6 (0.68)	155 (0.26)	34.3 (0.63)	69.3 (0.71)	24.1 (2.79)
benzene	(BEN)	4−120	13.5 (1.26)	12.8 (3.27)	3.95 (7.72)	6.79 (1.80)	15.0 (2.87)	5.57 (9.29)
toluene	(TOL)	10−250	40.0 (0.52)	31.4 (1.37)	9.25 (3.77)	17.7 (0.75)	34.7 (1.90)	12.4 (4.69)
m-xylene	(XYL)	10−200	89.2 (0.32)	54.4 (0.99)	16.2 (2.49)	31.0 (0.70)	59.9 (0.82)	20.9 (3.21)

Using Monte Carlo methods, random and systematic variations are applied to the calibrated responses to all of the vapors assuming a Gaussian error distribution. The population of error-enhanced synthetic responses is sampled iteratively, and each sample is treated as an unknown that is then assigned an identity and concentration by comparison with the EDPCR models established for arrays of 2−6 sensors from the calibration data in Table 1.[37] The number and nature of recognition errors observed from a large sample set (i.e., hundreds of simulations) are logged and evaluated with respect to the average rate of recognition, vapor-specific rates of recognition, and the identities of any incorrect assignments.

The simulated response data were generated according to the following equation:

$$r_{ij}' = r_{ij}(1 + k_1\alpha + k_2\beta_j) + k_{3j}\gamma_j + k_{4j}\delta \tag{1}$$

Here, r'_{ij} is the net synthetic response to vapor i from coated sensor j; r_{ij} is the starting-point response value generated by randomly selecting a point along the regression line derived from calibration; k_1 is the relative standard deviation (RSD) that accounts for variability in sample delivery to the sensor array from the preconcentrator; k_2 is the RSD of the sensitivity estimate obtained from repeated calibrations; k_{3j} is the root-mean-square (RMS) error in the baseline (in Hz) for each sensor due to random noise; k_{4j} is the RMS error attributable to the combination of inherent baseline drift and fluctuations in the response to residual water vapor; and α, β, γ, and δ are independent normally distributed variables with zero mean and unit standard deviation.

Detailed explanations of the terms in eq 1, the k_i values, and the implementation of the EDPCR/Monte Carlo model are given in the Supporting Information accompanying this article. The following k_i values were used: $k_1 = 0.05$; $k_2 = 0.03$; $k_3 = 2.9$ Hz (PIB), 4.5 Hz (PECH), 2.7 Hz (FPOL), 3.9 Hz (PDPP), 4.5 Hz (OV-25), 3.4 Hz (OV-275); and $k_4 = 5.7$ Hz (PIB), 14 Hz (PECH), 12 Hz (FPOL), 1.9 Hz (PDPP), 15 Hz (OV-25), 17 Hz (OV-275).

In our previous study examining the effect of concentration on recognition rates with an array of polymer-coated SAW sensors, it was found that above ∼5 LOD recognition rates were very high and showed little or no dependence on concentration.[2] As the concentration decreased below 5 LOD, a steady decrease in recognition was observed in most cases. In fact, the concentration at which errors in recognition became unacceptably large, which we refer to as the "limit of recognition" (LOR), was often above the concentration corresponding to the LOD. In light of these results, simulations performed here were divided into two different concentration ranges, 1−5 LOD and 5−25 LOD, where the LOD for the vapor under consideration is defined as that of the *highest* individual LOD among the six sensors. This ensures that there are measurable signals from all sensors for every simulation. Rates of (correct) recognition were then calculated and compiled separately for simulations within each of the two concentration intervals.

EDPCR modeling and Monte Carlo simulations were performed on a desktop computer using routines written in Visual Basic (version 7.0, Microsoft Corp.) and linked to spreadsheets in Excel (version 7.0, Microsoft Corp.). Additional statistical analyses were performed using SPSS (version 7.0, SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Response Data. Table 1 shows the sensitivities and limits of detection (LOD) for each vapor−sensor combination. Values were adjusted to reconcile the slight sampling flow-rate differences between the two instruments. Response curves were linear over the calibrated concentration ranges, and the linear regression correlation coefficients (r^2) were ≥0.98 for 93 of the 96 vapor/sensor combinations (for the three exceptions $r^2 \geq 0.96$). The LOD was defined as the vapor concentration corresponding to 3σ/(sensitivity), where σ is the standard deviation of the baseline response (Hz) at the time corresponding to the maximum sensor response, as determined by averaging the baseline responses from at least three blank (i.e., 50% RH air only) analyses.

With the binary mixtures, partial resolution of response maxima was observed in some cases as a result of the slow heating rate of the preconcentrator during thermal desorption. However, all peaks overlapped to some extent, and responses were equivalent to the sum of the component-vapor responses at each point along the response profiles, as observed previously.[1,3,18,21,26] The

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Table 2. Six-Sensor Pairwise Correlation Matrix

	FPOL	OV-25	OV-275	PDPP	PECH	PIB
FPOL	1					
OV-25	−0.821	1				
OV-275	0.242	−0.181	1			
PDPP	−0.817	0.918	0.005	1		
PECH	0.084	0.404	0.345	0.401	1	
PIB	−0.798	0.381	−0.528	0.349	−0.633	1

assumption of additivity was therefore applied to all mixture responses in the Monte Carlo simulations presented below.

