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Articles

An Investigation of the Concentration Dependence and Response to Analyte Mixtures of Carbon Black/Insulating Organic Polymer Composite Vapor Detectors

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The responses relative to an air background of carbon black/polymer composite vapor detectors have been determined as a function of the concentration of a homologous series of alcohols (n-C$_n$H$_{2n+1}$OH, $1 \leq n \leq 8$), a homologous series of alkanes (n-C$_n$H$_{2n+2}$, $5 \leq n \leq 10$ and $n = 12, 14$), and a set of diverse solvent vapors. In all cases, the steady-state relative differential resistance responses, $\Delta R/R_b$, of the carbon black/polymer composite vapor detectors were well-described by a linear relationship with respect to the analyte partial pressure, at least over the tested concentration range ($P/P° = 0.005-0.03$, where $P°$ is the vapor pressure of the analyte). When two vapors in air were simultaneously presented to the detectors, the $\Delta R/R_b$ response, relative to an air background, was the sum of the $\Delta R/R_b$ values obtained when each analyte was exposed separately to the carbon black/polymer composite detectors under study. Similarly, when an analyte was exposed to the detectors on top of a background level of another analyte, the $\Delta R/R_b$ values of the array of detectors were very close to those obtained when the test analyte was exposed to the detectors only in the presence of background air. The initial training requirements from the array response output data of such detectors are minimized because the $\Delta R/R_b$ response pattern produced by the analyte of concern can be associated uniquely with that odor, under the conditions explored in this work.

Arrays of several types of vapor detectors are actively being explored to produce an “electronic nose”.[1−5] In this type of system architecture, no individual detector is highly selective toward an individual analyte, as would be the case in the traditional “lock and key” approach to chemical sensing. Instead, each detector responds to many analytes, and each analyte elicits a response from many detectors. The resulting odor signature from the array of broadly cross responsive detectors is used to classify, and in some cases quantify, the analyte of concern. Detector modalities that have been employed in this architecture include surface acoustic wave (SAW) devices,[6−9] tin oxide detectors,[10−12] electrically conductive organic polymers,[2,13,14] coated fiber-optic detectors,[15] polymer-coated micromirrors,[16,17] quartz crystal microbalances (QCMs),[18,19] and carbon black−polymer composite chemiresistors.[1]

These types of broadly responsive detector arrays can be useful in at least two generic categories of sensing tasks. In one mode of operation, the array is only required to sense changes in an odor relative to a known prior condition. The changes of interest may have many different physical and/or chemical origins, some of which may not be anticipated in advance, but all of which should optimally be probed by the vapor detector array. This mode of operation is useful for applications in quality control and quality assurance of foodstuffs, fragrances, consumer goods, and similar

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applications.[14,20–22] For such purposes, the detector response need only be reproducible from trial to trial, and no constraints on the form of the detector response are necessarily required to perform the task at hand.

In another operational mode, a detector array could be used to identify a signature of an odor in the field on the basis of a comparison of the array response to the response signature that was recorded and stored for that analyte during a prior training/calibration run.[23–25] Such applications might include providing a warning when a particular odor becomes present above a certain concentration level in the vapor phase, tracking and/or localization of an odor in the environment, or determining the concentration of an analyte in a simple, but relatively time-independent, effluent mixture. In these types of applications, it is highly advantageous to utilize detectors that have a linear output signal in response to variations in the concentration of a particular odor, so that the pattern type allows identification of the odor while the pattern height can be straightforwardly related to the odor concentration. It is even more advantageous if the array response to the odor of concern is the same in the absence and presence of other odors. In this fashion, the initial training requirements from the array response output data are minimized because the pattern produced by the analyte of concern can be associated uniquely with that odor regardless of the changing environmental conditions under which the analysis is performed.

Prior work in our laboratory has demonstrated that insulating organic polymers interspersed with domains of electrical conductors can provide chemically sensitive detector materials that can be used to produce an "electronic nose" array.[1,2] The conducting polymer composites have been formed using either organic, inorganic, or carbonaceous materials as the conducting phase. Sorption of organic solvent vapors into these types of detectors produces a characteristic, reversible resistance change in the detector element.[1] Because every organic polymer will have a characteristic gas/polymer partition coefficient in response to the presence of a particular odor, a collection of insulating organic polymers provides a diversity in detector materials that produces the diagnostic response pattern of the detector array. Under certain circumstances, analysis of the pattern of signals produced by the detector array then allows information on odor classification and concentration to be extracted through signal processing methods.[26]

In this work, we describe the results of an extensive set of experiments designed to investigate the behavior of arrays of conductive polymer composite detectors when presented with a broadly construed, generic set of test organic vapors at varying analyte concentrations. In addition, we have probed the response when the detectors are exposed to various concentrations of members of homologous series of alkanes or alcohols. Additionally, the detector response properties have been investigated during exposure to various binary vapor mixtures to ascertain whether an array response pattern for a pure odor is transferable, weighted by the mole fraction of its vapor in an analyte mixture, to binary mixtures of analytes. Finally, we describe the results of experiments in which a small but rapidly changing odor concentration has been superimposed upon a relatively slowly varying baseline odor concentration.

EXPERIMENTAL SECTION

A. Materials. The carbon black used in the composites was Black Pearls 2000 (BP2000), a furnace black material that was generously donated by Cabot Co. (Billerica, MA). The following polymers were used in the composites (listed as detector number, polymer): **1**, poly(4-vinylphenol); **2**, poly(styrene-*co*-allyl alcohol), 5% hydroxy; **3**, poly(α-methylstyrene); **4**, poly(vinyl chloride-*co*-vinyl acetate), 10% vinyl acetate; **5**, poly(*N*-vinylpyrrolidone); **6**, poly(vinyl acetate); **7**, poly(methyl vinyl ether-*co*-maleic anhydride); **8**, poly(carbonate−bisphenol A); **9**, poly(styrene); **10**, poly(styrene-*co*-maleic anhydride), 50% styrene; **11**, poly(vinyl butyral); **12**, poly(sulfone); **13**, poly(methyl methacrylate); **14**, poly(vinylidene chloride-*co*-acrylonitrile), 80% vinylidene chloride; **15**, poly(caprolactone); **16**, poly(ethylene-*co*-vinyl acetate), 82% ethylene; **17**, poly(ethylene oxide); **18**, poly(butadiene), 36% *cis*-1,4-, 55% *trans*-1,4-, 9% vinyl-1,2-; **19**, poly(epichlorohydrin); **20**, poly(styrene-*co*-butadiene), 28% styrene; **21**, addition product of sodium menthoxide to poly(pentafluorostyrene); **22**, (+)-isopinocampheol-derivatized poly(*p*-chloromethylstyrene); **23**, poly(fluorostyrene); **24**, poly(styrene-*co*-isoprene) (Figure 1). All polymers were purchased from Polysciences Inc. or Aldrich Chemical Co. and were used as received, except polymers 20−23, which were kindly supplied by Prof. Robert H. Grubbs of Caltech. The solvents used in this study all were reagent grade and were used as received.

B. Fabrication of Detectors. Two substrates were used for the detectors. In one configuration, two parallel bands of gold, 50−100 nm thick and separated by either 1 or 5 mm, were deposited onto conventional 7.5 cm × 2.5 cm glass slides (Corning Inc.). The slides were then cut into strips to produce 0.7 cm × 2.5 cm pieces of glass, with each strip of glass having one pair of Au leads spaced 1 or 5 mm apart. In the second configuration, a commercial surface-mounting breadboard was slightly modified to be used as the substrate. The commercial product ("Surfboards") consisted of parallel leads of metal deposited onto the circuit board material. These leads were soldered to pins that were on 0.10 in. centers. The commercial product was cut into pairs of leads and was then coated with the composite films.

