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ABSTRACT

We describe herein the construction of a simple, low-power, broadly responsive vapor sensor. Carbon black-organic polymer composites have been shown to swell reversibly upon exposure to vapors. 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 the same carbon black conducting phase but 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 common organic solvents, including molecules of different classes (such as aromatics from alcohols) as well as those within a particular class (such as benzene from toluene and methanol from ethanol).

1. INTRODUCTION

Conventional approaches to chemical sensors have traditionally made use of a "lock-and-key" design, wherein a specific receptor is synthesized in order to bind strongly and highly selectively to the analyte of interest. A related approach involves exploiting a general physicochemical effect selectively toward a single analyte, such as the use of the ionic effect in the construction of a pH electrode. With both of these approaches, selectivity is achieved through precise chemical design of the receptor site. Such approaches are appropriate when a specific target compound is to be identified in the presence of controlled backgrounds and interferences. However, this type of approach requires the synthesis of a separate, highly selective sensor for each analyte to be detected. In addition, this type of approach is not particularly useful for analyzing, classifying, or assigning human value judgments to the composition of complex vapor mixtures such as perfumes, beers, foods, mixtures of solvents, etc.

An alternative approach to chemical sensing is closer conceptually to a design widely proposed for the mammalian sense of olfaction.[1,2] In such an approach, the strict "lock-and-key" design criterion of traditional sensing devices is abandoned. Instead, in this alternative sensor architecture, an array of incrementally different sensors is used, with every element in the sensor array chosen to respond to a number of different chemicals or classes of chemicals.[3-8] The elements of such an array should contain as much chemical diversity as possible, so that the array responds to the largest possible cross-section of analytes. Although in this design identification of an analyte cannot be accomplished from the response of a single sensor element, a distinct pattern of responses produced over the collection of sensors in the array could provide a fingerprint that would allow classification and identification of the analyte. The advantage of this approach is that it can yield responses to a variety of different analytes, including those for which the array was not originally designed. In addition, the broadly responsive sensors need not incorporate synthetically challenging, custom-designed, "lock-and-key" receptor sites in order to generate a response to an analyte. Also, an array of sensors naturally performs an integration to yield a unique signal for complex but distinctive odors (e.g., cheeses, beers, etc.) without requiring that the mixture be broken down into its individual components prior to, or during, the analysis.

We describe herein a simple, broadly responsive sensor array, based on carbon black composites[9-11] and demonstrate that this array can classify, detect, and quantify various test vapors and vapor mixtures. The 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.[9,12-18] Since 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 (Figure 1a). 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.
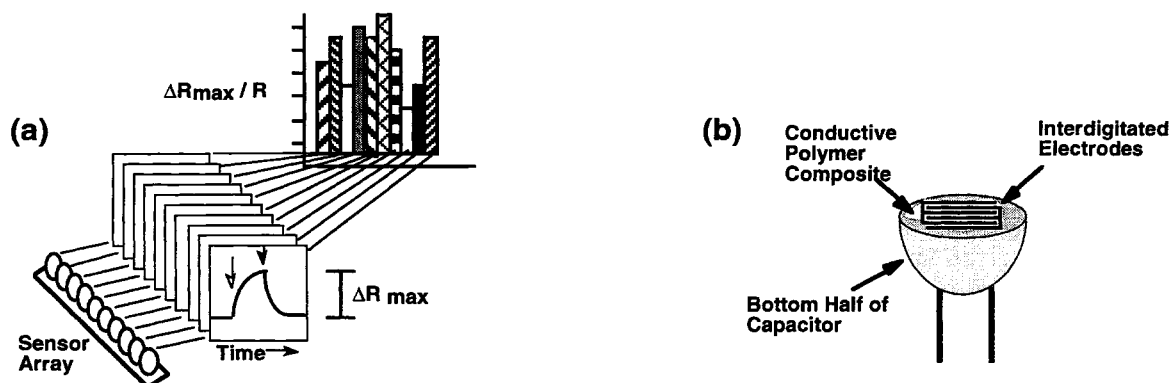

Figure 1. (a) Schematic of a chemiresistor sensor array and the response profiles generated by such an array. In this work, an array of 17 conducting carbon black-polymer composites has been used (the polymers of the composites are listed in Table 1). The resistance of each composite is monitored and observed to increase upon swelling by organic vapors. The open arrow in the schematic is a time marker corresponding to the introduction of solvent vapor and the solid arrow to its removal. The maximum relative differential resistance changes ($\Delta R_{max}/R$) for the elements of the array during exposure to the test vapor provide a fingerprint that can be used to classify various analytes. (b) Schematic showing a cleaved capacitor substrate.