Correlation and Principal Components Analysis. It is useful to start by assessing the pairwise correlations among the relative response patterns obtained for each vapor from the entire array of six sensors. Those vapor pairs with the largest positive correlation coefficients, r, are expected to be the most difficult to discriminate. The correlation matrix is presented in the Supporting Information accompanying this article. The largest r values are associated with the following vapor pairs: xylene + TCE, acetone + MEK, 1,4-dioxane + MEK, IPA + 2-ME, isooctane + *n*-hexane, and *n*-butyl acetate + isoamyl acetate. These exceptions notwithstanding, the r values are otherwise generally small or negative, indicating a fairly high degree of pairwise selectivity with this array of SAW sensors. Table 2 is a correlation matrix for the sensors also derived from an analysis of the relative response patterns. Only one pair of sensors has an r value >0.9 (i.e., 0.918 for the PDPP and OV-25 pair), indicating little redundancy in the contributions of each sensor to the response patterns.

The results of principal components analysis (PCA) for this data set, presented in Table 3, indicate that 98% of the variance in the responses to the vapors can be accounted for with only three principal components. According to Carey et al.,[38] although the first principal component explains most of the variance in the data, the most efficient approach to array construction entails selecting the one sensor providing the greatest contribution to each successive (orthogonal) principal component. This implies that the greatest information about vapor identities will be obtained from three well-chosen sensors and that adding a fourth sensor will yield only marginal improvement.[38] For the first principal component, sensors coated with FPOL, PDPP, and OV-25 contribute similarly, with a slight edge for the FPOL. The second and third principal components are influenced most by the sensors coated with PECH and OV-275, respectively. This suggests that the three-sensor array providing the greatest degree of discrimination would consist of sensors coated with FPOL, PECH, and OV-275. If a fourth coating were to be added, this analysis indicates that the PDPP-coated sensor would be the best selection.

The dendrogram in Figure 2 presents the results of a groupwise hierarchical cluster analysis of the data wherein the vectors in six-dimensional space for all of the vapors (derived from the relative sensitivities) are considered collectively, and the Euclidean distances between the vectors are compared. As shown, the vapors are divided according to polarity, with the top subset comprising the relatively polar vapors and the bottom subset comprising the relatively nonpolar vapors. Within each subset the pairs of vapors linked most closely to the origin (i.e., leftmost point) have the most closely situated vectors. The linkage distances correlate well with the r values from correlation analysis.

Recognizing Individual Vapors ($m = 16$). The first case considered in the EDPCR/Monte Carlo modeling was that in which only a single vapor is analyzed at a time, and the synthetic (i.e., error-enhanced) response patterns for that vapor are compared with the library of single-vapor response patterns created from the calibration curves for the entire vapor set ($m = 16$) or a subset ($m = 8$, see below). In a practical sense, this would apply to a situation in which the array might be used for several possible applications but only a single vapor was encountered at a time. Table 4 shows the rates of recognition for arrays comprising from 2 to 6 sensors for $m = 16$. Each array is ranked by the average recognition rate for the 16 vapors. The range of vapor-specific recognition rates is also included. Note that out of a total of six sensors, there are six possible 5-sensor arrays, 15 4-sensor arrays, 20 3-sensor arrays, and 15 2-sensor arrays. For brevity, Table 4 presents only the three highest ranking arrays for $n < 6$.

Evaluating these and subsequent results requires establishing tolerance limits on the rates of recognition error. Consistent with our previous analyses using Monte Carlo simulations,[2] we have arbitrarily applied a threshold of ≥95% average recognition (i.e., ≤5% recognition error) to define "good" performance. In addition, a threshold of ≥90% average recognition (i.e., ≤10% recognition error) has been adopted here to define "adequate" performance. Lower average recognition rates are considered to indicate unacceptable overall performance, despite the possibility for high recognition rates for specific vapors within the set.

For the higher concentration range (i.e., 5−25 LOD), Table 4 shows that as few as two sensors can provide a fairly high rate of recognition (i.e., >94%), but only one 2-sensor array, the array employing coatings of PIB and PECH, meets this performance standard. The next best 2-sensor array provides an average of only 88% recognition. In contrast, any of the top 3-, 4-, or 5-sensor arrays, as well as the 6-sensor array, provide excellent recognition rates (i.e., vapor-specific rates are ≥97% in all cases).