The detector films were made from a solution of the polymer into which carbon black had been suspended. A total of 160 mg of one of the insulating polymers (Figure 1) was dissolved in 20 mL of solvent, and carbon black (40 mg) was then suspended in this solution, to produce a composition of 80% polymer and 20% carbon black by weight of solids. The solvent was generally tetrahydrofuran, benzene, or methylene chloride, depending on the solubility of the polymer. The solutions were sonicated for 5 min to suspend the carbon black. Aromatics and chlorinated solvents yielded very good suspensions of the carbon black. A single solution that contained the polymer and the carbon black

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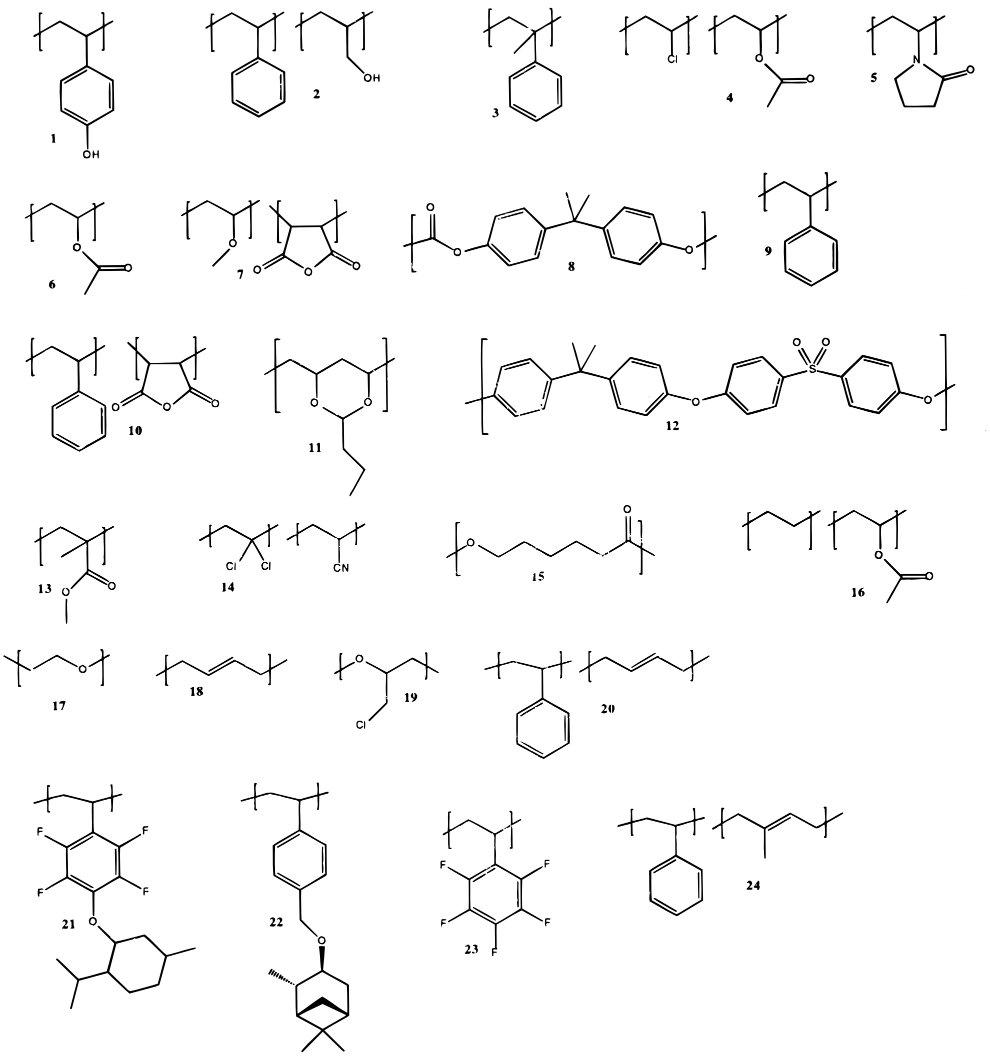

Figure 1. Structures of the polymers used in this work. Listed as detector number, polymer: **1**, poly(4-vinylphenol); **2**, poly(styrene-*co*-allyl alcohol), 5% hydroxy; **3**, poly(α-methylstyrene); **4**, poly(vinyl chloride-*co*-vinyl acetate), 10% vinyl acetate; **5**, poly(*N*-vinylpyrrolidone); **6**, poly(vinyl acetate); **7**, poly(methyl vinyl ether-*co*-maleic anhydride); **8**, poly(bisphenol A−carbonate); **9**, poly(styrene); **10**, poly(styrene-*co*-maleic anhydride), 50% styrene; **11**, poly(vinyl butyral); **12**, poly(sulfone); **13**, poly(methyl methacrylate); **14**, poly(vinylidene chloride-*co*-acrylonitrile), 80% vinylidene chloride; **15**, poly(caprolactone); **16**, poly(ethylene-*co*-vinyl acetate), 82% ethylene; **17**, poly(ethylene oxide); **18**, poly(butadiene), 36% *cis*-1,4-, 55% *trans*-1,4-, 9% vinyl-1,2-, **19**, poly(epichlorohydrin); **20**, poly(styrene-*co*-butadiene), 28% styrene; **21**, addition product of sodium menthoxide to poly(pentafluorostyrene); **22**, (+)-isopinocampheol-derivatized poly(*p*-chloromethylstyrene); **23**, poly(fluorostyrene); **24**, poly(styrene-*co*-isoprene)

was used to prepare all the detectors of a given composition that were used in this work. An aliquot of the suspension was spin coated, at 1000 rpm, onto a glass substrate using a Headway (Garland, TX) spin coater, and the resulting film was allowed to dry in air. Multiple coatings of the suspension were applied to each substrate to yield detectors having resistance values of approximately a few hundred kiloohms. For the fiberglass substrates, the film was applied by dip-coating the substrate two or three times until the desired resistance was achieved. Before use, the detectors were dried in open air and then were placed in air flowing at 20 L min^{-1} for 12−24 h.

C. Instrumentation and Apparatus. An automated flow system consisting of LabVIEW software, a Pentium computer, and electronically controlled solenoid valves and mass flow controllers was used to produce and deliver selected concentrations of solvent vapors to the detectors.[27] To obtain the desired analyte concentration, a stream of carrier gas was passed through a bubbler that had been filled with the solvent of choice. Saturation of the carrier gas with the solvent vapor was verified through measurement of the rate of mass loss of the solvent in the bubbler.[28] The vapor-saturated carrier gas was then diluted with pure carrier gas through the use of mass flow controllers (MKS Instruments, Inc). Calibrations of the flow system using a flame ionization detector (model 300 HFID, California Analytical Instruments, Inc.) verified that the analyte concentrations delivered to the sensors were those expected from the settings of the mass flow controllers.

The carrier gas for all experiments was oil-free air, obtained from the general compressed air laboratory source, containing

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1.10 ± 0.15 ppth (parts per thousand) of water vapor. The air was filtered to remove particulates, but deliberately was not dehumidified or otherwise purified. Fluctuations in laboratory temperature, 21.5 ± 1.5 °C, could cause a ~10% error in setting and controlling the vapor concentrations between nominally identical exposures over the course of the data collection analyzed in this work. No temperature control of the apparatus or of the carbon black–polymer composite detectors was performed. The flow rate of the vapor stream entering the exposure chamber (~1 L in total volume) was maintained at 15 L min^{-1}.

