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Vapor Sensing with Arrays of Carbon Black-Polymer Composites

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ABSTRACT

Thin films of carbon black-organic polymer composites have been deposited across two metallic leads, with swelling-induced resistance changes of the films signaling the presence of vapors. To identify and classify vapors, arrays of such vapor-sensing elements have been constructed, with each element containing a different organic polymer as the insulating phase. The differing gas-solid partition coefficients for the various polymers of the sensor array produce a pattern of resistance changes that can be used to classify vapors and vapor mixtures. This type of sensor array has been shown to resolve all organic vapors that have been analyzed, and can even resolve H_2O from D_2O. Blends of poly(vinyl acetate) and poly(methyl methacrylate) have been used to produce a series of sensors that respond to vapors with a change in resistance of a magnitude that is not simply a linear combination of the responses of the pure polymers. These compatible blend composite detectors provided additional analyte discrimination information relative to a reference detector array that only contained composites formed using the pure polymer phases. Vapor signatures from chemicals used in land mine explosives, including TNT, DNT, and DNB, have been detected in air in short sampling time and discriminated from each other using these sensor arrays.

INTRODUCTION

Prior work in our lab has utilized broadly responsive sensor array,s based on carbon black composites[1-3] for various vapor detection tasks. In this approach, individual sensor elements are constructed from films consisting of carbon black particles dispersed into insulating organic polymers. The carbon black endows electrical conductivity to the films, whereas the different organic polymers are the source of chemical diversity between elements in the sensor array. Swelling of the polymer upon exposure to a vapor increases the resistance of the film, thereby providing an extraordinarily simple means for monitoring the presence of a vapor.[1,4-10] Because different polymer compositions are present on each sensor element, an array of elements responds to a wide variety of vapors (or complex mixtures of vapors) in a distinctive, identifiable fashion. The electrical resistance signals that are output from the array can be readily integrated into software- or hardware-based neural network processors, allowing for an integration of sensing and analysis functions into a compact, low-power, simple vapor sensor.

RESULTS

A typical set of polymers used to construct an array is given in Table 1.

Table 1. Polymers Used in Sensor Array

Sensor #	Polymer
1	poly(4-vinyl phenol)
2	poly(styrene - co - allyl alcohol), 5.7% hydroxyl
3	poly(α-methylstyrene)
4	poly(vinyl chloride - co - vinyl acetate), 10% vinyl acetate
5	poly(vinyl acetate)
6	poly(N -vinylpyrrolidone)
7	poly(carbonate bisphenol A)
8	poly(styrene)
9	poly(styrene - co - maleic anhydride), 50% styrene
10	poly(sulfone)
11	poly(methyl methacrylate)
12	poly(methyl vinyl ether - co - maleic anhydride), 50% maleic anhydride
13	poly(vinyl butyral)
14	poly(vinylidene chloride - co - acrylonitrile), 80% vinylidene chloride
15	poly(caprolactone)
16	poly(ethylene - co- vinyl acetate), 82% ethylene
17	poly(ethylene oxide)