The recognition rates for all of the arrays decline at lower vapor concentrations, as expected, and the difference in performance among the possible arrays of a given size is greater. This is most striking in the performance of the 2- and 3-sensor arrays. Apparently, the LOR for many of the vapors suffering significant confusion with the 2- and 3-sensor arrays is within the concentration range of 1−5 LOD. As observed at higher concentrations, the best 4- and 5-sensor arrays perform similar to the 6-sensor array and still provide very high average and vapor-specific recognition rates at lower concentrations.

Recognition matrices for the 6-sensor array and for the highest-ranked 2-sensor array (presented in the Supporting Information) illustrate the nature of the errors in recognition as a function of array size in the more difficult 1−5 LOD concentration range. For the 6-sensor array, confusion of both acetone and 1,4-dioxane with MEK (and vice versa) is prevalent, as well as confusion of isooctane with *n*-hexane. The lowest vapor-specific recognition rate is 93% (for MEK). Most other vapors are recognized with less than ∼3% error, though a consistent low-level error is seen in

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(38) Carey, W. P.; Kowalski, B. R. *Anal. Chem.* **1986**, *58*, 149−153.

Table 3. Percentage of the Total Variance Attributable to Each Principal Component (PC) and the Contribution of Each Sensor to Each PC

principal component	variance (%)		contribution to each PC (%)					
	each	cumulative	PIB	PECH	FPOL	PDPP	OV-25	OV-275
1	52.9	52.9	17.1	0.0	**29.9**	23.7	25.3	4.0
2	33.6	86.5	20.7	**43.8**	0.2	10.0	7.2	18.0
3	11.5	98.0	4.3	13.4	5.6	0.8	2.7	**73.3**
4	1.1	99.2	6.9	15.0	10.1	**60.5**	5.7	1.9
5	0.8	100.0	10.6	24.8	4.7	4.1	55.1	0.8

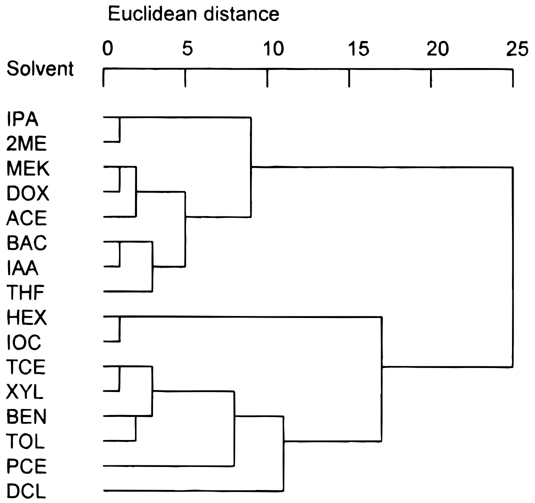

Figure 2. Dendrogram depicting average Euclidean linkage distances derived from hierarchical cluster analysis for the 6-sensor array.

attempting to discriminate between homologous vapor pairs. For the top-ranked 2-sensor array in this low concentration range, errors are distributed among a larger number of vapors. Problems recognizing acetone, MEK, and 1,4-dioxane are most apparent, and significant confusion of TCE with *m*-xylene also emerges. The lowest vapor-specific recognition rate is 57% (for acetone); however, seven of the vapors are recognized at rates >90%. Note that most of these recognition errors become “acceptably small” at higher concentrations (see Table 4).

The recognition problems encountered are consistent with the *r* values derived from correlation analysis and with the results shown in Figure 2, but the level of recognition error observed, at least for the 6-sensor array, is less than might have been expected on the basis of the high *r* values, particularly for the isoamyl acetate/butyl acetate pair. Other vapor pairs giving somewhat high *r* values in the pairwise analysis ($0.90 \le r \le 0.99$) do not present significant recognition/discrimination problems.

According to Table 4, a 3-sensor array is capable of recognizing these 16 vapors with relatively low error. This is consistent with the PCA results in Table 3, but the highest ranking sensor arrays listed in Table 4 differ from what would have been selected from the contributions shown in Table 3. In particular, PIB is included in all of the top-ranked 3-sensor arrays from the Monte Carlo/EDPCR analyses, whereas the PCA results suggest that other sensors should be more important. We believe this is due to the low noise level and relatively high sensitivity exhibited by PIB for many of the vapors (Table 1)—a factor that is accounted for in the Monte Carlo simulations but not accounted for in PCA. We note, however, that while PIB does not contribute predominantly to any single principal component, the sum of its fractional contributions to the variance accounted for by the first two principal components exceeds that of the other sensors. The sensors providing the largest cumulative fractional contributions to the first three principal components are PIB, FPOL, and OV-275, followed closely by PECH. The order of these contributions is consistent with the 2- and 3-sensor array rankings presented in Table 4.

