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Progress in the development of an electronic nose using arrays of chemically sensitive, carbon black-polymer resistors

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ABSTRACT

Response data were collected for a carbon black-polymer composite electronic nose array during exposure to homologous series of alkanes and alcohols. At a fixed partial pressure of odorant in the vapor phase, the mean response intensity of the electronic nose signals varied significantly for members of each series of odorants. However, the mean response intensity of the electronic nose detectors, and the response intensity of the most strongly-driven set of electronic nose detectors, was essentially constant for members of a chemically homologous odorant series when the concentration of each odorant in the gas phase was maintained at a constant fraction of the odorant's vapor pressure. Because the thermodynamic activity of an odorant at equilibrium in a sorbent phase is equal to the partial pressure of the odorant in the gas phase divided by the vapor pressure of the odorant, and because the activity coefficients are similar within these homologous series of odorants for sorption of the vapors into specific polymer films, the data imply that the trends in detector response can be understood based on the thermodynamic tendency to establish a relatively constant concentration of sorbed odorant into each of the polymeric films of the electronic nose at a constant fraction of the odorant's vapor pressure. This phenomenon provides a natural mechanism for enhanced sensitivity to low vapor pressure compounds, like TNT, in the presence of high vapor pressure analytes, such as diesel fuel. In a related study to evaluate the target recognition properties of the electronic nose, a statistical metric based on the magnitudes and standard deviations along Euclidean projections of clustered array response data, was utilized to facilitate an evaluation of the performance of detector arrays in various vapor classification tasks. This approach allowed quantification of the ability of a fourteen-element array of carbon black-insulating polymer composite chemiresistors to distinguish between members of a set of nineteen solvent vapors, some of which vary widely in chemical properties (e.g. methanol and benzene) and others of which are very similar (e.g. n-pentane and n-heptane). The data also facilitated evaluation of questions such as array performance as a function of the number of detectors in the system.

1. INTRODUCTION

We have previously reported the use of carbon black-polymer composites for array-based vapor sensing applications.[1] In such an array, no individual detector responds solely to a specific molecule, but the collective response of the entire array of detectors yields a unique fingerprint for the vapor of interest. Such arrays are often referred to as "electronic noses" and are not designed in advance to perform a specific task, but are instead developed to identify and quantify vapors based on pattern recognition algorithms.[2-7] This approach to vapor sensing takes advantage of the collective output of an array of broadly responsive detectors. In the polymer composite array configuration, the signal transduction is extremely simple: swelling of the polymeric phase of the composite, in the presence of a vapor, leads to an increase in the electrical resistance of the composite, which is monitored using simple electronics. The pattern of responses produced by an array of chemically different carbon black-polymer composites identifies the odorant, and the pattern height is correlated with the odorant concentration. The resistance change of a detector is reversible, is linear over at least an order of magnitude of odorant concentration, and is quite reproducible.[1]

In this work, we have measured the response intensities of an electronic nose,[1] based on an array of carbon black polymer composite detectors, to straight chain alkanes and alcohols. Lower sensitivity is observed towards relatively higher vapor pressure odorants, and higher sensitivity is observed towards lower vapor pressure analytes. This provides a built-in advantage in detecting lower vapor pressure odorants. We use a fundamental, first-order explanation for the observed trends in response intensity of the detectors in the electronic nose, based on the thermodynamic tendency for odorants to partition into sorbent phases as a function of the odorant's vapor pressure.

In addition, a statistical metric was used to quantify the resolving power of detector arrays, and to evaluate how array resolving power improves as the number of detectors increases. It has been hypothesized that a fairly small number of

detectors is sufficient to span odor space (a multi-dimensional space, containing all odorants, where every possible orthogonal chemical difference between any two odorants is represented by a separate dimension).[8] Small numbers of carefully chosen detectors are thought to be optimal because it is hypothesized that additional detectors add noise, but not classifying ability, to the data produced by a well-designed detector array. In contrast, others have hypothesized that it is desirable to have as many detectors as possible in an array.[9,10] Current research suggests that in mammalian olfaction there are approximately 10^3 different receptor genes and approximately 10^7 total receptor cells.[11] Thus, it is not clear whether functional models of the mammalian olfactory system can be satisfactorily constructed with a small detector basis set or whether such models will require thousands, or even millions, of different detector compositions. A quantitative measure (i.e. a metric) of the resolving power of a detector array as a function of the number of detectors in the system can allow evaluation of some of these questions in a meaningful fashion.