Array-based vapor sensing has been demonstrated previously in several systems, including those using surface acoustic wave devices,[8,19-21] tin oxide sensors,[7,22,23] and conducting organic polymers.[24-26] In general, desirable design criteria for the elements of such an array are as follows: (1) they should readily transduce environmental information into an easily monitored signal, using a minimum of hardware and energy; (2) they should exhibit reversible, reproducible responses with a minimum of baseline drift; (3) they should be broadly tunable to respond in a predictable manner to a wide range of chemical species and concentrations; (4) they should be easily fabricated, preferably from inexpensive, commercially-available materials using well-established techniques; (5) they should permit miniaturization to facilitate the construction of compact sensors with a large number of elements; and (6) they should be robust and stable in many different environments. SnO_2 gas sensors[7,22,23] are among the most well-established sensing elements, and several commercial "electronic noses" have been based on SnO_2 arrays.[6] Although such arrays yield diagnostic responses for several gases, the incomplete understanding of catalytic processes at the doped SnO_2 surface makes chemical control of the response properties, and thus deliberate introduction of desired chemical diversity into the array, difficult to accomplish. Surface acoustic wave (SAW) devices are extremely sensitive to the presence of vapors, but involve somewhat sophisticated electronics to sustain surface Rayleigh waves in the piezoceramic crystals. Chemical diversity in a SAW array can be readily attained by coating the SAW crystals with different polymer films having differing gas-solid partition coefficients towards a vapor of interest. To our knowledge, primarily because of the electronic complexity involved in a SAW device and the resulting engineering challenges associated with micromanufacturing large numbers of such systems into an integrated system, the largest SAW array reported to date contains approximately 12 sensor elements.[8,19-21] In contrast, over 1000 receptor genes have recently been discovered in the mammalian olfactory system, and it is therefore estimated that the dimensionality of smell in humans is approximately 10^3.[27] There is thus great intellectual interest in constructing sensor arrays that have large numbers of chemically distinct sensor elements so that a large number of diverse sensing tasks can be accommodated within one array structure, and to investigate fundamentally the behavior of systems that are functionally, if not structurally, analogous to the mammalian olfactory response. Conducting organic polymers have also been used to form sensor arrays,[24,25] and commercial "electronic nose" devices have recently been announced using poly(pyrroles).[28] . However, since there are only a few classes of stable conducting polymers, and since to date the conducting polymers have been synthesized electrochemically to yield insoluble, intractable materials, additional variation in the array elements has been largely confined to changes in the counterion of the polymer or to the more synthetically challenging task of varying the substituents on the polymer backbone.

The scope of conducting polymer-based sensors has recently been broadened through the use of a set of polymer blends that possess a common conducting element, poly(pyrrole), for signal transduction, and a variety of insulating,

swellable, organic polymers to achieve chemical diversity in the array.[26] These devices have been shown to function quite well, but the long-term stability of poly(pyrrole) is of concern for practical use of such systems. The advantages of the approach described herein are that the conductive element is a very stable species, carbon black, and that chemical diversity in the sensor array can be readily obtained through the use of simply prepared, conventional organic polymers that function as the insulating phase of the carbon black composites. Individual carbon black composites have been widely explored as humidity sensors[9,13-15] and, to a somewhat lesser extent, as sensors for organic vapors or liquids such as gasoline.[12,16-18] To our knowledge, however, carbon black composites have yet to be incorporated into an array-based sensing configuration. In this paper, we demonstrate the feasibility of using carbon black-organic polymer composites in a broadly responsive, multi-component vapor sensor.

2. EXPERIMENTAL

2.1. 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 polymers used in the composites are listed in Table 1. All polymers were purchased from Polysciences Inc. or Aldrich Chemical Co. and were used as received. The solvents used in this study were toluene, benzene, ethyl acetate, methanol, ethanol, 2-propanol, hexane, chloroform and tetrahydrofuran (THF); all were reagent grade and were used as received from EM Scientific.

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(a-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)
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)

2.2. Apparatus

Standard glassware was used to construct a bubbler apparatus (to provide known partial pressures of various vapors) and a flow chamber to control the resulting gas stream. The bubblers were large test tubes (30 cm long with a 3 cm inside diameter) equipped with exit sidearms. To provide a pathway for gas flow, a glass tube terminated by a coarse filter frit was inserted into a rubber stopper and then placed into the top of each bubbler. The carrier gas was compressed air from the general lab source, and was neither filtered nor dehumidified. The measurements were performed at room temperature, which was in the range 22 ± 2 °C over the course of the experiments described herein. The carrier gas was introduced into the solvent through the porous ceramic frit, and the solvent-saturated gas mixture exited the bubbler via the sidearm of the glass tube. Saturation of the gas streams in our experimental apparatus was verified for the highest flow rates (1.0 L min^{-1}) used in this work through measurement of the rate of mass loss of liquid in the bubbler,[29] thus saturation conditions were assumed to have been obtained for the lower flow rates used in other experiments described in this work. The experimentally measured vapor pressures at the highest gas flow rate through the bubbler were within 2% of the values calculated from the literature[30] for the measured temperatures of the solvent in the bubblers during the period of gas flow. The experimentally measured vapor pressures, and corresponding solvent temperatures, were: acetone: 176 torr (19°C); benzene: 83 torr (22°C); chloroform:

158 torr (20°C); ethanol: 50 torr (22°C); ethyl acetate: 82 torr (22°C); hexane: 114 torr (19°C); methanol: 102 torr (21°C); 2-propanol: 37 torr (22°C); toluene: 25 torr (23°C). The saturated vapor was carried out the sidearm of the bubbler, blended with a controlled background flow of pure carrier gas and then introduced into a sensing chamber. This chamber consisted of a glass tube (22 cm long with a 2.6 cm inside diameter) to which inlet and outlet sidearms had been attached. The sensing elements were introduced into the chamber through a 24/40 taper ground glass opening attached at one end of the chamber. The chamber was then sealed with a ground-glass stopper through which the electrical lead wires had been sealed. The gas flow rates were controlled with needle valves and stopcocks.