Recognizing Individual Vapors ($m = 8$). Reducing the number of possible vapors considered does not necessarily improve performance. Two 8-vapor subsets were created by dividing the vapors at the midpoint of the dendrogram in Figure 2. The first subset, abbreviated n8, comprises relatively nonpolar vapors and the second, abbreviated p8, comprises relatively polar vapors. Simulations were then run for each group separately. As shown in Table 5, the performance is similar between the two vapor groups. For arrays of ≥3 sensors, average recognition rates are above 98.5% within the high concentration range, similar to the results obtained with all 16 vapors. Within the lower concentration range, results are also similar to those obtained with the 16-vapor set, but there is a slightly greater dependence of performance on the number of sensors in the array. For the 2-sensor arrays, however, the performance of the best arrays improves markedly compared with that obtained with the 16-vapor set, particularly in the low concentration range where the highest average recognition rates improve to >91% (from 83%).

It is important to note the difference in rankings and recognition rates between the two 8-vapor sets with the smaller arrays. All of the top-ranked 2-sensor arrays contain PIB, but PECH is a more important coating for recognition of the nonpolar vapors, while FPOL and OV-275 are more important for the polar vapors. This makes sense in light of the structures of these coatings (Figure 1), but the differences in recognition rates imply that two different 2-sensor arrays (or one 3-sensor array) would be needed to analyze these 8-vapor subsets. Differences in the members of the top-ranked coating sets for the 3-sensor arrays are also apparent, though less significant than for the 2-sensor arrays.

The performance of the two highest ranked 2-sensor arrays at low concentrations for these two 8-vapor subsets is considered adequate by our criteria, and in both cases at least six of the eight vapor-specific recognition rates are >92%. But confusion of xylene with TCE occurs at a rate of 32% in the n8 subset, and confusion of acetone with MEK or 2-propanol occurs at a rate of 21% in the p8 subset. For the 3-sensor arrays (and larger arrays) all of the vapor-specific recognition rates exceed 91% at low concentrations and 99% at higher concentrations.

To further characterize the performance limits of the arrays,

Table 4. Top-Ranked Sensor Arrays and Corresponding Average and Vapor-Specific Recognition Rates for Individual-Vapor Analysis of 16 Vapors

no. of sensors	1−5 LOD sensor array	1−5 LOD recognition (%) av	1−5 LOD recognition (%) range[a]	5−25 LOD sensor array	5−25 LOD recognition (%) av	5−25 LOD recognition (%) range[a]
6	all	97.8	93.0−99.6	all	99.6	98.4−100.0
5	PIB, PECH, FPOL, PDPP, OV-25	97.8	90.8−100.0	PIB, PECH, PDPP, OV-25, OV-275	99.7	99.0−100.0
	PIB, PECH, FPOL, PDPP, OV-275	97.5	91.6−100.0	PIB, PECH, FPOL, PDPP, OV-25	99.6	99.0−100.0
	PIB, PECH, PDPP, OV-25, OV-275	97.2	87.6−99.8	PIB, FPOL, PDPP, OV-25, OV-275	99.6	99.0−100.0
4	PIB, PECH, FPOL, PDPP	96.8	87.4−99.8	PIB, PECH, OV-25, OV-275	99.7	98.8−100.0
	PIB, PECH, FPOL, OV-25	96.1	87.8−100.0	PIB, PDPP, FPOL, OV-25	99.6	98.4−100.0
	PIB, PECH, FPOL, OV-275	95.7	89.2−99.8	PIB, FPOL, OV-25, OV-275	99.4	97.8−100.0
3	PIB, FPOL, PDPP	95.8	87.8−100.0	PIB, FPOL, PDPP	99.2	97.0−100.0
	PIB, FPOL, OV-25	94.5	82.8−100.0	PIB, PECH, OV-275	99.2	93.8−100.0
	PIB, PECH, OV-275	93.9	74.4−100.0	PIB, FPOL, OV-25	98.2	88.2−100.0
2	PIB, PECH	82.0	56.6−99.6	PIB, PECH	94.6	87.6−99.6
	PIB, FPOL	80.2	54.4−97.2	PIB, FPOL	88.1	72.4−100.0
	PIB, OV-25	72.3	48.4−99.8	PIB, OV-25	80.2	68.4−99.4

[a] Range of vapor-specific recognition rates for 16 vapors.

two additional 8-vapor subsets were created. For the first additional subset, the preceding results were used to assemble the eight vapors expected to give the highest rate of recognition error. Since this subset was expected to represent the most difficult recognition/discrimination problem, it has been abbreviated d8. The second additional subset was created to provide the easiest recognition/discrimination problem (i.e., least expected recognition error), on a similar basis, and is abbreviated e8.

Results are summarized in Table 5. Performance for the arrays with ≥3 sensors is similar to that observed with the previous vapor sets, though the 3-sensor arrays performed significantly better for the e8 vapor subset than for the n8 or p8 subsets in the low concentration range. For the 2-sensor arrays, there is a dramatic difference in performance between e8 and d8. For e8, two of the 2-sensor arrays provide >90% average recognition even at the low concentration range. For d8, overall performance for the 2-sensor arrays is similar to that for the 16-vapor set, with the maximum average recognition rate being ~84%. Differences in the rankings of the 2-sensor arrays are also apparent between these two 8-vapor subsets. Vapor-specific recognition for the e8 vapor subset was >90% for the highest ranked arrays of ≥3 sensors. With the notable exception of TCE (83%), vapor-specific recognition even for the d8 subset was >91%.