D. Measurements. The dc electrical resistance of each detector was monitored in response to the presence of various test vapors and mixtures of vapors. Resistance measurements were performed using a simple two-point configuration across the gold leads that bridged the sensing element. The detectors were multiplexed through a Keithley model 7001 channel switcher to a Keithley model 2002 multimeter that measured the dc resistance of each detector once every 3–5 s, with the exact time interval depending on the particular experiment.

To initiate an experiment, the detectors were placed into the flow chamber and a background flow of compressed air was introduced until the resistance of the detectors stabilized. Each exposure consisted of a three-step process that began with 60 s of air flow to achieve a smooth baseline resistance. After this period, the detectors were exposed to solvent vapor at a controlled concentration in flowing air. The solvent exposure was then followed by a flow of clean air for a time equal to the total exposure time, to restore the baseline resistance values. For the linearity studies, the 60 s baseline period was followed by 240 s of exposure to the test analyte. To probe the dependence of the detector response on the order of presentation, in some measurements of the mixture studies, the exposure phase consisted of two parts. In the sequential mixture measurements, the first analyte (denoted as s_1) was exposed for 120 s, at which time the second solvent, s_2, was introduced and exposed for an additional 120 s. During the exposure of the second analyte, the first analyte was continually flowing (this protocol is denoted as s_1, $s_1 + s_2$). In the measurements, when a mixture of two analytes was exposed simultaneously to the sensors (denoted $s_1 + s_2$), the two analytes of the mixture were presented to the detectors for a total of 240 s.

In studies of mixtures, the eight bubblers of the system were divided into two sets of four bubblers each. One mass flow controller was present for "set A" and one for "set B" (Table 1). One-way valves ensured that significant gas back flow did not occur during the experiments. Analytes in the same solvent set could not be exposed simultaneously to the detectors. Therefore, 16 pairs of solvents were available for use in the first set of mixture studies. Only six solvents were used in the second mixture study, three in each set, so nine solvent pairs were available. The detectors used for the eight-solvent experiment were formed from polymers **1**–**18**, **21**, and **23** (Figure 1). The detectors used for the six-solvent experiment, the alcohol linearity study, and the alkane linearity study were formed using polymers **8**, **12**, and **15**–**24** (Figure 1). In all experiments, one copy of each type of detector was used.

In both the eight-solvent and six-solvent mixture experiments, the detectors were exposed to individual solvents (s_1), to pairs of solvents presented simultaneously ($s_1 + s_2$), and to one solvent followed by addition of another solvent (s_1, $s_1 + s_2$). The individual solvents and the preselected pairs of s_1, s_2 solvents were exposed to the detectors at analyte concentrations that corresponded to 0.5, 1.0, and 1.5% of each solvent's vapor pressure, $P°$. In the six-solvent experiment, individual solvents were additionally presented at 2.0 and 2.5% of $P°$. Solvents forming every compositionally distinct binary mixture were permuted in their order of presentation to the detectors, so that for each solvent pair (one from set A and one from set B) at every distinct analyte concentration, the trials included the exposure protocol s_A, $s_A + s_B$ as well as the exposure protocol s_B, $s_B + s_A$. Each unique exposure protocol, for each type of mixture and pure analyte presentation, was repeated 5 times. The eight-solvent experiment thus contained 2280 total exposures (8 solvents, 3 concentrations, 5 repeats of each for the individual solvent exposures, 6 × 8 × 5 simultaneous mixture exposures, and 16 × 8 × 2 × 5 sequential mixture exposures). The six-solvent experiment contained 1365 total exposures (6 × 5 × 5 individual solvent exposures, 3 × 9 × 5 simultaneous mixture exposures, and 9 × 6 × 2 × 5 sequential mixture exposures). Within each experiment, every exposure was assigned a randomly generated index number using the Microsoft Excel random number generator. The exposures were then presented to the detector array in ascending order of the assigned index values.

Table 1. Two Groups of Solvents Used in the Eight-Solvent Binary Mixture Study and the Six-Solvent Binary Mixture Study[a]

set A	set B
Eight-Solvent Experiment	
benzene	chloroform
ethyl acetate	ethanol
heptane	hexane
methanol	toluene
Six-Solvent Experiment	
benzene	nitrobenzene
2-propanol	chloroform
cyclohexanone	heptane

[a] Binary mixtures were formed between solvents of set A and solvents of set B of each group. Solvents common to one set could not be paired.

In the studies designed to quantify the detector response as a function of analyte concentration, two homologous series of vapors, one consisting of straight-chain alcohols and the other of straight-chain alkanes, were exposed to the detectors. The following alcohols were used: methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol. In a separate run, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-tetradecane were used. In another, related set of experiments, the broad test set of solvents used in the studies of mixtures (Table 1) was exposed to the detectors over a wider concentration range ($0.005P° \leq P \leq 0.03P°$) than was used in the runs to determine the detector's response to mixtures of these particular solvent vapors. Additionally, one run with the straight-chain alcohols was performed using vapor concentrations that were in the range $0.01P° \leq P \leq 0.06P°$. In each of these experiments, each unique presentation of an analyte was repeated 10 times, with the entire presentation order (within

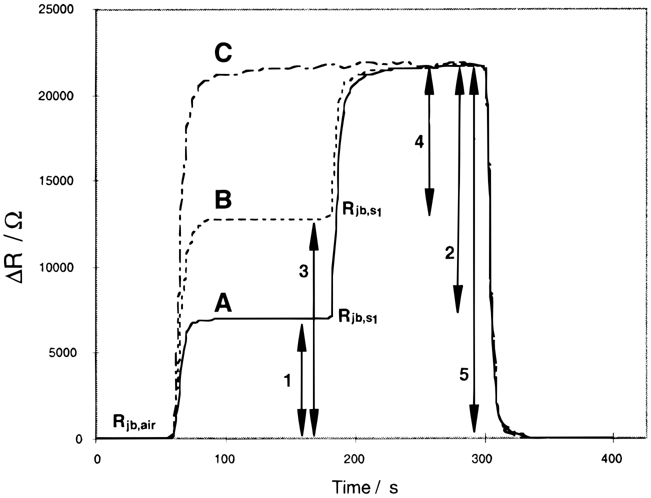

Figure 2. Representative differential resistance responses for three types of vapor presentations to a poly(ethylene-*co*-vinyl acetate)–carbon black composite vapor detector. (A) Exposure to benzene at $P/P^{\circ} = 0.02$ ($\Delta R_{js1,max}$ indicated by arrow 1) followed by exposure to benzene at $P/P^{\circ} = 0.02$ and chloroform at $P/P^{\circ} = 0.02$ ($\Delta R_{js2,max}$ indicated by arrow 2). The combined response, $\Delta R_{js1,max} + \Delta R_{js2,max}$, is indicated by arrow 5. (B) Exposure to chloroform at $P/P^{\circ} = 0.02$ ($\Delta R_{js1,max}$ indicated by arrow 3) followed by exposure to chloroform at $P/P^{\circ} = 0.02$ and benzene at $P/P^{\circ} = 0.02$ ($\Delta R_{js2,max}$ indicated by arrow 4). The combined response, $\Delta R_{js1,max} + \Delta R_{js2,max}$, is also indicated by arrow 5. Arrow 1 ≈ arrow 4; arrow 3 ≈ arrow 2. (C) Benzene at $P/P^{\circ} = 0.02$ and chloroform at $P/P^{\circ} = 0.02$ both presented simultaneously to the detector (response, $\Delta R_{js1+s2,max}$ is again indicated by arrow 5).

a run) randomized with respect to solvents, concentrations of solvents, and repeated exposures to a solvent.