2.3. Fabrication of substrates

Ceramic capacitors (22 nF, approx. 2 x 4 x 4 mm) from Kemet Electronics (Greenville, SC) were found to provide a very convenient electrical contact and physical support for the composite films of each sensor (see Figure 1b). First, the interdigitated electrodes inside the capacitor were exposed by using progressively finer grades of sandpaper and polishing paste to remove the top of the capacitor. During this process, the bulk of the material was removed with diamond-impregnated sanding paper on a sanding belt. The path of the grinding paper or paste was parallel to the interdigitated electrodes to avoid shorting the capacitor. Following the diamond paper treatment, the capacitors were sanded on a disk sander using 3M Tri-M-ite Fre-Cut, Open Coat, 360 grit paper. The tops of the capacitors were then polished on a 48-1581-BXXR polishing wheel (Buehler LTD, Lake Bluff, IL) using 0.3 mm diameter Buehler a-alumina micropolish grit. After the polishing step, the capacitors were sonicated in acetone or 2-propanol for 5-10 min to remove any residual alumina. All capacitors that were used as sensors had an initial resistance after polishing of greater than 10 MΩ (greater than the upper measurement limit of our ohmmeter).

2.4. Fabrication of composite films and individual sensor elements

Individual sensor elements were prepared by a single dip of the polished, cleaved capacitors into 10 mL solutions that contained 80 mg of dissolved polymer and 20 mg of suspended carbon black. After removal from the solution, any excess liquid was shaken off or blotted off, and the film was then dried in air prior to use. The solvent was generally THF, but benzene was the solvent for composites prepared from poly(ethylene - co - vinyl acetate) and poly(ethylene oxide), and dichloro-methane was the solvent for composites made from poly(caprolactone). Prior to immersion of the capacitor, the solutions were sonicated for 5-10 min to aid in the suspension of the carbon black.

2.5. Measurements

To determine the response of the sensor elements to various vapors, the dc resistance of each sensor was determined as a function of time. Resistance measurements were performed using a simple two-point configuration. Sensors fabricated with the capacitor supports were plugged directly into a 40 pin bus strip that was then connected to a multiplexing ohmmeter via a ribbon cable. Generally, resistance data were acquired using a Hydra 2620A Data Acquisition Unit (John Fluke Mfg. Co.) interfaced to a personal computer. All of the prepared samples had resistances less than the 10 MΩ limit of the Hydra 2620A.

To initiate an experiment, the sensors were placed into the glass chamber and a background flow of compressed air was introduced until the resistance of the sensors stabilized. Solvent vapor streams of various concentrations and compositions were then passed over the sensors. The flow rates in the bubblers were controlled using flow meters obtained from Gilmont Instruments, Inc., with the lower and upper limits of the flow meters being either 0.2 L min^{-1} and 15.0 L min^{-1}, 0.0010 L min^{-1} and 0.280 L min^{-1}, 0.0015 L min^{-1} and 0.310 L min^{-1}, or 0.0048 L min^{-1} and 0.673 L min^{-1} respectively. Analyte gas flows were kept low enough (< 1 L min^{-1}) to ensure that the vapor was saturated with solvent prior to dilution with the background gas. In a typical experiment, resistance data on the sensor array elements were collected for 1 min (to serve as a baseline), followed by a 0.25 - 1.5 min collection during exposure to the solvent vapor stream, and then were followed by a 5 min recovery time.

3. RESULTS

3.1. Sensor element response characteristics

Figure 2 shows the resistance change of a carbon black-polymer composite film during repeated, periodic exposures to a test solvent vapor. The resistance of the film increased when the solvent vapor was present and then returned to the original baseline value after the vapor flow was discontinued. For example, Figure 2 shows data for the exposure of a PVP (poly(N-vinylpyrrolidone))-carbon black composite film to 1.5 parts per thousand (ppt) methanol in air, 15 times interlaced with recovery periods. For the PVP composite, resistance changes of 2.95 ± 0.07 kΩ (2.28% of the baseline value) were