2. EXPERIMENTAL

The electronic nose is an array of vapor detectors, with each detector consisting of a dispersion of carbon black particles in a swellable, insulating organic polymer film. The composite films used in the homologous odorant series experiments were cast by dipping surface mount universal boards (surfboards, part number 6012 from Capital Advanced Technologies Inc.) into solutions containing 20 mL of solvent, 40 mg of suspended Black Pearls 2000 carbon black (Cabot Co., Billerica, MA) and 160 mg of dissolved polymer, and then allowing the films to dry. The thirteen polymers (Aldrich and Polysciences), each used for a different detector, in this portion of the study were: poly(4-vinyl phenol), poly(α-methyl styrene), poly(vinyl acetate), poly(sulfone), poly(caprolactone), poly(ethylene-co-vinyl acetate) (82% ethylene), poly(ethylene oxide), poly(ethylene), poly(butadiene), poly(vinylidine fluoride), poly(n-butyl methacrylate), poly(epichlorohydrin) and poly(ethylene glycol). To explore the detector response vs. analyte vapor pressure relationships, the detectors were exposed to the various odorants at partial pressures equal to 10% of their vapor pressures in air. The odorants and their concentrations were: n-pentane at $6.0 \cdot 10^1$ parts per thousand (ppth), n-hexane at $1.7 \cdot 10^1$ ppth, n-heptane at 5.1 ppth, n-octane at 1.6 ppth, n-nonane at 0.49 ppth, n-decane at 0.15 ppth, n-dodecane at 0.014 ppth, n-tetradecane at 0.0011 ppth, methanol at $1.4 \cdot 10^1$ ppth, ethanol at 6.5 ppth, 1-propanol at 2.2 ppth, 1-butanol at 0.75 ppth, 1-pentanol at 0.26 ppth, 1-hexanol at 0.096 ppth, 1-heptanol at 0.021 ppth and 1-octanol at 0.0077 ppth.

In studying the odorant resolving power of arrays, a different detector fabrication method was used, with different polymers. Substrates for the carbon black-polymer detectors were made by cutting Corning micro glass slides into 10 mm x 25 mm strips. Two gold electrodes, each $\approx$ 50 nm thick, 10 mm wide and 10 mm long, were evaporated onto the ends of each slide. A gap of 5 mm was left between the electrodes and this region was used to probe the resistance of the carbon black-polymer composite films. To prepare the carbon black-polymer composites, 40 mg of carbon black and 160 mg of one of the insulating polymers (poly(4-vinyl phenol), poly(vinyl chloride-co-vinyl acetate), poly(N-vinylpyrrolidone), poly(vinyl acetate), poly(methyl vinyl ether-co-maleic anhydride), poly(carbonate bisphenol A), poly(styrene), poly(sulfone), poly(methyl methacrylate), poly(vinylidene chloride-co-acrylonitrile), poly(caprolactone), poly(ethylene-co-vinyl acetate), poly(ethylene oxide) or poly(9-vinylcarbazole)) were added to 20 mL of solvent. The solvent was generally tetrahydrofuran, but benzene was the solvent for detectors prepared from poly(ethylene-co-vinyl acetate) and poly(ethylene oxide), and dichloromethane was the solvent for detectors made from poly(caprolactone). The solutions were sonicated for 5 min to suspend the carbon black, and the films were then cast by dipping a modified glass slide substrate into the solution and then removing the slide into air. The dipping procedure was repeated 2 or 3 times until a measurable film resistance was obtained. Before use, the detectors were dried in open air for 12-24 h and were then placed in air flowing at 7.5 L min^{-1} for 5 hours. The detectors were then exposed 12 times each to 19 odorants (1,2-dimethoxyethane, acetone, acetonitrile, anisole, benzene, butylamine, chloroform, cyclohexane, dichloromethane, ethanol, ethyl acetate, isopropanol, methanol, n-heptane, n-pentane, tetrahydrofuran, toluene, triethylamine and α,α,α-trifluorotoluene) in random order with a gas phase concentration of approximately 6.7 ppth.