E. Data Processing. Sample responses for a single exposure and for a sequential mixture exposure are shown in Figure 2. Although the resistance of each detector was sampled once every 3–5 s during each exposure, only the maximum relative differential resistance change, $\Delta R_{js,max}/R_{jb,air}$, where $\Delta R_{js,max}$ produced by exposure to an individual solvent is the maximum resistance change of the *j*th detector during exposure to solvent s and $R_{jb,air}$ is the baseline resistance of the *j*th detector exposed to the initial 60 s period of exposure to background air, was used in analysis of the data. In the mixture studies when solvents were exposed sequentially to the detectors, three separate $\Delta R/R$ values, $\Delta R_{j,s1,max}/R_{jb,air}$, $\Delta R_{j,s2,max}/R_{jb,s1}$, and $\Delta R_{j,s1,s1+s2}/R_{jb,air}$ were calculated from the data from each exposure protocol s_1, $s_1 + s_2$ (Figure 2).

For these solvents and detectors, the exposure time was sufficiently long that the maximum response value, $\Delta R_{js,max}/R_{jb}$, was a very good approximation to the change in the steady-state resistance value of the detectors in response to the specified analyte concentration relative to the baseline resistance of the detector in an air background flow alone. Examples of the temporal dependence of individual carbon black/insulating polymer composite detectors are shown in Figure 2. For some exposures in the eight-solvent system, the value $R_{jb,s1}$ had not completely reached steady state. Therefore, to calculate $\Delta R_{js2,max}/R_{jb,s1}$ in those cases, the slope of the resistance values 30 s prior to the start of the exposure was calculated and subtracted from the R_{js2} values. If this correction were not made, then the detector's response to s_2 would have been overestimated.

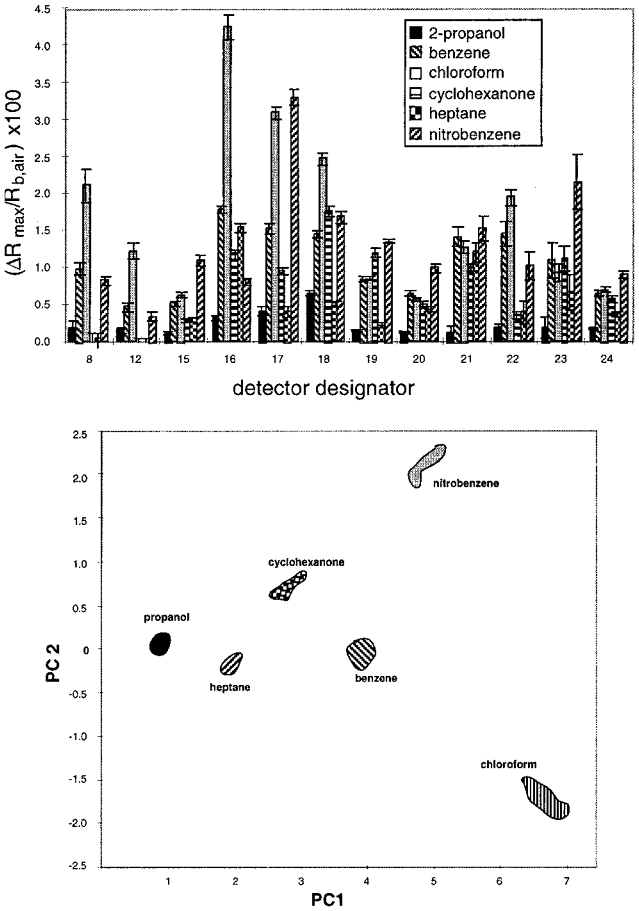

Figure 3. (a) histogram of the maximum relative differential resistance response of 12 carbon black/polymer composite detectors exposed to *n*-heptane, cyclohexanone, benzene, chloroform, nitrobenzene, and 2-propanol each presented at $P/P^{\circ} = 0.03$ in air. Each analyte was presented 10 times to the array, with the order of presentation randomized over all repetitions of all test solvents. (b) Results from the exposures described in (a) as represented by the first two dimensions of principal component space, which contain 96% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte in principal component space.

RESULTS

A. Linearity of Detector Response for Pure Odors. Figure 3a displays the maximum relative differential resistance data, $\Delta R_{js,max}/R_{jb,air}$, for a 12-element conducting organic polymer composite detector array toward a series of test analytes when each analyte was maintained at a partial pressure, *P*, in air equal to 3% of its vapor pressure, P°, at 22 °C. Each analyte can be seen to produce a distinct $\Delta R_{js,max}/R_{jb,air}$ response pattern on the array of conducting polymer composite detectors. Principal component analysis was used in order to aid visualization of the differences between $\Delta R_{js,max}/R_{jb,air}$ patterns produced by the various analytes.[29] Figure 3b presents the $\Delta R_{js,max}/R_{jb,air}$ data in principal component space, with the axes representing the first and second principal components of the data set. All analytes were well-separated from each other on the basis of the differences between their characteristic $\Delta R_{js,max}/R_{jb,air}$ response patterns on the array of detectors.

The concentration of each analyte was then varied over six even steps in the range $0.005P^{\circ} \leq P \leq 0.03P^{\circ}$. Figure 4 depicts

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Table 2. Statistics for $\Delta R/R_b$ Response vs $P/P°$ for Representative Polymers and Analytes[a]

	poly(butadiene)				poly(epichlorohydrin)		
	R^2	intercept	slope		R^2	intercept	slope
1-propanol	0.9998	−0.0136	0.2200	ethanol	0.9956	0.0024	0.0367
benzene	1.0000	−0.0429	0.5017	1-propanol	0.9990	−0.0048	0.0542
chloroform	0.9998	−0.0563	0.8509	1-butanol	0.9997	−0.0031	0.0629
cyclohexanone	1.0000	−0.0668	0.6128	1-pentanol	0.9992	−0.0060	0.0670
n-heptane	0.9993	−0.0003	0.1682	1-hexanol	0.9998	−0.0036	0.0703
nitrobenzene	0.9995	−0.0397	0.5656	1-heptanol	0.9991	−0.0033	0.0691
n-hexane	0.9994	−0.0344	0.1788				
n-heptane	0.9999	−0.0175	0.1659				
n-octane	0.9994	−0.0223	0.1688				
n-nonane	0.9995	−0.0294	0.1713				
n-decane	0.9988	−0.0162	0.1599				
n-dodecane	0.9997	−0.0136	0.1478				

[a] Correlation coefficients, intercepts, and slopes for three sets of analytes exposed at $P/P° = 0.005-0.03$.

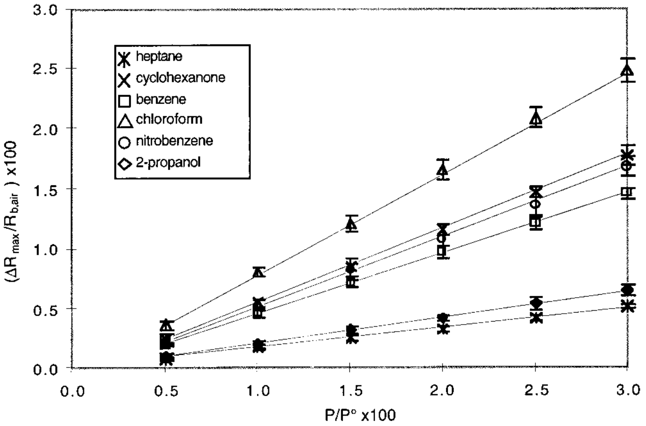

Figure 4. Average maximum relative differential resistance responses, $\Delta R_{js,max}/R_{jb,air}$, of composite detector films consisting of carbon black and poly(butadiene), when exposed to *n*-heptane, cyclohexanone, benzene, chloroform, nitrobenzene, and 2-propanol, each at $P/P° = 0.005-0.03$ in air in six even steps. Each analyte was presented 10 times to the array, with the order of presentation randomized over all repetitions of all test solvents. The error bars represent 1σ values computed from 10 exposures at each $P/P°$.

the responses of a representative detector to all of the test solvent vapors. The data were well fit by a linear dependence of $\Delta R_{js,max}/R_{jb,air}$ on $P/P°$ over the $P/P°$ ranges probed in this experiment. A summary of the correlation coefficients calculated for these lines is presented in Table 2, while statistics for all of the sensor−analyte combinations are provided in the Supporting Information that accompanies this work. For some sensor−analyte combinations, the correlation coefficients were low because the sensor exhibited only a very small response to the analyte. For example, poly(sulfone) had a small response to nonpolar solvents and so the correlation coefficients for these presentations are low. Similarly, essentially no response was exhibited by poly(sulfone) to dodecane. The intercepts of such plots were statisticallly indistinguishable from zero for all sensor−analyte combinations investigated.