Recognizing Vapor-Mixture Components. The remaining series of simulations considered the more difficult problems of recognizing/discriminating among vapors when it is possible for mixtures to be present. Analyses were performed for specific subsets of 2−6 vapors. For each subset, the analysis determined whether each array could recognize and discriminate among the individual vapor components under all possible levels of mixture complexity. For example, for the analysis of three specific vapors, simulations were run on each individual vapor to determine if that vapor could be differentiated from the other two individual vapors, from all three possible binary mixtures that could be created from the three vapors, and from the ternary mixture. Then simulations were run for each possible binary mixture to determine if that mixture could be recognized and differentiated from the three individual vapors, the two other binary mixtures, and the ternary mixture. Finally, the ternary mixture was tested against the three individual vapors and three binary mixtures. For each of the 3500 iterations (i.e., 500 × 7) involved in a given 3-vapor simulation trial, the concentrations of the vapors were selected randomly from within the specified range for each vapor. This set of analyses was repeated for each subset of three vapors selected. Similar analyses were performed for selected subsets of two, four, five, and six vapors. Table 6 shows the number of mixture components tested for each case considered and illustrates how complex the problem becomes with more than a few vapors.

This type of modeling represents the case in which one has knowledge of all vapors that *might* possibly be present, but not which vapors are *actually* present or in what combination. This would be applicable to, say, an industrial chemical facility where a materials inventory would have been performed to determine all processing chemicals as part of a routine qualitative hazard assessment, but air monitoring was needed to determine which, if any, chemicals were being released into the working environment and at what concentrations.

The problem of analyzing binary mixtures was considered first. A total of nine binary subsets was considered—three from each of three categories of difficulty (easy, moderate, and difficult) as determined from the preceding analyses. Results are summarized in Table 7. For convenience, only results for the highest ranked array of each size are presented. Excellent results were obtained for sensor arrays of all sizes for the 2-vapor subsets considered to present easy and moderate recognition/discrimination problems. For the more difficult subsets, the performance is marginally adequate by our criterion.

Contrary to intuition, *increasing the number of sensors in the array does not improve performance significantly*. That is, regardless of whether the performance with a 2-sensor array is good or poor, adding more sensors provides little or no increase in the recognition rate. This point is illustrated graphically in Figure 3 for two binary mixtures where the average recognition rate (5−25 LOD range) is plotted versus the number of sensors in the array. Each point in the figure represents the performance for a specific array of a given size. The dichloromethane/trichloro-

Table 5. Average Recognition Rates for Four Different 8-Vapor Subsets as a Function of Array Size and Polymer Coatings

	1−5 LOD		5−25 LOD	
no. of sensors	sensor array	recog (%)[a]	sensor array	recog (%)[a]
n8 Vapor Subset (includes BEN, TOL, XYL, DCL, TCE, PCE, HEX, IOC)				
≥4	see Table 4[b]	≥96.5	see Table 4	≥99.6
3	PIB, PECH, PDPP	96.8	PIB, PECH, OV-275	99.8
	PIB, PECH, OV-275	96.4	PIB, PECH, PDPP	99.6
	PIB, PECH, OV-25	95.8	PIB, FPOL, PDPP	99.3
	PIB, PDPP, OV-25	94.9	PIB, FPOL, OV-275	98.8
	PIB, FPOL, OV-25	93.4	PIB, PDPP, OV-25	98.6
2	PIB, PECH	91.1	PIB, PECH	93.6
	PIB, OV-25	84.9	PIB, FPOL	92.8
	PIB, PDPP	79.9	PIB, PDPP	91.8
	PIB, OV-275	73.3	PIB, OV-275	87.4
	PIB, FPOL	65.9	PIB, OV-25	87.3
p8 Vapor Subset (includes ACE, MEK, IPA, THF, IAA, BAC, 2ME, DOX)				
≥4	see Table 4	≥95.6	see Table 4	≥99.0
3	PIB, OV-25, OV-275	96.9	PIB, OV-25, OV-275	99.8
	PIB, PECH, OV-275	96.2	PIB, FPOL, PDPP	99.1
	PIB, FPOL, OV-25	95.8	PIB, FPOL, OV-25	99.0
	PIB, PECH, FPOL	95.3	PIB, PDPP, OV-275	99.0
	PIB, PDPP, OV-275	92.6	PIB, PECH, FPOL	98.8
2	PIB, FPOL	91.4	PIB, OV-275	96.4
	PIB, OV-275	89.2	PIB, FPOL	95.7
	PECH, FPOL	79.1	PIB, OV-25	86.5
	PIB, PECH	77.4	PIB, PECH	85.9
	PIB, OV-25	74.7	PDPP, OV-275	84.2
e8 Vapor Subset (includes TCE, TOL, HEX, DCL, IOC, IPA, MEK, IAA)				
≥4	see Table 4	≥97.2	see Table 4	≥99.8
3	PIB, PECH, FPOL	98.1	PIB, PECH, OV-275	99.8
	PIB, PECH, OV-275	97.8	PIB, PECH, OV-25	99.8
	PECH, OV-25, OV-275	97.8	PIB, PECH, FPOL	99.8
	PIB, PECH, OV-25	97.7	PECH, FPOL, OV-275	99.8
	PIB, FPOL, OV-25	97.5	PECH, PDPP, OV-275	99.7
2	PIB, PECH	94.9	PIB, FPOL	99.7
	PIB, FPOL	90.2	PIB, PECH	98.5
	PECH, OV-25	86.9	PECH, OV-25	93.6
	PIB, OV-25	84.1	FPOL, OV-25	90.0
	FPOL, OV-25	82.5	PIB, OV-25	88.4
d8 Vapor Subset (includes BEN, TOL, XYL, TCE, IPA, 2ME, MEK, DOX)				
≥4	see Table 4	≥93.0	see Table 4	≥99.2
3	PIB, FPOL, OV-25	93.8	PIB, FPOL, OV-275	99.4
	PIB, OV-25, OV-275	93.4	PIB, FPOL, PDPP	99.2
	PIB, PECH, OV-275	92.9	PIB, PECH, OV-275	98.9
	PIB, PECH, FPOL	90.2	PIB, OV-25, OV-275	98.5
	PIB, OV-275, FPOL	89.9	PIB, PDPP, OV-25	98.0
2	PIB, FPOL	83.7	PIB, FPOL	97.3
	PIB, OV-275	82.7	PIB, OV-275	92.4
	PIB, PECH	80.5	PIB, OV-25	86.5
	PIB, OV-25	78.3	PIB, PECH	86.4
	FPOL, PDPP	66.9	FPOL, PDPP	81.4