observed for exposure to methanol. The form of the time response of these sensors was representative of all sensor elements studied in this work, with response times under these experimental conditions generally varying from <2 s to 4 s for the film thicknesses used in this study (2 s was the minimum time resolution of the multiplexing ohmmeter in this experiment). As can be seen from the data of Figure 2, the baseline resistance value drifted by approximately <0.15% for the PVP composite over a 20 min time period. These relative resistance changes and baseline drift rates were representative of the behavior of all sensor elements studied in this work under these experimental conditions.
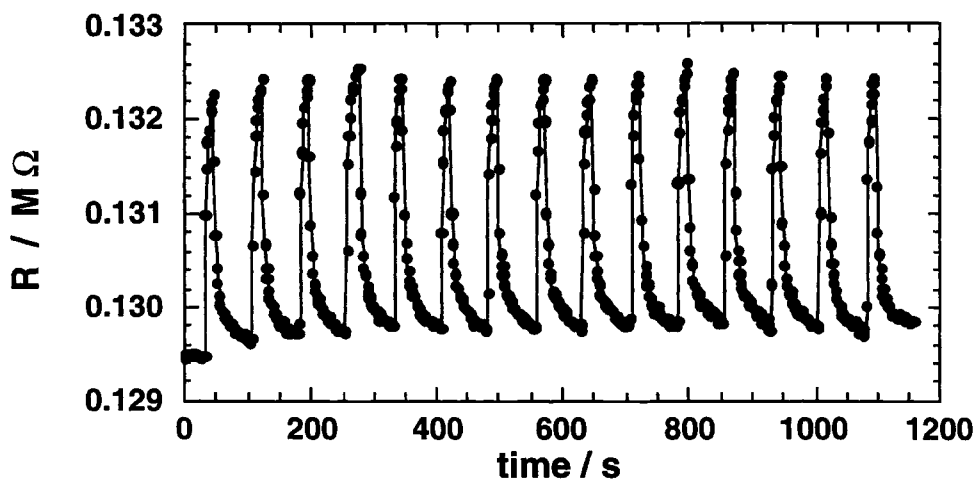

Figure 2. The resistances, R, of a PVP carbon black composite upon 15 repeated exposures to methanol (at 1.5 ppt). The PVP composite was fabricated from a 45% (w/w) carbon black mixture. The exposure periods were for 15 s during which time the resistances increased as shown. These exposures were interlaced between recovery periods in which the resistances decreased.

3.2. Array-based vapor sensing
3.2.1. Response patterns for various vapors

Although each individual sensor element had a characteristic relative differential resistance response, such data from an isolated sensor element would only be useful in a controlled environment that contained a single, known gas species. In more complex situations, data from a number of different sensors would be required. For this purpose, resistance data were obtained for arrays of carbon black-polymer composite sensor elements during exposure to various chemically different gaseous species.

To evaluate the performance of a modestly sized sensor array, a set of 17 carbon black-polymer composites was fabricated, with each sensor element having a different polymer in the composite (see Table 1). Modified capacitors served as substrates for the composite films in the sensor array. Air (at a flow rate of 1 L min^{-1}) saturated with one of nine common organic solvents: acetone, benzene, chloroform, ethanol, ethyl acetate, hexane, 2-propanol, methanol, or toluene was combined with a background air flow (6 L min^{-1}) and the mixture then introduced into a chamber containing the sensor array. This produced the following concentrations of each solvent: acetone: 49±2 ppt; benzene: 17.1±0.7 ppt; chloroform: 40±2 ppt; ethanol: 10.0±0.4 ppt; ethyl acetate 16.0±0.6 ppt; hexane: 29±1 ppt; methanol: 23.0±0.8 ppt; 2-propanol: 7.4±0.3 ppt; toluene: 4.7±0.2 ppt. Solvent vapors were introduced for 60 s, in random order, six times each (except for acetone, for which only three exposures were performed), over a total period of 10 h. Between vapor exposures, the sensors were exposed only to the solvent-free background flow (air) for a minimum of 6 min, although shorter recovery times could have been employed in most cases.

Figure 3 displays the normalized, relative differential resistance data for this array during exposure to three representative solvents: methanol, ethyl acetate and benzene. These three solvents have similar vapor pressures (113, 85, and 87 torr at 296 K, respectively) but the solvents clearly differ in their chemical properties. To facilitate comparison between various sensors, a normalized signal, S'_{sj}

$$S'_{sj} = \frac{\Delta R_{sj,\max} / R_j}{\sum_s (\Delta R_{sj,\max} / R_j)},$$ (1)

has been plotted, where s = methanol, ethyl acetate, or benzene, j is the sensor number, R_j is the baseline resistance of sensor j before exposure to the solvent, and $\Delta R_{sj,max}$ is the largest differential resistance change observed for the jth sensor during the 60 sec exposure to solvent s. For the film thicknesses and solvent concentrations used in this series of experiments, almost none of the sensors reached equilibrium so the recorded $\Delta R_{sj,max}$ value also incorporated temporal aspects of the resistance response of the array. Nevertheless, the histogram in Figure 3 clearly shows that the differential resistance response patterns generated by these solvents at this test pressure can be easily distinguished from each other using this modestly-sized sensor array.