Figure 5 presents the concentration-dependent $\Delta R_{js,max}/R_{jb,air}$ response data for the entire detector array in principal component space. For each test vapor, the analytes produced a unique signal response pattern, with the pattern direction in principal component space diagnostic of the analyte and the pattern height proportional to the analyte concentration in the vapor phase. This behavior is further illustrated by normalization of the detector response patterns with respect to analyte concentration according to eq 1,

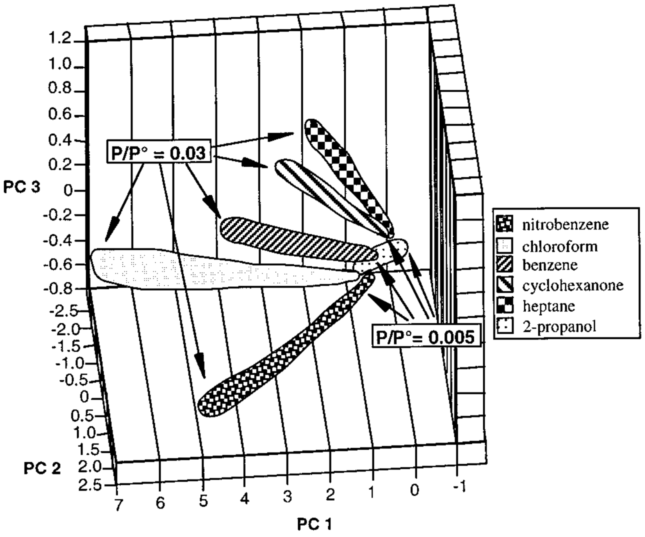

Figure 5. Data in principal component space from a 12-detector array exposed to *n*-heptane, cyclohexanone, benzene, chloroform, nitrobenzene, and 2-propanol each at $P/P° = 0.005-0.03$ in air in six even steps. The first three principal components depicted contained 98% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte. Each analyte was presented 10 times to the array, with the order of presentation randomized over all repetitions of all test solvents.

$$S_{js} = (\Delta R_{js,max}/R_{jb,air})(P°/P) \qquad (1)$$

where S_{js} is the normalized signal for 12 detector films exposed to benzene, chloroform, and nitrobenzene, each presented at $P/P° = 0.005-0.03$ in six even steps. As can be seen from Figure 6, the characteristic S_{js} pattern of each test vapor was maintained, within experimental error, as the analyte concentration was varied.

Additional experiments were performed using a homologous series of alkanes, and then using a homologous series of alcohols, as test analytes. Figures 7 and 8 display the $\Delta R_{js,max}/R_{jb,air}$ values for selected detectors. The statistical information on these runs is summarized in Table 2. Again the data were well fit by a linear dependence of $\Delta R_{js,max}/R_{jb,air}$ on $P/P°$ over the $P/P°$ range probed in these experiments.

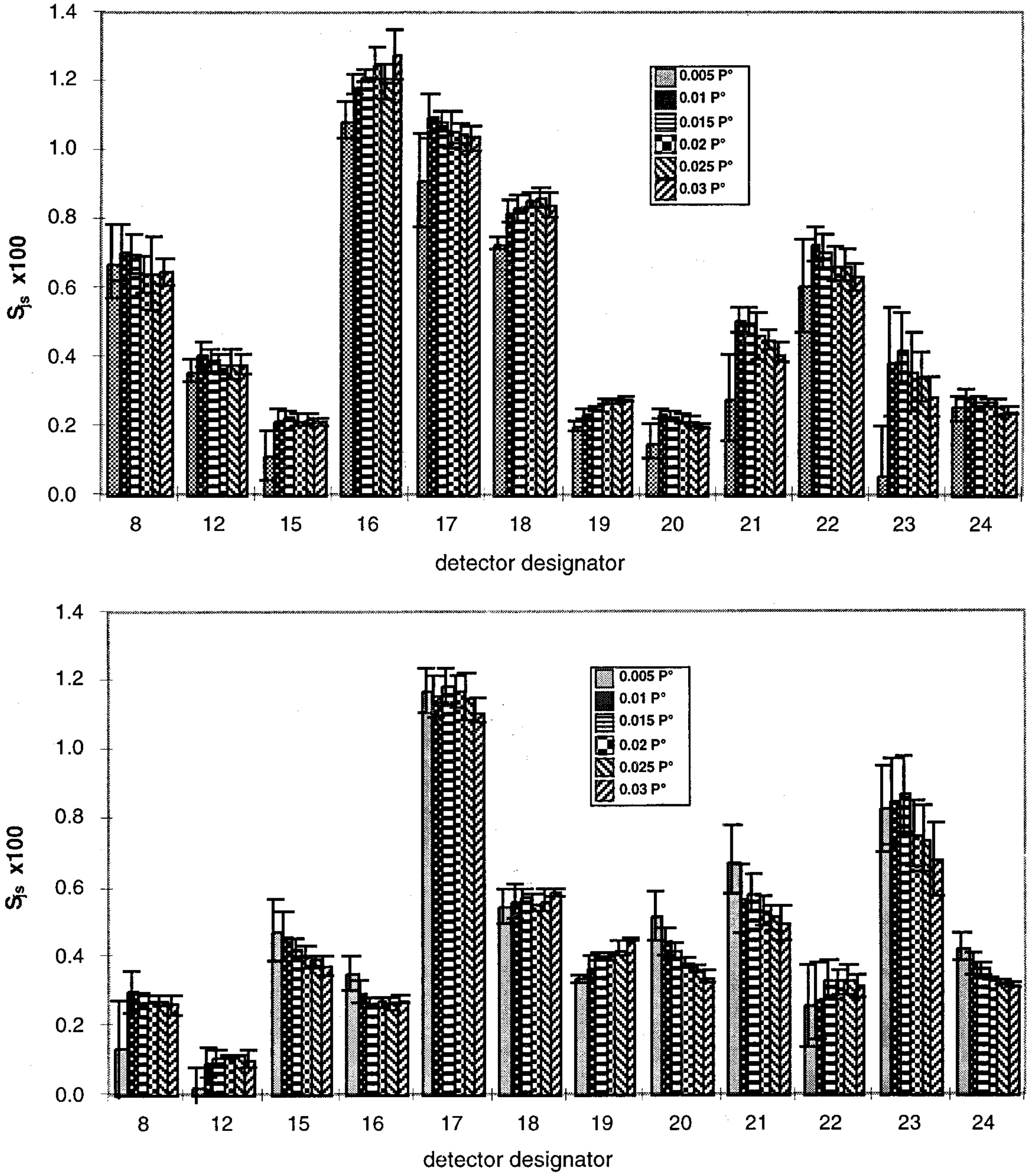

Figure 6. Histogram of the average normalized response of a 12-element array of carbon black/polymer detector films exposed to two analytes; (a) chloroform and (b) nitrobenzene, each presented 10 times at $P/P° = 0.005-0.03$ in air in six even steps. The data were normalized according to eq 1 in the text.