[a] Average of the vapor-specific recognition rates. [b] Similar to the 16-vapor case.

Table 6. Combinations of Components in the Vapor Mixtures Tested

size of vapor subset	number of components tested[a]							total simulations
	1°	2°	3°	4°	5°	6°	total	
two	2	1					3	1500
three	3	3	1				7	3500
four	4	6	4	1			15	7500
five	5	10	10	5	1		31	15500
six	6	15	20	15	6	1	63	31500

[a] 1°, individual; 2°, binary; 3°, ternary; etc.

ethylene vapor subset represents a relatively easy discrimination problem, while the benzene/toluene subset represents a more difficult problem. In both cases, however, the performance of the top-ranked 2-sensor array is about as good as that of the 6-sensor array.

The recognition matrices (not shown) for the more difficult vapor pairs in Table 7 indicate similar confusion among the vapors with all of the arrays. Importantly, the degree of confusion among these difficult 2-vapor subsets when their mixtures are considered is generally higher than that observed when they are tested individually among all 14 other vapors (see confusion matrices in the Supporting Information). This is a critical point that is rarely addressed in assessing sensor-array performance.

Analyses were then performed of several subsets of three vapors spanning the range of expected difficulty. As for the 2-vapor subsets, the components of the easy and moderate 3-vapor subsets are recognized at a high rate with three or more sensors (Table 7) (note: it is not possible to analyze a 3-vapor subset with less than three sensors because the problem is statistically underdetermined when there is only one output parameter being measured from the sensors). For the difficult 3-vapor subsets, the performance with an array of three sensors is quite poor, but increasing the number of sensors does not increase the average recognition rate or alter the nature of the recognition errors. Once again, the degree of confusion among the components of these 3-vapor mixtures is generally higher than that observed when considering them only as individual vapors among a set of 13 other individual vapors.

Not shown in Table 7 are the sensors comprising the top-ranked arrays. As it turns out, the top-ranked 2- and 3-sensor arrays differ among the different cases tested. The PIB/FPOL array ranks highly in four of the nine 2-vapor subsets shown in Table 7, but for the remaining 2-vapor subsets either PIB or FPOL is paired with another polymer. PDPP is included in the fewest 2-sensor arrays. PIB and FPOL are also included among the top-ranked 3-sensor arrays in eight of the nine 2-vapor subsets in Table 7. Notably, for the TCE + xylene subset, PIB is not among the top-ranked sensors. The third sensor varies among all of the remaining four possible sensors. For the 3-vapor subsets, all of the top-ranked 3-sensor arrays include PIB, but the remaining two sensors vary with the specific 3-vapor subset being considered. Thus, as noted above for the individual-vapor analyses of the 8-vapor subsets (Table 5), different arrays (or one slightly larger array) might be needed to optimize performance for different applications.

Analyses of several 4-vapor subsets provided results similar to those for the preceding mixtures, except that significant errors are observed even for the so-called moderate vapor sets (Table 7). Results are quite good for the easy subsets, however, and once again, increasing the number of sensors provides no performance improvement regardless of the recognition rate. In all cases PIB, FPOL, and OV-275 are included among the two or three highest ranking 4-sensor arrays, with the fourth sensor varying among the remaining three possibilities.