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The normalized signal response, S', of the 17 chemiresistors in the array for 60 s exposures to methanol, ethyl acetate, and benzene is shown graphically below. The concentrations of each solvent vapor were: benzene: 16.4±0.7 ppt; ethyl acetate 16.0±0.6 ppt; methanol: 21.2±0.8 ppt. Each recorded S value is the average of six separate exposures. As a visualization aid, each sensor's relative differential resistance response was individually normalized by dividing the $\Delta R_{max}/R$ value observed for exposure to a particular vapor by the sum of that sensor's $\Delta R_{max}/R$ responses to methanol, ethyl acetate, and benzene. The normalization factors (in %) are given parenthetically following the sensor numbers. For instance, for sensor #1, $\Delta R_{max}/R$ was 0.12 (i.e., 12%) in response to methanol. The fingerprints for the three solvents are clearly different, demonstrating the ability of this array to distinguish these vapors.
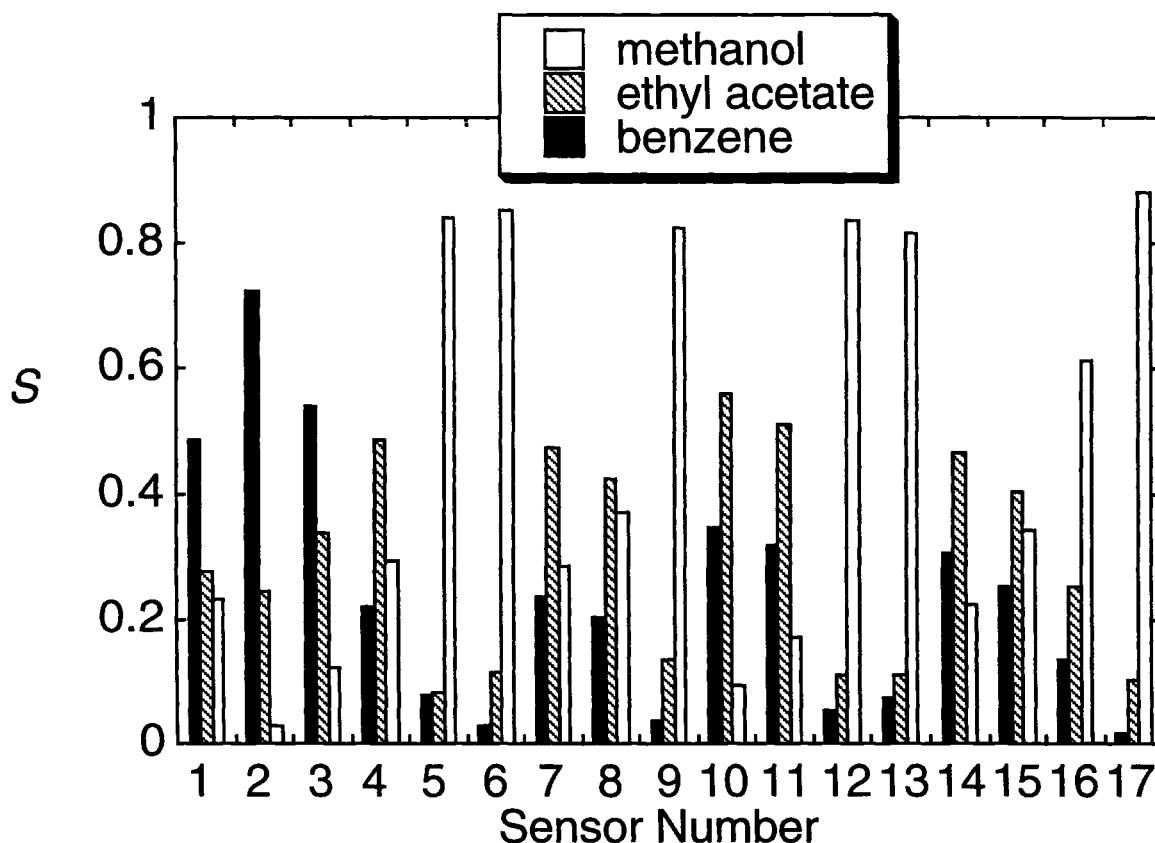
The Fisher linear discriminant method[11] was used to analyze the data collected. A resolution factor for any solvent pair can be obtained along any vector, $\vec{w}$, from the vector projection onto $\vec{w}$ of the distance between the cluster centroids, $d_{\vec{w}}$, divided by the sum of the projected standard deviations, $\sigma_{a,\vec{w}}$ and $\sigma_{b,\vec{w}}$, for the data arising from repeated exposures to the two vapors, a and b. The resulting numerical resolution factor along $\vec{w}$ is defined as:

$$\text{rf} = \frac{d_{\vec{w}}}{\sqrt{\sigma_{a,\vec{w}}^2 + \sigma_{b,\vec{w}}^2}} \ . \tag{2}$$

The Fisher linear discriminant searches for the projection vector, $\vec{w}$, in detector space which maximizes the pairwise resolution factor for each set of analytes, and reports the value of rf along this optimal linear discriminant vector. It can be shown that this rf value is an inherent property of the data set and does not depend on whether principal component space or original detector space is used to analyze the response data. This resolution factor is basically a multi-dimensional analogue to the separation factors used to quantify the resolving power of a column in gas chromatography, and thus the rf value serves

as a quantitative indication of how distinct two patterns are from each other, considering both the signals and the distribution of responses upon exposure to the analytes that comprise the solvent pair of concern.