Figure 9a shows that all of the test alcohols could all be distinguished from one another visually in principal component space when the responses of all detectors in the array are considered. Additionally, like the analytes in the broad test set, the normalized patterns of $\Delta R_{js,max}/R_{jb,air}$ were essentially invariant as the analyte concentration was varied. Identical behavior was observed for the alkanes, as seen in Figure 9b. Thus, the $\Delta R_{js,max}/R_{jb,air}$ pattern type is diagnostic of the analyte and the pattern height indicates the concentration of each of these analytes, at least under the conditions of these test runs.

B. Detector Response to Analytes in the Presence of Background Odors. The response of the detectors to various test vapors was also investigated when the detectors were first exposed to, and then maintained in the presence of, a fixed concentration of another solvent vapor. Figure 10 exhibits the $\Delta R_{js,max}/R_{jb,air}$ values displayed by poly(ethylene-*co*-vinyl acetate) and poly(caprolactone) detectors in response to varying concentrations of heptane in the range $0.005P° \leq P \leq 0.025P°$, relative to an air background gas flow. The responses for heptane vapor at $0.005P° \leq P \leq 0.015P°$ in air were then recorded when the detector was exposed to the analyte gas stream in the presence of a constant background gas that consisted of air with 2-propanol, benzene, or cyclohexanone at $P/P° = 0.005$, 0.010, and 0.015 for each background gas. As displayed in Figure 10, $\Delta R_{jheptane,max}/R_{jb,s1}$ and $\Delta R_{jheptane,max}/R_{jb,air}$ were essentially constant for s_1 = benzene, cyclohexanone, and 2-propanol at the three values of $P/P°$. Figure 11 shows the same result in principal component space for the responses of the entire array of detectors, illustrating

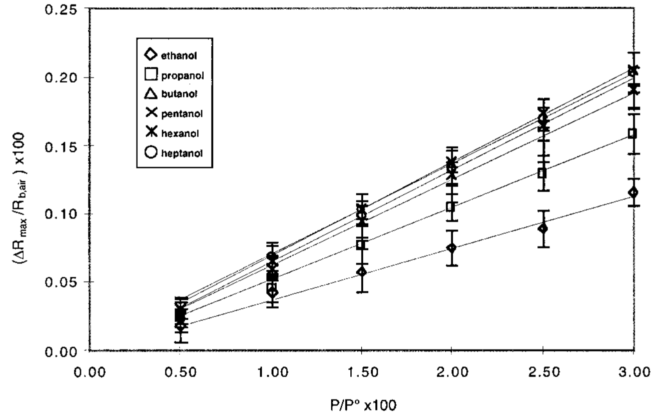

Figure 7. Maximum relative differential resistance responses, $\Delta R_{\mathrm{js,max}}/R_{\mathrm{jb,air}}$, of composite detector films consisting of carbon black and poly(epichlorohydrin), when exposed to ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol each at $P/P^{\circ} = 0.005-0.03$ in six even steps in air. Each analyte was presented 10 times to the array, with the order of presentation randomized over all repetitions of all test solvents. The error bars represent 1σ values computed from 10 exposures at each P/P°.

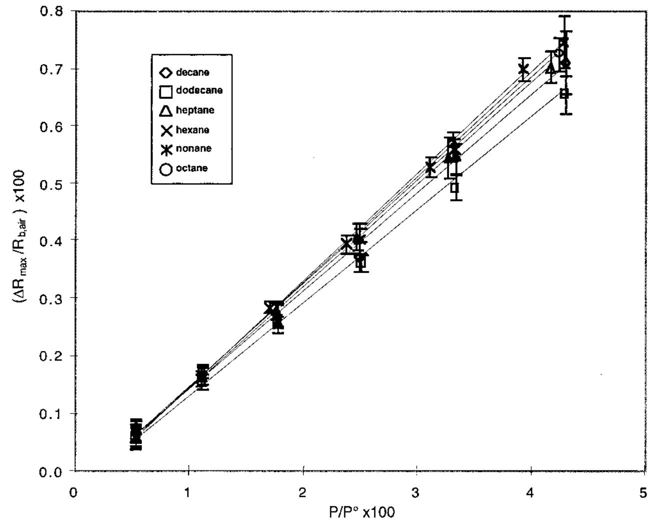

Figure 8. Maximum relative differential resistance responses, $\Delta R_{\mathrm{js,max}}/R_{\mathrm{jb,air}}$, of composite detector films consisting of carbon black and poly(butadiene), when exposed to *n*-dodecane, *n*-decane, *n*-nonane, *n*-octane, *n*-heptane, and *n*-hexane each at $P/P^{\circ} = 0.005-0.03$ in six even steps in air. Each analyte was presented 10 times to the array, with the order of presentation randomized over all repetitions of all test solvents. The error bars represent 1σ values computed from 10 exposures at each P/P°.

that this behavior is characteristic of the response pattern in the detector array as well as of the individual detectors displayed in Figure 10.

C. Detector Response to Binary Analyte Mixtures. Figure 12 shows the $\Delta R_{\mathrm{s2,max}}/R_{\mathrm{jb,s1}}$ and $\Delta R_{\mathrm{s1,s1+s2,max}}/R_{\mathrm{jb,air}}$ values of a carbon black/poly(ethylene oxide) detector to mixtures of benzene and heptane. For this detector for both the $\Delta R_{\mathrm{s2,max}}/R_{\mathrm{jb,s1}}$ and $\Delta R_{\mathrm{s1,s1+s2,max}}/R_{\mathrm{jb,air}}$ values, s_1 and s_2 were each presented to the detectors at $P/P^{\circ} = 0.005$, 0.010, and 0.015. The linear dependence of $\Delta R_{\mathrm{js,max}}/R_{\mathrm{jb}}$ on P/P° exhibited by an individual detector was maintained when the analyte was a constituent of a binary solvent mixture. The lines that have been drawn in Figure 12 to connect the data points also correspond to the change in response that would be expected based on the $\Delta R_{\mathrm{js,max}}/R_{\mathrm{jb,air}}$ behavior of the detector when presented with corresponding changes in the concentration of the individual solvent vapor in an air background. Additionally, the total $\Delta R_{\mathrm{js1+s2,max}}/R_{\mathrm{jb,air}}$ response to two solvents relative to a background air baseline was