The dc resistance of each detector was monitored as a function of time using a simple two-point resistance configuration. Electrical contacts were made to the detectors by pressure-contacting electrical leads using flat-jawed alligator clips. Resistance data were acquired using a multiplexing multimeter interfaced to a personal computer. A flow system was used to deliver the known analyte concentrations in air by dilution from their saturated vapor concentrations in air (at 20-23°C), as calculated from the literature vapor pressure values.[12]

3. RESULTS AND DISCUSSION

3.1. Responses to homologous series of n-alkane and 1-alcohol odorants

Straight chain alcohols and straight chain alkanes were investigated because they define two homologous series of odorants that vary regularly in their chemical properties as the carbon chain length is increased. Figures 1a and 1b display the responses, $\Delta R_{max}/R_b$, where R_b is the baseline resistance of the detector immediately prior to the exposure and ΔR_{max} is the amplitude of the maximum resistance change during the 5 minutes the detector was exposed to the odorant, for an array of carbon black-polymer composite detectors exposed to methanol, 1-butanol, 1-octanol, n-pentane, n-nonane and n-tetradecane at partial pressures, P, corresponding to 10% of the vapor pressure of the odorant, P^o. The different response patterns across the array of detectors correspond to differences in odor quality data produced by the electronic nose, while the signal intensities correspond to differences in odor intensity that are obtained from the raw, unprocessed signals of the detectors.
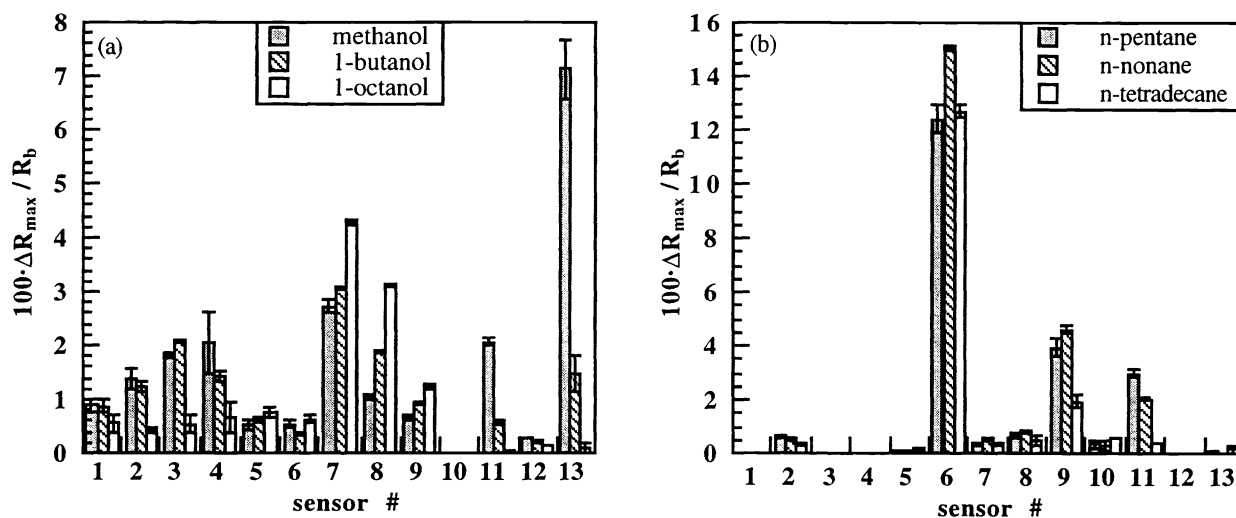

Figure 1. Histograms showing the response patterns of an array of 13 carbon black-polymer detectors exposed in air to (a) methanol at 11 torr, 1-butanol at 0.57 torr and 1-octanol at $5.8 \cdot 10^{-3}$ torr and (b) n-pentane at 46 torr, n-nonane at 0.37 torr and n-tetradecane at $8.5 \cdot 10^{-4}$ torr. The odorant partial pressures correspond to 10% of their vapor pressures in ambient air. Each histogram bar represents the average over 6 exposures of a single detector to a single odorant, with each exposure performed for 5 minutes. The error bars represent one standard deviation in the responses.