Assuming a Gaussian distribution relative to the mean value of the data points that are obtained from the responses of the array to any given analyte, the probabilities of correctly identifying an analyte as a or b from a single presentation when a and b are separated with resolution factors of 1.0, 2.0 or 3.0 are approximately 76%, 92% and 98% respectively. Since the multiple exposures to each analyte allow only an estimate of the statistical distributions of the clustered data, the resolution factors can be overestimated. The overestimations will typically be less than 30% in the cases involving a fourteen-detector array, decreasing to approximately 3% in the cases involving single-detector arrays. However, especially large rf's should be interpreted cautiously as these could be overestimated by larger amounts. Autoscaling has no effect, and thus was not used, in the evaluation of the array resolving power using the Fisher linear discriminant methodology.

Resolution factors for organic vapors range from about 10 for pairs of very similar molecules up to over 200 for disparate pairs of molecules. An average resolution factor from a 20-sensor array for a pair of organic molecules is 80-100, corresponding to an extremely high confidence in identifying an unknown belonging to one of the two groups. A pair of extremely similar molecules was sought to challenge the resolving ability of the polymer array. One hundred exposures each to H_2O and D_2O were collected, and the resolution factor between the two was calculated to be about 9. The data was evenly divided into a test and training set, and all unknown exposures were correctly identified as H_2O or D_2O.

Polymer Blends

Improved target recognition and clutter rejection is expected when increased diversity is incorporated into the array of sensors. In this fashion, there ought to always be some set of sensors that can probe molecular properties that can uniquely identify clutter from the desired target signal. To explore increasing sensor diversity through use of combinations of commercial materials, blends of poly(vinyl acetate) and poly(methyl methacrylate) have been used to produce a series of sensors. These sensors were then exposed to ethyl acetate, ethanol, acetonitrile, acetone, and methanol. For each analyte, a statistically significant nonlinearity was observed for the detector response vs. the mole fraction of the base polymer feedstocks. Since the nonlinearity is not the same for all solvents, this indicates that useful information is available through use of such compatible blend materials in a detector array for vapor classification.

A different metric, closely related to Fisher's linear discriminant, was used to evaluate the performance of the polymer-blend sensors. Instead of projecting the data onto an optimized $\vec{w}$ vector, it was instead projected onto the vector that passes through the means of the two analytes under study. This simplified metric was selected because of its ease of calculation. It is important to realize that the results are coupled to the metric used to evaluate the responses, and different algorithms, such as Fisher's linear discriminant, which are linear data analysis methods that are not confined to pass through the mean response values of the analytes of concern,[11] may well yield different conclusions from the same response data. The detector responses were autoscaled to account for the different dynamic ranges of different detectors. The autoscaled response of the jth detector to the ith exposure, A_{ij}, was thus

$$A_{ij} = \frac{\Delta R_{ij,max} / R_b - \alpha_j}{\beta_j} \ . \tag{1}$$

where α_j and β_j are the mean and standard deviation, respectively, in the responses of the jth detector to all analytes.

The responses produced by a set of 99 detectors, 14 detectors with pure PMMA, 10 with 11% PVA, 10 with 28% PVA, 15 with 44% PVA, 10 with 64% PVA, 15 with 78% PVA, 10 with 91% PVA and 15 with pure PVA, were investigated using this approach. The performances of 8-detector combinations from different sets of detectors were evaluated to determine if arrays containing some of the compatible blend polymer detectors would perform better than arrays containing only detectors made from the base polymers, for certain test tasks. The performance of each studied array was measured by its ability to pairwise resolve the solvents, as given by the calculated rf values obtained using the simple linear data analysis method described above.

Results are presented for four sets of detectors. Set A contained all 14 detectors with 0% PVA and all 15 detectors with 100% PVA (i.e. all the base polymer detectors). Set B contained all 99 of the prepared detectors ranging from 0% through to 100% PVA content. Set C contained only the 10 detectors with 91% PVA. Set D contained all 14 of the 0% PVA detectors, all 10 of the 91% PVA detectors and all 15 of the 100% PVA detectors. Since there are extremely large numbers of possible 8-detector combinations from within sets A, B and D ($\approx 10^{11}$ unique 8-detector combinations out of 99 set B detectors), 500 member subsets of the total number of 8-detector array combinations were selected randomly and their corresponding rf values were calculated. For set C, rf values for all 45 possible 8-detector combinations out of 10 detectors were calculated. The results of the calculated resolution factors for arrays of 8-detectors within each set were averaged and presented in Table 2.