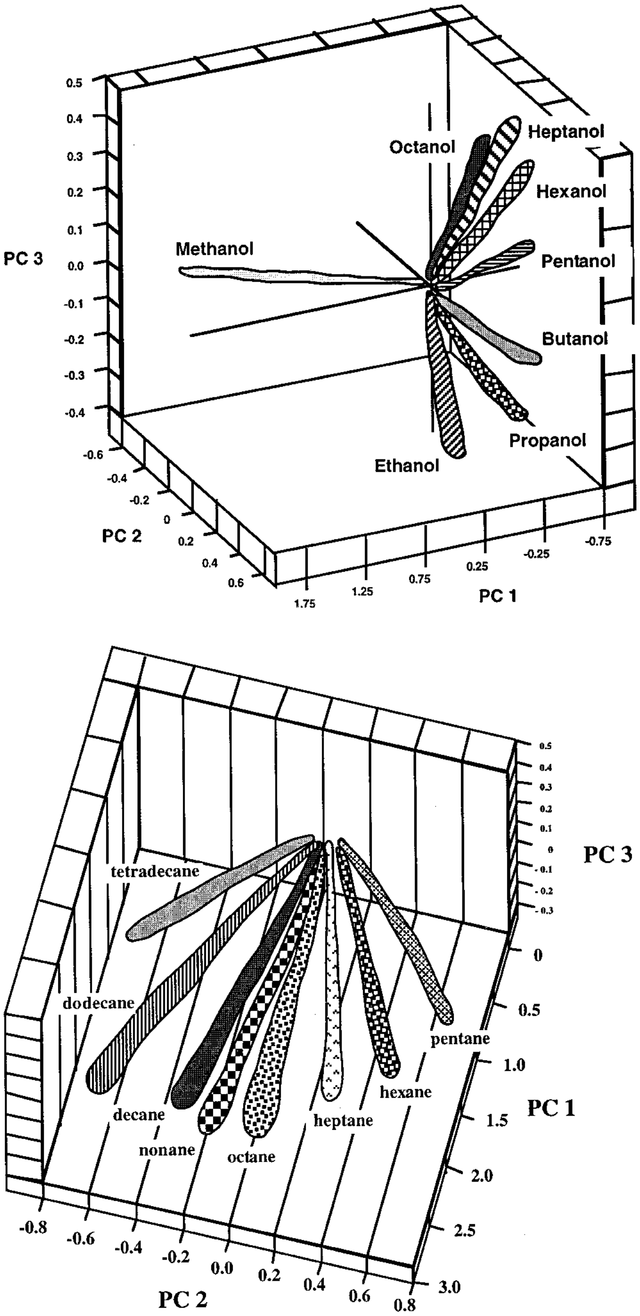

Figure 9. (a) Data in principal component space from a 20-detector array exposed 10 times each to methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1- heptanol, and 1-octanol each at $P/P^{\circ} = 0.005$ to 0.03 in air in 27 even steps. The first three principal components contain 99% of the total variance in the data. The ellipsoids contain 99% of the data for each analyte. (b) Data in principal component space from a 20-detector array exposed 5 times each to *n*-tetradecane, *n*-dodecane, *n*-decane, *n*-nonane, *n*-octane, and *n*-heptane each at $P/P^{\circ} = 0.005-0.03$ in air in 27 even steps. The first three principal components contain 99% of the total variance in the data. The ellipsoids contain 99% of the data for each analyte. All presentations in each set were randomized over all repetitions of all test solvents.

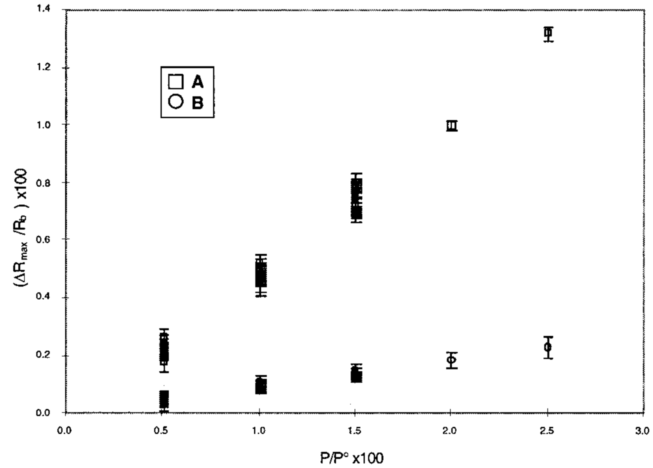

Figure 10. Maximum relative differential resistance responses, $\Delta R_{js,max}/R_{jb,air}$, of composite detector films consisting of carbon black and (A) poly(ethylene-*co*-vinyl acetate) and (B) poly(caprolactone), when exposed to *n*-heptane at $P/P^\circ = 0.005-0.025$ in air in five even steps (represented by the open symbols). Additional exposures (solid symbols) to *n*-heptane were performed at $P/P^\circ = 0.005$, 0.01, and 0.015 while the detector film was exposed to either benzene, cyclohexanone, or 2-propanol at $P/P^\circ = 0.005$, 0.01, or 0.015.

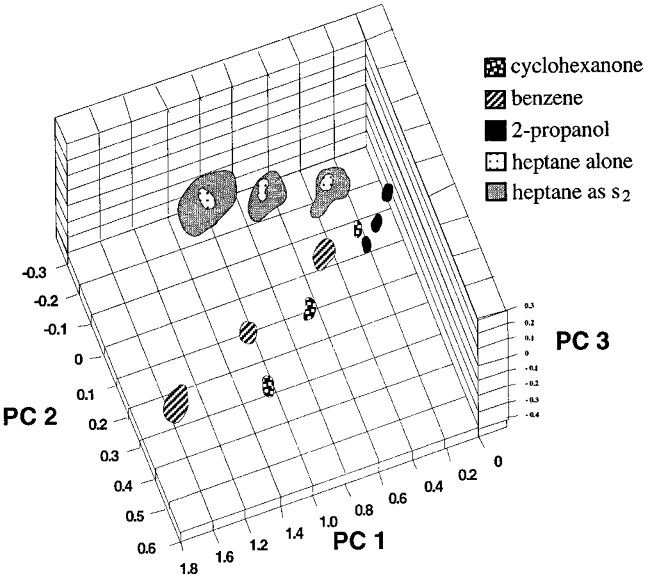

Figure 11. Data in principal component space from a 12-detector array exposed to *n*-heptane, benzene, cyclohexanone, or 2-propanol at $P/P^\circ = 0.005$, 0.01, and 0.015, and to exposures of *n*-heptane at $P/P^\circ = 0.005$, 0.01, and 0.015 while the detector film was exposed to either benzene, cyclohexanone, or 2-propanol each at $P/P^\circ = 0.005$, 0.01, or 0.015. The first three principal components contain 98% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte. Each analyte was presented five times to the array, with the order of presentation randomized over all repetitions of all exposure types.

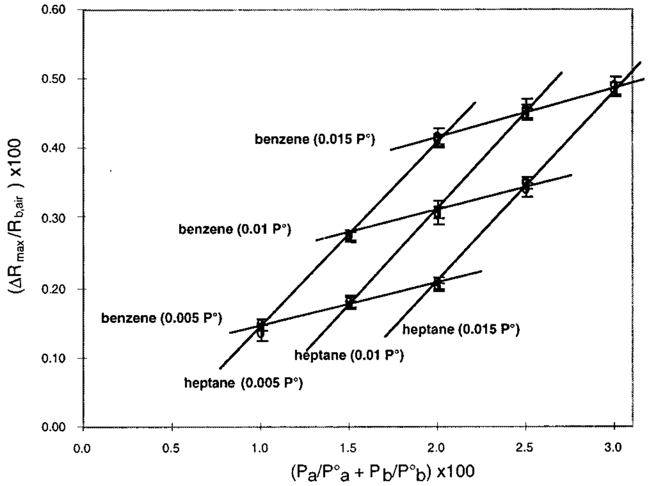

Figure 12. Maximum relative differential resistance responses of a poly(ethylene-*co*-vinyl acetate)−carbon black composite detector film when exposed to simultaneous and sequential binary mixtures of benzene at $P/P^\circ = 0.005$, 0.01, or 0.015, and *n*-heptane at $P/P^\circ = 0.005$, 0.01, or 0.015. Each of the nine binary mixture combinations was presented five times to the array, with the order of presentation randomized over all repetitions. The error bars represent 1σ values computed from five exposures at each P/P°.