The error bars in Figure 3 represent the standard error over the various exposures to each solvent. These experiments were conducted at much higher vapor concentrations than those in Figure 2. At these higher concentrations, small decreases in responses and/or shifts in baselines were observed upon repeated solvent exposures of certain composites, but the small baseline shifts could be compensated for electronically if so desired and such minor shifts did not preclude the use of the sensor array, even under these stressing conditions, to separate the various vapors based on their array responses. The error bars depicted in Figure 3 reflect this effect , and also incorporate errors due to instabilities in our flow system and random errors in the resistance measurements. The presence of impurities in the background air stream, such as oil vapor from the compressed air source used to provide the carrier gas flow, would only minimially affect the data of Figure 3 since any signals arising from the presence of such impurities would be present in the resistance readings taken before and after exposure to the test vapors. Additionally, a slow baseline drift was also noted for most sensors. Over a three month period under ambient conditions, the baseline resistances of the composites in our 17-element array increased an average of 16%, with the maximum increase being 55% (for poly(vinyl chloride - co - vinyl acetate)) and the minimum being <1% (poly(methyl vinyl ether - co - maleic anhydride), although this baseline drift did not significantly affect the $\Delta R/R$ performance of the sensor array.
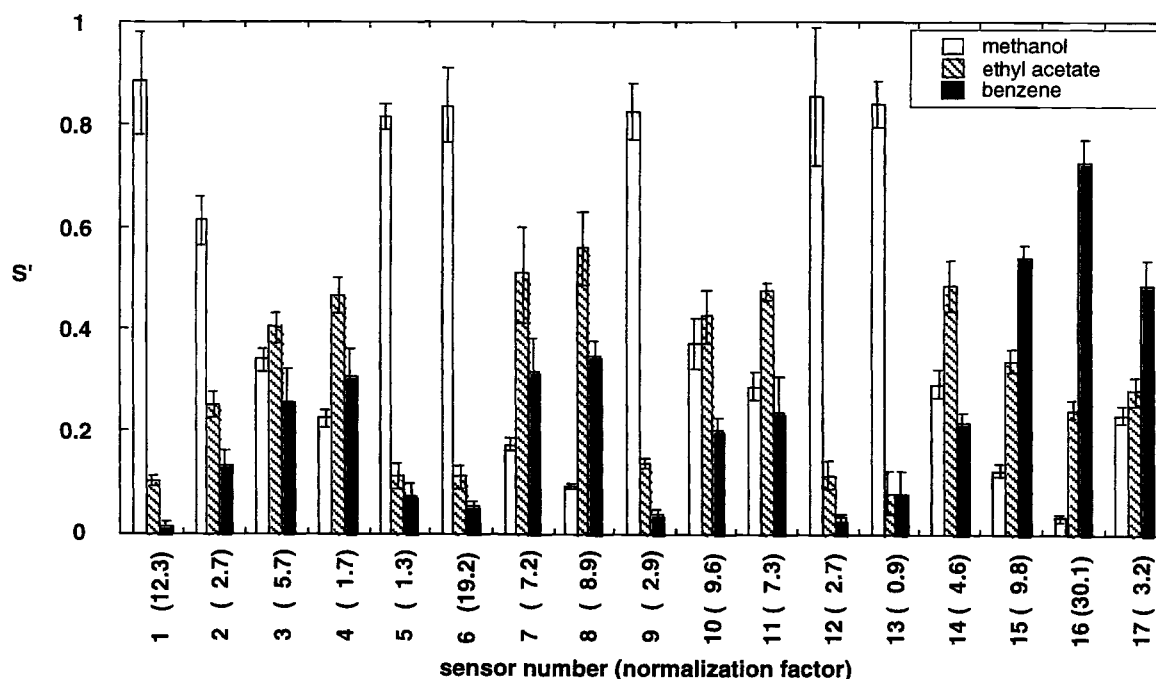

Figure 3. The normalized signal response, S', of the 17 chemiresistors in the array (see Table 1) for 60 s exposures to methanol, ethyl acetate, and benzene. The concentrations of each solvent vapor were: benzene: 16.4±0.7 ppt; ethyl acetate 16.0±0.6 ppt; methanol: 21.2±0.8 ppt. Each recorded S value 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.

3.2.2. Principal component analysis for data reduction of an array response

A more quantitative approach to evaluating the performance of the sensor array is provided by principal component analysis. Principal component analysis transforms multivariate data sets into a coordinate space that allows for the variance in the data to be represented in the minimum number of dimensions. The vectors in this new coordinate set are the principal components of the data stream, and the separation between various vapors (e.g., various presentations to the array) is therefore readily visualized in this transformed data space.[31,32]

The principal components are linear combinations of descriptors (in our case, the relative differential resistance responses):

$$\mathbf{P} = \mathbf{DC}, \tag{2}$$

where $\mathbf{D} = \{d_{ij}\}$ and $\mathbf{P} = \{p_{ij}\}$ are $m \times n$ matrices and $\mathbf{C} = \{c_{ij}\}$ is an $n \times n$ matrix containing the coefficients of the linear combination. For a sensor array (with n sensors) exposed m times to various analytes, d_{ij} represents the response of the jth sensor to the ith exposure and p_{ij} the jth principal component for the ith exposure. The power of principal component analysis stems from the fact that the coefficient matrix, $\mathbf{C}$, (containing as its columns the eigenvectors of the covariance matrix $\mathbf{D}^T\mathbf{D}$) is chosen such that the principal components are mutually orthogonal, even though the original descriptors may have been heavily correlated.