Subsets of five and six vapors were also examined. In these cases, even the relatively easy subsets could not be analyzed

Table 7. Recognition Rates for Specific Subsets of 2−6 Vapors as a Function of Concentration, Sensor Array Size, and Anticipated Difficulty in Discrimination

no. of vapors	class	vapor subset	no. of sensors	av recog rate (%) for highest ranked array 1−5 LOD	av recog rate (%) for highest ranked array 5−25 LOD
2	easy	PCE + DOX	≥2	≥99.3	≥99.4
		ACE + HEX	≥2	≥99.1	≥99.6
		TOL + MEK	≥2	≥98.9	≥99.5
	moderate	2ME + THF	≥2	≥98.9	≥99.5
		IPA + MEK	≥2	≥98.9	≥99.5
		DCL + TCE	≥2	≥98.9	≥99.5
	difficult	TCE + XYL	6	88.3	91.0
			5	91.5	92.2
			4	87.3	91.3
			3	89.9	92.9
			2	85.3	92.9
		BAC + IAA	6	87.3	88.7
			5	90.0	90.6
			4	89.4	89.5
			3	89.0	88.8
			2	84.3	86.5
		TOL + BEN	6	85.4	89.3
			5	88.0	90.2
			4	89.6	89.3
			3	87.6	90.0
			2	87.1	87.8
3	easy	IOC + DCL + ACE	≥3	≥99.5	≥99.6
		HEX + TCE + 2ME	≥3	≥98.9	≥98.9
	moderate	TOL + DCL + HEX	≥3	≥96.8	≥97.6
		IPA + DOX + IAA	≥3	≥92.2	≥92.1
	difficult	MEK + DOX + ACE	6	65.0	69.1
			5	63.6	73.1
			4	68.0	74.7
			3	65.4	73.3
		BEN + TOL + XYL	6	63.8	66.9
			5	65.5	66.2
			4	64.9	67.8
			3	63.6	65.5
4	easy	IPA + BAC + IOC + DCL	≥4	≥97.9	≥97.9
		2ME + IAA + HEX + TOL	≥4	≥96.4	≥96.7
	moderate	HEX + BEN + DCL + PCE	6	84.8	87.2
			5	84.2	87.5
			4	82.3	86.8
		IPA + DOX + IAA + THF	6	78.3	79.0
			5	77.3	78.6
			4	73.1	75.5
	difficult	BEN + TOL + XYL + TCE	6	52.9	54.5
			5	51.1	55.4
			4	48.0	55.6
		MEK + DOX + ACE + BAC	6	52.2	54.4
			5	53.2	57.0
			4	52.9	55.2
5	easy	2ME + IAA + HEX + TOL + DCL	6	86.5	86.7
			5	85.2	86.2
		IPA + ACE + IOC + BEN + PCE	6	75.8	78.1
			5	74.8	77.2
	moderate	IPA + DOX + IAA + TOL + XYL	6	72.9	73.9
			5	73.5	73.9
		DCL + TCE + PCE + ACE + MEK	6	58.6	60.5
			5	59.0	59.9
	difficult	ACE + MEK + DOX + IAA + BAC	6	37.3	39.0
			5	37.1	39.9
		BEN + TOL + XYL + TCE + PCE	6	37.0	39.6
			5	35.9	39.2
6	easy	IPA + DOX + IAA + IOC + TOL + PCE	6	66.6	69.1
		2ME + MEK + BAC + HEX + BEN + DCL	6	66.5	67.9
	moderate	MEK + DOX + IPA + HEX + IOC + TOL	6	47.6	49.4
		BAC + IAA + THF + TCE + XYL + BEN	6	39.5	41.2
	difficult	DCL + TCE + PCE + BEN + TOL + XYL	6	30.6	31.6
		MEK + DOX + ACE + BAC + IAA + THF	6	29.0	31.3

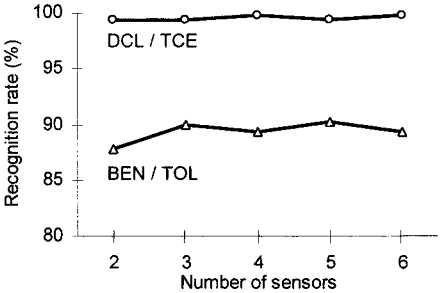

Figure 3. Recognition rates for two different 2-vapor subsets showing no significant change in vapor recognition with increasing number of sensors in the array. The upper set of points is for the dichloromethane/trichloroethylene subset, and the lower set is for the benzene/toluene subset.

effectively. This is undoubtedly due, in large part, to the number of components included in these subsets: 31 for the 5-vapor subsets and 63 for the 6-vapor subsets.

Quantification Error. Up to this point, only errors in recognition have been considered. It was of interest to explore errors in quantification as well. To this end, several of the simulations discussed above were assessed in terms of quantification accuracy.