A striking feature of the electronic nose data is that, when the mean signal intensity, defined as the mean value of $\Delta R_{max}/R_b$ that was observed for all 13 detectors in the array upon exposure to an odorant, is plotted vs. the partial pressure of odorant present in the vapor phase, the electronic nose exhibits increased sensitivity (i.e. a similar response intensity to a lesser odorant concentration) to lower vapor pressure alkanes and alcohols (Figure 2a). The 13 polymers in the array of detectors (poly(4-vinyl phenol), poly(α-methyl styrene), poly(vinyl acetate), poly(sulfone), poly(caprolactone), poly(ethylene-co-vinyl acetate) (82% ethylene), poly(ethylene oxide), poly(ethylene), poly(butadiene), poly(vinylidine fluoride), poly(n-butyl methacrylate), poly(epichlorohydrin) and poly(ethylene glycol)) were chosen to include a broad range of chemical properties, thereby minimizing biases that would result from averaging the responses over sets of detectors that had a limited chemical diversity. Data are also displayed in Figures 2b and 2c for the largest responding detectors to the alkanes and alcohols, respectively. These data confirm the trend observed in Figure 2a, and show that the response intensity of an individual detector is relatively independent of the odorant in the series, if the odorant is present in the gas phase at a constant fraction of its vapor pressure. Thus, the electronic nose detectors produced nearly the same odor intensity from their raw signal outputs for $P=0.1 \cdot P^o$ of pentane ($P=46$ torr in 707 torr of air=61 parts per thousand) as they did for $P=0.1 \cdot P^o$ of tetradecane ($P=8.5 \cdot 10^{-4}$ torr in 707 torr air=1.1 parts per million).

The trends displayed in Figure 2 were also observed in an analysis of gas chromatography data. Retention volumes[13] for odorants having a wide range of vapor pressures were converted into gas/support partition coefficients,[14] K, and the data were collated for two selected stationary phases, one polar (tricresyl phosphate) and one nonpolar (squalane) in