Prior to performing principal component analysis, the data from the 17-element sensor array were normalized and autoscaled. The maximum differential resistance change for the jth sensor to the ith exposure, $\Delta R_{ij,max}$, was normalized by the sum of the responses for all 17 sensors to that same exposure to produce a value S_{ij}:

$$S_{ij} = \frac{\Delta R_{ij,\text{max}}}{\sum\limits_j \Delta R_{ij,\text{max}}} \tag{3}$$

where S_{ij} is the normalized signal. This normalization involves a summation over the entire array for a given exposure rather than over a collection of exposures for a given sensor, as in eq 1. The normalization of eq 3 helps correct for differences in the exposure concentrations, which are a consequence of the solvents' differing vapor pressures. In the limit of linear response, the normalization process assures that the solvents are not being distinguished on the basis of their concentrations alone. The normalized maximum relative differential resistance changes were then autoscaled, resulting in a set of descriptors, d_{ij}, that were defined as:

$$d_{ij} = \frac{S_{ij} - \bar{S}_j}{\sigma_j} \tag{4}$$

Here, $\bar{S}_j$ and σ_j are the mean and standard deviation, respectively, of all of the normalized signal responses of sensor j to the entire range of solvents. This autoscaling procedure provides a means of accounting for differences in the dynamic ranges of the sensors. After normalizing and autoscaling, the data were transformed into principal component space. The principal components were numbered in accord with the amount of variance they contained: the lower the number, the more variance contained along that direction in principal component space.

The first five principal components (Figure 4) contained greater than 98% of the total variance in the data. The patterned areas in Figure 4 encompass all of the responses of the array that were produced during the repeated exposures to each specified vapor. The representation in principal component space clearly shows not only that, at the test concentrations used in this work, the carbon black-polymer composite array can readily distinguish nonpolar from polar solvents (e.g., benzene or toluene from methanol or acetone) but also illustrates that such an array can readily distinguish members of a related class of materials (e.g. methanol from ethanol from 2-propanol, or benzene from toluene). A notable feature of this

type of sensing device is that the sensor elements were not designed *a priori* to have specific responses to any particular vapor or class of vapors, yet the array could nevertheless separate a broad range of chemical species having relatively subtle differences in their chemical/physical properties.
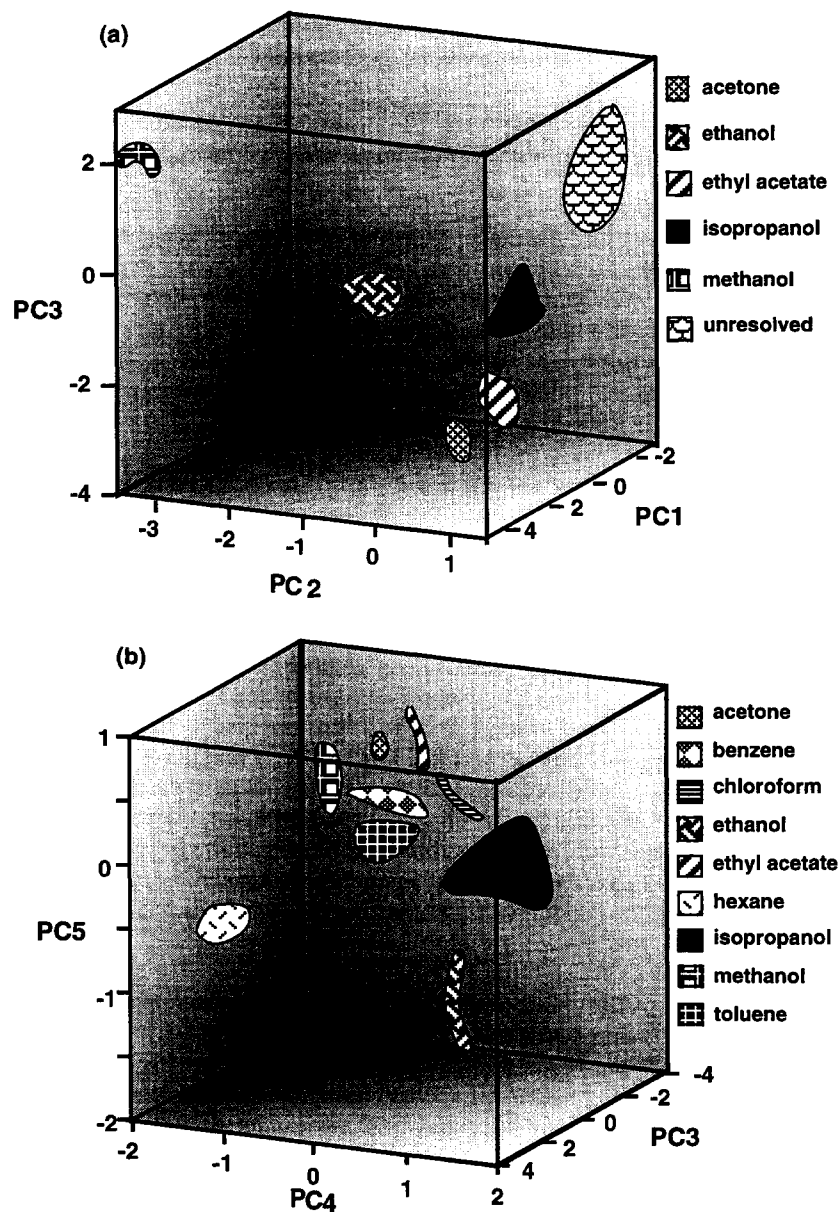