Results in Table 8 are representative of the levels of error in quantification observed for the 2-, 3-, and 4-vapor subsets examined. As shown, the range of errors for correctly recognized vapors and vapor mixtures is quite reasonable, and the averages of the absolute values of the errors of 5−8% are extremely good. Thus, quantification does not appear to be a limiting factor in array performance.

CONCLUSIONS

The most significant conclusion that can be drawn from this study is that large arrays of polymer-coated SAW sensors are not necessary for accurate multivapor analysis. As shown, an array of just two or three sensors can *recognize and discriminate among* 16 individual vapors with very low error over a wide range of concentrations. Furthermore, for the analysis of mixtures of up to four vapors the number of sensors in the array required for recognition of the components, alone or in any combination, is equal to the total number of vapors being considered. Although high rates of confusion were observed among mixture components in some cases, increasing the number of sensors in the array did not improve performance significantly, if at all. In light of these

Table 8. Quantification Errors (1−5 LOD range) for Representative Analyses of 2−4 Vapors

vapor subset[a]	sensor array	recognition (%)	quantification error (%)[b]	
			av[c]	95% conf interval
PCE + DOX	FPOL, PDPP	99.6	5.4	−13.6 − 13.6
IOC + DCL + ACE	PIB, PECH, FPOL	99.5	5.7	−14.2 − 14.4
TOL + HEX + IAA + 2ME	PIB, FPOL, OV-25, OV-275	96.8	7.9	−21.1 − 21.6

[a] All possible combinations. [b] Calculated for correctly recognized cases only. [c] Absolute error.

results, the need for large arrays of sorption-based sensors, such as those being incorporated into "electronic nose" instrumentation, is called into question.

We believe these findings to be general. That is, similar results are likely to be obtained not only with other SAW sensor arrays but also with arrays of other types of vapor sensors employing isotropic-polymer interface layers, such as optical-fiber sensors, chemiresistors, and other acoustic-wave sensors. Several features of this study support this conclusion. First, coating selection was based on a rational process guided by LSER concepts to ensure that the polymer coatings employed contained functional groups that collectively represented most of the recognized interaction forces known to affect the strength of vapor sorption. In addition, the test vapors were selected from several functional-group classes, but also included members within a given class. Exposures were performed in humid air under well-controlled environmental conditions, and quality control procedures were used to ensure the reproducibility of responses and the stability of the sensor coatings over the course of the six-month data collection period. The error model used to generate the synthetic responses for the Monte Carlo simulations accounted quantitatively for all known sources of response variation in the sensors, and the performance testing addressed the problems of recognizing individual vapors from a large set of possibilities as well as recognizing mixture components in mixtures of up to six vapors. Vapor concentration was also taken into account in these performance tests and was shown to be an important cofactor affecting recognition rates as well as optimal sensor selection. The scope of these analyses exceeds that of any previous study.

The general applicability of these findings is further supported by the results, though not the authors' conclusions, of a recent study of arrays of carbon-loaded polymer-coated chemiresistors, tin-oxide sensors, and conducting-polymer sensors.[19] That study examined the pairwise resolution of 19 different vapors as a function of array size and showed no statistically significant increase in discrimination with any of the sensor technologies for arrays of more than 3−4 sensors. PCA of their chemiresistor data also support this finding.

Mixtures containing homologous vapor pairs or vapors with very similar functional-group interaction strengths pose the greatest challenge when using isotropic polymers as sensor coatings, and differentiating the components of mixtures of such vapors is more difficult than differentiating the individual vapors.

Although arrays of 2−4 polymer-coated SAW sensors can perform multivapor analyses effectively, given that different sensors are required to optimize recognition/discrimination for different mixtures, an array of 4−6 sensors may be necessary for multiple applications, even though not all of these sensors will be required for a given analysis. According to our results, analyses of more than four vapors become intractable if all possible subsets/combinations of the vapors are considered. Furthermore, even for less complex mixtures, cases were found where members of the mixtures or their combinations could not be sufficiently discriminated for accurate analysis regardless of the size of the array. While the use of polymers with more subtle differences in structure may improve discrimination, such improvements are bound to be small. This is supported by the results of PCA and correlation analysis presented here indicating a high degree of chemical diversity among the polymer coatings employed and by the successful recognition/discrimination of all 16 vapors in the individual-vapor analyses. The nonselective dispersion forces governing most vapor−polymer interactions will tend to mitigate any improvements in selectivity accruing from the addition or substitution of other functionalized polymers in the array.

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SUPPORTING INFORMATION AVAILABLE

A detailed rationale for the form of eq 1 and the k_i values employed are provided along with a more complete description of the EDPCR methodology. Also provided are the correlation matrix for the 16-vapor set and recognition matrices for the 6-sensor array and the top-ranked 2-sensor array in the low (i.e., 1−5 LOD) concentration range, which illustrate the nature of the recognition errors observed. This material is available free of charge via the Internet at http://pubs.acs.org.

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