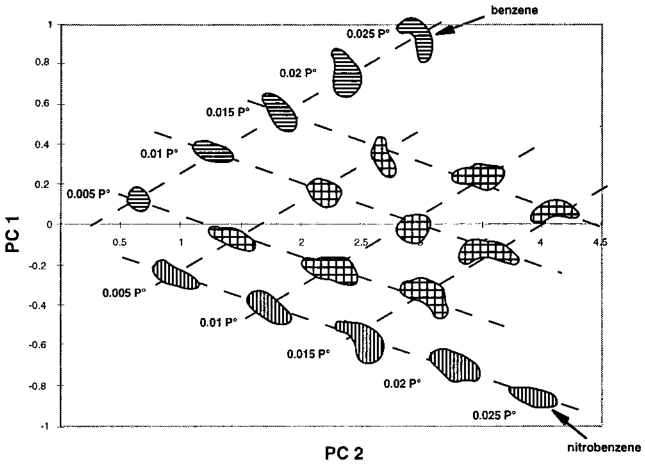

Figure 13. Data in principal component space from a 12-detector array exposed to benzene at $P/P^\circ = 0.005-0.025$ in air in five even steps, nitrobenzene at $P/P^\circ = 0.005-0.025$ in air in five even steps, and binary mixtures of benzene at $P/P^\circ = 0.005$, 0.01, or 0.015, and nitrobenzene at $P/P^\circ = 0.005$, 0.01, or 0.015. The first three principal components contain 99.6% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte. Each analyte was presented five times to the array, with the order of presentation randomized over all repetitions of all exposure types. The error bars represent 1σ values computed from five exposures at each P/P°.

independent of whether the two solvents were exposed simultaneously or sequentially to the detector. Furthermore, in the case of sequential solvent vapor exposures, the maximum relative differential response values for a given solvent were independent of the order in which the solvents were presented to the detector. Figure 13 shows similar data, in principal component space, that were produced by an entire array of carbon black/polymer composite detectors during individual analyte exposure, and simultaneous and sequential exposures of binary mixtures of benzene and nitrobenzene. Similar behavior was observed for all nine binary mixtures explored in this work (see part D in the Experimental Section for a description of the binary mixtures explored).

DISCUSSION

A. Linearity of Detector Response vs Analyte Concentration. The linearity in $\Delta R_{js,max}/R_{jb}$ response of the conducting organic polymer composite detectors versus the concentration of a pure analyte is readily understood based on the signal transduction mechanism of these types of vapor detectors. Sorption of the vapor into the detector leads to swelling of the polymer, which then produces an increase in the electrical resistance through the network of conducting regions in the composite film. Although the absolute $\Delta R_{js,max}$ of the composite is sensitive to the fractional loading of the conductive filler in the insulating polymer of the conductive material,[30-32] the relative swelling of the film in response to the presence of an analyte vapor should remain constant provided that the filler material does not significantly affect the properties of the insulating portion of the composite. Under such conditions, the ratiometric quantity $\Delta R_{js,max}/R_{jb}$ is expected to be the key parameter that characterizes the response of conducting polymer composite vapor sensors to various analytes of interest. The present work quantitatively confirms these expectations.

On the basis of the expectations discussed above, for small fractional film swellings, the observed $\Delta R_{js,max}/R_{jb}$ response should be a linear function of the concentration of the vapor that partitions into the film. This appears to be the case for the solvents studied during the course of this work. This type of behavior has been observed for poly(pyrrole) conducting polymer vapor sensors[33] and for vapor sensors that monitor the capacitance change of dielectric polymer films in response to the presence of vapor analytes, where again the response is a linear function of the analyte concentration.[34-36] Polymer films that are exposed to analytes that either bind very strongly to the polymer or that induce significant structural distortions in the chains of the polymeric material could certainly produce a saturation of the detector response at concentrations well below the vapor pressure of the analyte; however, such behavior was not observed for any of the solvents or detectors explored in this work.

For mixtures, as long as the concentration of analyte molecules is dilute in the polymer film, the linear swelling relationship as a function of the analyte concentration in the vapor phase is expected to be a good microscopic description of the signal transduction properties of the detectors when exposed to combinations of these same gaseous analytes. Thus, the swelling response of a polymer to binary analyte mixtures is expected to be a weighted linear combination of the response to the individual analytes in the vapor phase. Previous work in our laboratory has shown that the fraction of the partial pressure of the odorant, as opposed to the concentration of the odorant, is the key variable in determining the response of the carbon black/organic polymer composite vapor detectors.[37] Thus, to first order, the response of a polymer composite detector array to a mixture of solvents should be readily obtained by calculating the fractional composition of the constituents in the mixture relative to their individual vapor pressures under the experimental test conditions of concern. This additive behavior is, in fact, in excellent accord with experimental observations for the response of the conducting polymer composite arrays to the binary mixtures studied during the course of this work.

B. Implications for Algorithm Development/Pattern Recognition Requirements. All architectures that rely on array-based sensing require some type of training set and signal-processing algorithm in order to classify and/or identify an analyte upon presentation to the detector array. In this respect, the performance and range of applicability of such detector arrays is intimately coupled to the data reduction algorithms and computational capabilities that are required to achieve the sensing task of concern.

The minimum possible training set, and the minimum requirements on computational capabilities to analyze a mixture or to classify and/or identify a particular analyte, are clearly achieved when the detector response is a linear function of the analyte concentration and when the differential detector response to the analyte of concern is independent of whether other analytes are present in the environment. Both of these conditions were met for the carbon black/organic polymer composite chemiresistor response characteristics over the ranges of concentrations and for the ranges of analyte background concentrations that were explored during the course of this study. This behavior contrasts with the properties reported for tin oxide chemiresistors[38] or for dye-impregnated organic polymer coatings on fiber optics,[5,38] whose responses are nonlinear with analyte concentration and/or with variations in environmental background. Such nonlinearities imply that significantly more computational resources and algorithm development will be required to achieve similar system performance in varying background environments or when an analyte concentration is to be quantified either alone or in a mixture of vapors. The exact tradeoffs imposed by more complex data reduction and more involved computational requirements, relative to the opportunity to exploit possibly increased information content of a richly varying signal response pattern, will be array and task specific and will require a detailed analysis for the specific task of interest.

For odors that are more complex compositionally than simple binary or ternary mixtures of analytes, it could be envisioned that a single array-based detector response fingerprint would not be sufficient to produce a unique vector decomposition of the mixture into the signatures of each of the components of a training set of vapors. Thus, one response pattern might not be sufficient to provide a unique solution to the chemical composition of the odor mixture of concern. For example, if most of the variance among the data is contained in three to five principal components and if the cannonical variance tracks the total variance in the data, then mixtures of only three to five components can be decomposed uniquely from the use of the equilibrium response data alone. It is likely that, even for complex odors, useful information will be obtained, however, if some temporal or spatiotemporal variation in the composition of the odor is present. Under such conditions, changes in detector response can be identified with individual

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portions of the analyte based on their differential response patterns relative to the integrated baseline response of the odor on the detector array. The detector response characteristic that is least demanding on the signal processing and computational resources under such circumstances is when the pattern for an analyte remains linearly proportional to the analyte concentration regardless of the composition, or concentration, of the other components of the background ambient. This behavior was observed experimentally for the conducting polymer composite detectors for the various solvents and background ambient vapors evaluated in this work.

CONCLUSIONS

Under the conditions of this study, carbon black/organic polymer composite vapor detectors displayed a linear steady-state relative differential resistance signal in response to changes in the concentration of analyte vapor in the gas phase. This behavior was observed relative to either an air background or a background that contained an organic solvent vapor in air. Moreover, the steady-state relative differential resistance response patterns produced by an array of carbon black/polymer composite detectors upon exposure to a test series of binary mixtures of analytes were the arithmetic sums of the maximum relative differential resistance responses that were obtained upon independent exposure of the array to each individual component of the mixture. This behavior implies that, under our test conditions, a relatively simple algorithm and training set, based on identifying a solvent vapor through its pattern type and quantifying the vapor concentration through the pattern height, would be sufficient to identify and quantify the test vapors and test vapor mixtures studied in this work.

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SUPPORTING INFORMATION AVAILABLE

Statistics for all of the sensor−analyte combinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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