Figure 4. The results from the exposure of the 17-element array to nine solvents as represented in (a) the first three dimensions of principal component space, and (b) the third, fourth and fifth dimensions of principal component space. These five principal components contain over 98% of the total variance in the data. The concentrations of each solvent vapor were: acetone: 40 ± 2 ppt; benzene: 16.4 ± 0.7 ppt; chloroform: 34 ± 2 ppt; ethanol: 10.0 ± 0.4 ppt; ethyl acetate 16.0 ± 0.6 ppt; hexane: 26 ± 1 ppt; methanol: 21.2 ± 0.8 ppt; 2-propanol: 7.5 ± 0.3 ppt; toluene: 4.9 ± 0.2 ppt. Each patterned region contains six points corresponding to six exposures of each solvent, except for acetone which only contained data for three exposures. The unresolved region in PC1-PC2-PC3 space contains the responses to benzene, chloroform, hexane, and toluene. Each loci of

points for each solvent occupies a unique region of principal component space, indicating that the array distinguished all nine test analytes.

3.3. Classification and identification of vapors using the chemiresistor array

The success of modestly-sized arrays of chemically sensitive resistors in the detection and classification of vapors underscores the advantages of an approach to chemical sensing that utilizes broadly responsive sensing elements. The use of a common conducting phase, combined with the use of conventional insulating organic polymers to achieve the differential swelling properties of the various sensor elements, allows fabrication of such arrays from readily available, stable materials. An additional attractive feature of the present system is the simplicity of the signal transduction process. A chemical sorption event is directly transduced into an electrical resistance signal that can be readily integrated with inexpensive, conventional, signal processing circuitry.

Despite the lack of chemical specificity in the binding of an analyte to an individual array element, the carbon black-polymer composite chemiresistor array discriminated between a variety of vapors, some of which displayed very subtle chemical differences. This array also was able to identify and quantify the vapor mixture tested in this initial study. In fact, the 17-element carbon black-based sensor array was able to distinguish all of the nine test analytes from each other at the specific test concentrations used in this work, even though this test set required distinguishing molecules from very different classes, such as alcohols from aromatics, as well as those within a particular class, such as benzene from toluene or methanol from ethanol from 2-propanol.

The ability to resolve various vapors is quantified by their separation in principal component space. The best resolved vapors generally showed the largest separation in the early principal components, i.e., in those components containing the most variance in the data. For exposure of our array to the nine test analytes at the test concentrations used in this work, the first five principal components (shown in Figure 4) contained 49%, 25%, 17%, 4%, 2%, and 1%, respectively, of the total variance. The greatest resolution was observed between the polar compounds, which were distinguished in the first three dimensions of principal component space (Figure 4a). This is reasonable because nearly all of the sensor elements were reasonably polar, with many being able to participate in hydrogen bonding, so gas-solid interactions based on polarity dominated the binding of the various analytes into the composite films of the sensor array. The more non-polar molecules were separated collectively from the polar compounds in the first three principal components, but separation of the non-polar compounds from each other was based on more subtle effects. These effects only become evident through an analysis of the higher principal components of the sensor array response (see Figure 4b). Of course, principal component analysis is a purely statistical approach to data reduction, and a neural network could easily be trained, without additional array design, to assign an increased weighting to the response of certain sensors if the primary function of the array were, for example, to separate benzene from toluene. Even restricting the data evaluation to principal component analysis, resolution of non-polar analytes should improve significantly with the incorporation of additional sensor elements having composite films fabricated from carbon black and non-polar organic polymers.

Ideally, the swelling-induced relative differential resistance response of each of the chemiresistors could be related to solubility parameters that correlate with the partition coefficients for binding of a given vapor into a given polymer film. Such a correlation has been drawn for the swelling of a commercial carbon black-polymer composite with a variety of saturated vapors.[16] For some of our chemiresistors, the relative differential resistance response did indeed track with the extent of swelling predicted by solubility parameters. For other chemiresistors, however, the agreement between maximum relative differential resistance changes and solubility parameters was poor. There was some difficulty in drawing definitive conclusions from our experiments because the vapor concentrations for the nine solvents were different (thus requiring correction based on linear response) and because the short exposure times used to investigate the array responses to various vapors did not permit equilibrium to be reached on the sensor elements at the test concentrations and composite film thicknesses used in this study. However, as long as the exposure period was maintained constant, the data of Figures 3 and 4 show that the various vapors could be distinguished even without reaching an equilibrium differential resistance signal (which could be obtained in a specified time period through use of thinner films, if so desired). The data of Figure 3 do qualitatively show the selectivity of the sensors for different solvents and demonstrate that these responses agree with simple chemical ideas. For instance, the $\Delta R_{max}/R$ response of the protic poly (4-vinyl phenol) composite, sensor #1, to methanol was 55 times greater than that its response to benzene. The situation is reversed for one of the non-polar sensor elements, PEVA (sensor #16), with benzene producing a 42 times larger $\Delta R_{max}/R$ signal than methanol. Note that although it is possible to analyze the data to ascertain which subset of sensor elements provided the "best" discrimination for a given pair of

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vapors, this assessment is very task-dependent (i.e., the "best" subset of sensors for separating benzene from toluene are different from the "best" subset of sensors for separating methanol from ethanol and are different yet again from the "best" subset of sensors for separating benzene and toluene in the presence of methanol or ethanol, etc.), so this type of evaluation has not been performed extensively at this time.