Clearly, the inclusion of compatible blend detectors produced a statistically significant improvement in maximizing the overall average rf, which is the average ability of all calculated 8-detector array combinations within a set of detectors to

resolve all analyte pairs using the metric defined above. For example, sets B, C and D, which contained compatible blend detectors, had overall average rf's of 60, 81 and 60, respectively, whereas the base polymer detector arrays (set A) had an overall average rf of 52. The array performance in separating the pair of solvents, ethyl acetate vs. acetone, that was worst resolved by set A (base polymer detectors) could also be improved by using 8-detector arrays containing only 91% PVA detectors (set C) or by including these detectors into arrays that contained the base polymer detectors (set D). Set D arrays, containing blended polymers, exhibit a larger overall average rf, a larger rf for the worst resolved analyte pair, and resolved 7 of the 10 analyte pairs better than did the base polymer arrays of set A.

The results presented in Table 2 show that each of the 4 detector sets produce arrays with at least one advantage over the others, such as the ability to resolve at least one analyte pair better than the other selected arrays. This reinforces the concept that more detector diversity is desirable, since it provides a larger basis of chemically unique detectors from which to tailor arrays for specific tasks.

Table 2. Comparison of performance of polymer blend-based arrays.

sensors used	overall average rf	methanol vs. ethanol	methanol vs. ethyl acetate	methanol vs. acetonitrile	methanol vs. acetone	ethanol vs. ethyl acetate
set A	52	25	61	90	44	58
set B	60	19	67	104	81	67
set C	81	4.6	122	102	181	103
set D	60	23	84	93	60	82
		ethanol vs. acetonitrile	ethanol vs. acetone	ethyl acetate vs. acetonitrile	ethyl acetate vs. acetone	acetonitrile vs. acetone
set A		93	42	58	20	27
set B		110	81	31	17	26
set C		93	148	16	31	8.7
set D		96	58	55	22	26

Sensing of Nitroaromatics for Land Mine Detection

The excellent sensitivity of the Caltech electronic nose and its ability to differentiate between compounds which have only subtle structural variations makes it an attractive device for sensing nitroaromatic vapors. These compounds, the vapors of which are smelled by land mine detecting dogs, are challenging targets for any sensing method because they posses very low volatility and are similar structurally (Figure 2). Our initial efforts have focused primarily on the most plentiful components of the headspace above TNT-based land mines: 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 1,3-dinitrobenzene (DNB).
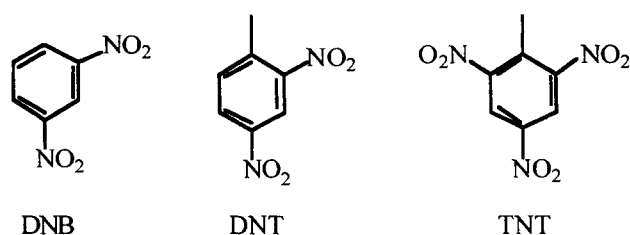

DNB   DNT   TNT

Figure 2. Nitroaromatic components in the headspace above TNT-based land mines.

Room temperature detection of compounds with low volatility was initially quite challenging because of the slow kinetics associated with partitioning into the polymeric sensors. The problem was ultimately solved by utilizing thin films of polymer-carbon black composites deposited by spray deposition onto ceramic substrates. This problem is illustrated for films of polycaprolactone responding to benzophenone (Figure 3).
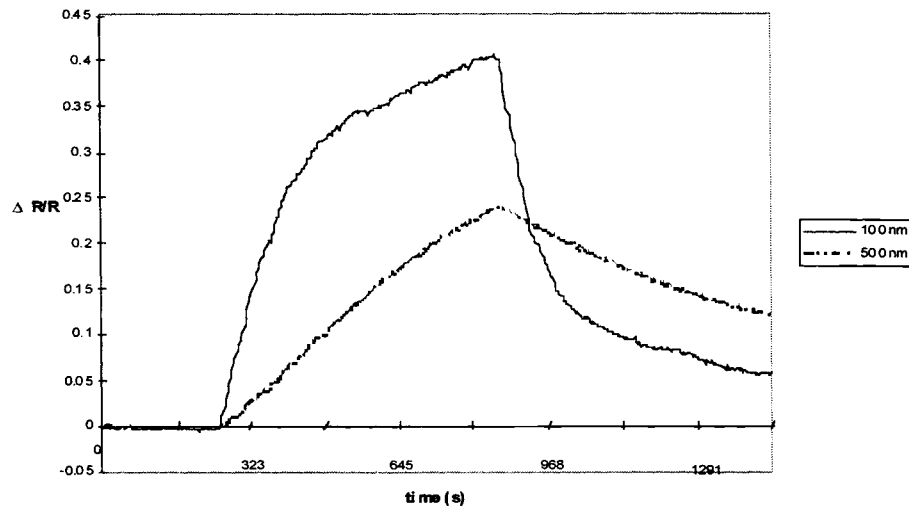
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Figure 3. Effect of film thickness on response time of polycaprolactone films to benzophenone.