Further improvements in the resolving power of the sensor array are expected when the temporal information provided by each solvent is incorporated into the data analysis algorithm. The time course of the resistance change is a potentially valuable additional discriminant because it will reflect the diffusion rate of a vapor into a particular film.[33] In fact, the concentration of $CHCl_3$ or CCl_4 above a poly(vinyl chloride)-carbon black composite has been determined previously on the basis of temporal response information alone and potentially can take advantage of data involving specific molecular interactions that affect the binding and diffusion kinetics of various analytes into the sensor elements.[18] We are currently investigating the best means by which test analytes can be classified by our sensor array; however, since it is unlikely that a single algorithm will be optimal for all tasks on a given sensor array, we have not pursued this scenario-specific analysis extensively at the present time.

4. CONCLUSIONS

A broadly responsive, easily monitored vapor sensor has been developed using thin film, carbon black-polymer composites. The chemiresistor elements have been shown to give distinctive, low-power, dc, signal patterns in response to the presence of test concentrations of various organic solvent vapors. This type of sensor is inexpensive and easily fabricated. Furthermore, the ease with which it can be modified as well as customized for specific chemical and environmental monitoring tasks makes it potentially attractive for such applications.

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REFERENCES

(1)   Lancet, D.; Ben-Arie, N. *Curr. Biol.* **1993**, *3*, 668.
(2)   Reed, R. R. *Neuron* **1992**, *8*, 205.
(3)   Lundstrom, I.; Erlandsson, R.; Frykman, U.; Hedborg, E.; Spetz, A.; Sundgren, H.; Welin, S.; Winquist, F. *Nature* **1991**, *352*, 47.
(4)   Zaromb, S.; Stetter, J. R. *Sens. Actuators* **1984**, *6*, 225.
(5)   Shurmer, H. V.; Gardner, J. W. *Sens. Actuators B* **1992**, *8*, 1.
(6)   Gardner, J. W.; Bartlett, P. N. *Sens. Actuators B* **1994**, *18*, 211.
(7)   Gardner, J. W.; Shurmer, H. V.; Tan, T. T. *Sens. Actuators B* **1992**, *6*, 71.
(8)   Nakamoto, T.; Fukuda, A.; Moriizumi, T. *Sens. Actuators B* **1993**, *10*, 85.
(9)   Norman, R. H. *Conductive Rubbers and Plastics*; Elsevier: Amsterdam, 1970.
(10)   *Carbon Black-Polymer Composites*; Sichel, E. K., Ed.; Marcel Dekker, Inc.: New York, 1982.
(11)   Medalia, A. I. *Rubber Chem. Tech.* **1986**, *59*, 432.
(12)   Ford, C. J. In U.S. Patent 2,691,134, 1951; pp .
(13)   Newton, R. G. *J. Rubber Res.* **1946**, *15*, 35.
(14)   Sands, A. G.; McDowell, M. V. *Rubber Age, New York* **1956**, *80*, 500.
(15)   Boyd, J.; Bulgin, D. *J. Text. Inst. Proc.* **1957**, *48*, 66.
(16)   Lundberg, B.; Sundqvist, B. *J. Appl. Phys.* **1986**, *60*, 1074.
(17)   Ruschau, G. R.; Newnham, R. E.; Runt, J.; Smith, B. E. *Sens. Actuators* **1989**, *20*, 269.
(18)   Talik, P.; Zabkowskawaclawek, M.; Waclawek, W. *J. Mater. Sci.* **1992**, *27*, 6807.
(19)   Ballantine, D. S.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, *58*, 3058.

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

(21)   Grate, J. W.; Rosepehrsson, S. L.; Venezky, D. L.; Klusty, M.; Wohltjen, H. *Anal. Chem.* **1993**, *65*, 1868.

(22)   Gardner, J. W.; Shurmer, H. V.; Corcoran, P. *Sens. Actuators B* **1991**, *4*, 117.

(23)   Corcoran, P.; Shurmer, H. V.; Gardner, J. W. *Sens. Actuators B* **1993**, *15*, 32.

(24)   Shurmer, H. V.; Corcoran, P.; Gardner, J. W. *Sens. Actuators B* **1991**, *4*, 29.

(25)   Pearce, T. C.; Gardner, J. W.; Friel, S.; Bartlett, P. N.; Blair, N. *Analyst* **1993**, *118*, 371.

(26)   Freund, M. S.; Lewis, N. S. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 2652.

(27)   Merrifield, R. B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 799.

(28)   Nunez, E. M.; Myerson, A. S.; Kwei, T. K. *Polym. Eng. Sci.* **1991**, *31*, 1172.

(29)   Sarin, V. K.; Kent, S. B.; Mitchell, A. R.; Merrifield, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 7845.

(30)   Merrifield, R. B. *Makromol. Chem.* **1988**, *19*, 31.

(31)   Hecht, H. G. *Mathematics in Chemistry: An Introduction to Modern Methods*; Prentice Hall: Englewood Cliffs, NJ, 1990.

(32)   Gardner, J. W. *Sens. Actuators B* **1991**, *4*, 109.

(33)   *Diffusion in Polymers*; Crank, J.; Park, G. S., Ed.; Academic Press: London and New York, 1968, pp 452.