Utilizing thin films of the polymer-carbon black composites allowed room temperature detection of nitroaromatics. Resolution factors for these nitroaromatics from each other and from a few organic solvents were determined for three minute exposures to saturated vapors. The results clearly show that these compounds can be detected and resolved at room temperature using an array of four different polymers: polyethylene-co-vinyl acetate, polycaprolactone, polymethyloctadecylsiloxane, and polystyrene-co-butadiene. The magnitude of the resolution factors was found to roughly correlate with the chemical similarity of the compounds with the smallest resolution factors being observed between TNT and the other nitroaromatics.

	DNT	TNT	toluene	hexanes	ethanol
DNB	32.64	11.47	26.68	32.50	25.88
DNT		10.43	40.45	43.15	28.80
TNT			30.17	53.69	46.46
toluene				93.99	161.30
hexanes					137.06

Figure 4. Resolution factors for various nitroaromatic compounds.

To aid in our efforts to develop efficient nitroaromatic sensors commercial polymers were screened for their ability to sorb DNT. The partition coefficients (α) were determined by quartz crystal microbalance and are expressed as mass of analyte per mass of polymer divided by grams of analyte per cc of air. The values vary by less than two orders of magnitude. These results confirm predictions that the dominant effect in determining the partitioning of a giving analyte into a polymer is the fraction of the vapor pressure to which the sensor is exposed and not the absolute vapor pressure of the analyte, as described in a previous general evaluation of the factors that control the sensitivity of these sorption devices to a variety of compounds.
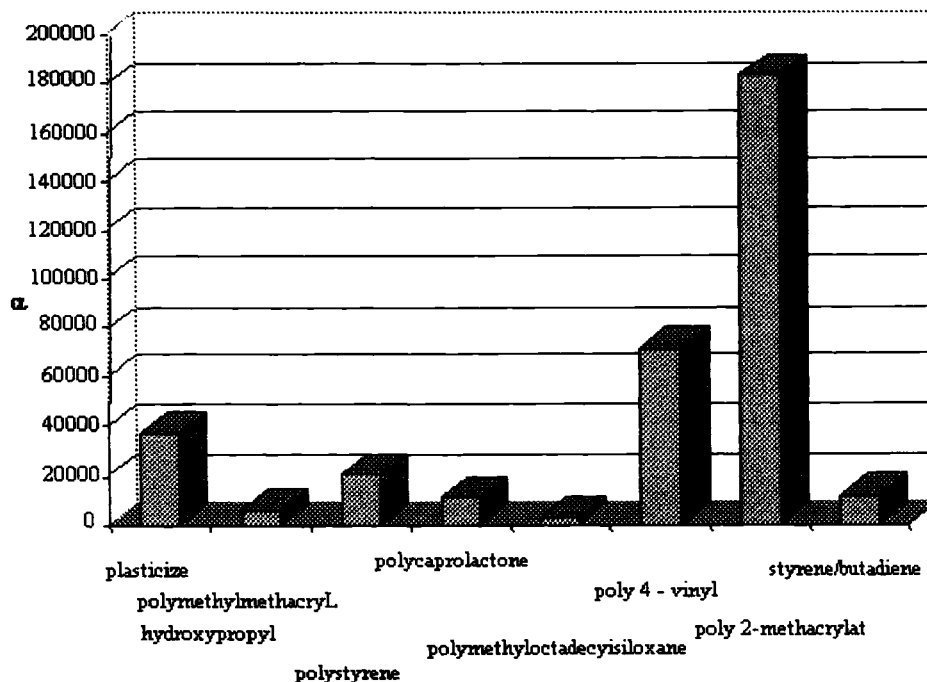
Figure 5. Partition coefficients for DNT into various polymers.

The final goal is to improve the response time to nitroaromatic vapors as well as to increase the detection limits/sensitivity of the sensors. The response time can be improved through better control over vapor transport and sampling to and through the boundary layer to the sensors, while the sensitivity can be improved through use of more sensors, less noisy sensors, and novel signal transduction mechanisms that provide up front gain to the sensor/signal transduction events. Work in all of these areas is being pursued at present and will be described in future reports.

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