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character. The values of log K for each odorant into each sorbent phase were then regressed against log P^o for every odorant in the data set. As displayed in Figures 3a and 3b, the regressions yielded straight lines with slopes of -0.87±0.07 and -0.80±0.04 and had r^2 values of 0.86 and 0.93 respectively. Taking a cut through the sample set to leave only odorants in either the alkane or alcohol homologous series yielded a much better fit to a straight line dependence of log K on log P^o. Slopes were approximately -1.0, and r^2 values were 1.0, for both the alcohol and alkane homologous series partitioning into both stationary phases. This reduction in variance is expected because the variation in chemically-based gas/support partition coefficients that contribute to the variance in the entire data set is reduced when only partition coefficients for a series of homologous odorants are considered. The activity coefficients at infinite dilution for these series of alcohols and alkanes in the two stationary phases are presented in Table 1.[13] It is apparent that the activity coefficients for members of each homologous series are relatively similar relative to the variation in vapor pressures, which spans many orders of magnitude, for each series of odorants.
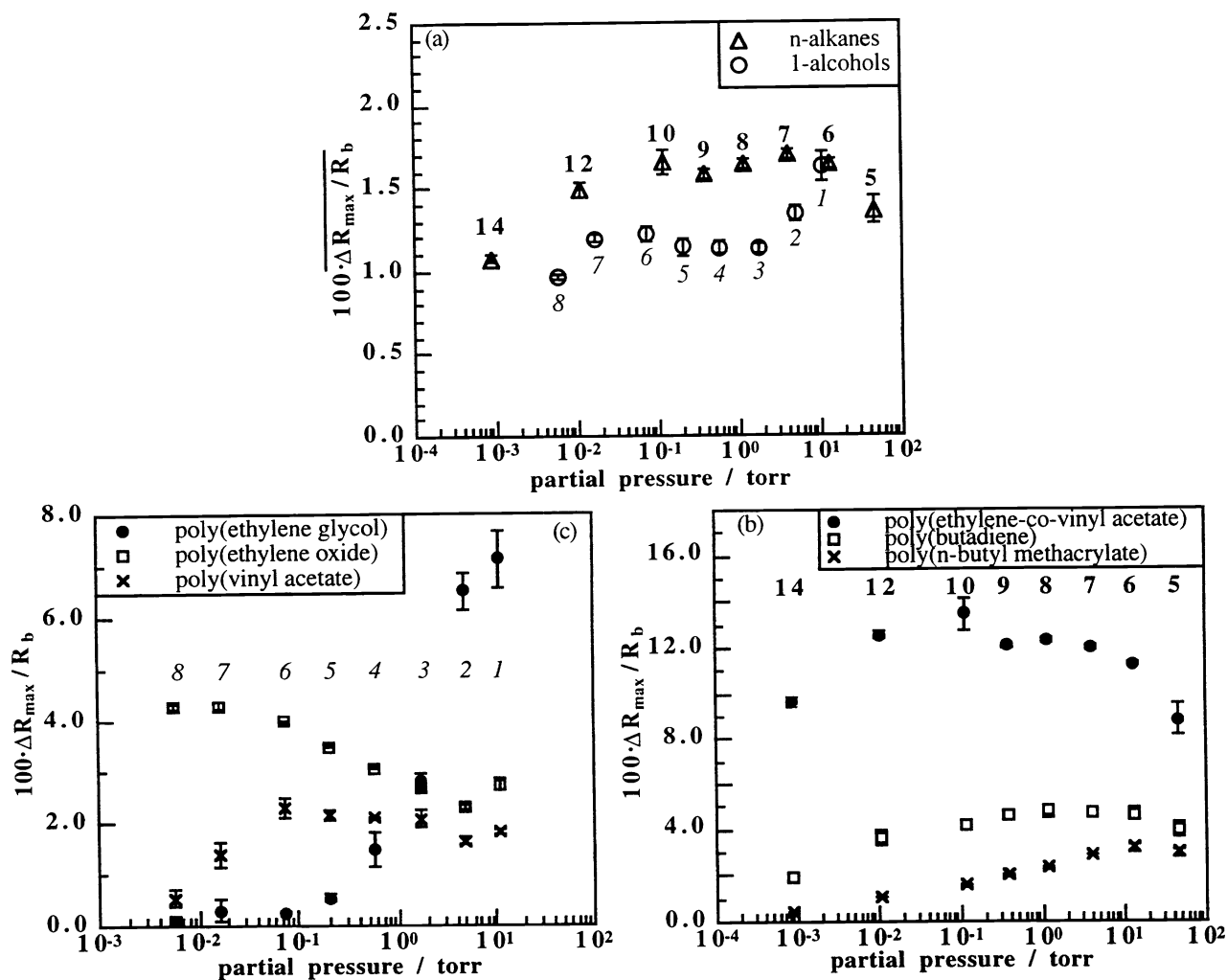

Figure 2. (a) The mean signal intensity, $\overline{\Delta R_{max}/R_b}$, defined as the average over all thirteen detector responses in the electronic nose array to an odorant, plotted versus the partial pressures of homologous series of alkane and alcohol odorants. (b) Responses, $\Delta R_{max}/R_b$, of three individual electronic nose detectors (poly(ethylene-co-vinyl acetate), poly(butadiene) and poly(n-butyl methacrylate) which produced the largest responses to a homologous series of straight chain alkanes, plotted versus the partial pressures of the odorants in each series. (c) Responses of three individual detectors (poly(ethylene glycol), poly(ethylene oxide) and poly(vinyl acetate)), which produced the largest responses to a straight chain homologous series of 1-alcohols, plotted versus the partial pressures of the odorants in each series. The alkanes used in (a) and (b) were: n-pentane,

n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane and n-tetradecane. The straight chain alcohols used in (a) and (c) were: methanol, ethanol, 1-propanol , 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. Each odorant was maintained at a partial pressure equivalent to 10% of its vapor pressure, and the background was ambient air. For clarity, the number of carbons in each odorant is indicated for each data point, in italics for the alcohols and plain text for the alkanes. The error bars represent one standard deviation unit in the 6 responses to each odorant.

Activity coefficient data were also culled from the literature[13,15] for some of the specific polymers in the electronic nose detectors. Data for poly(vinyl acetate), poly(ethylene oxide) and poly(ethylene glycol) are presented in Table 1. The activity coefficients at infinite dilution for the odorants within either the alcohol or alkane series, sorbed into these specific polymers, are clearly similar relative to the large variation in the vapor pressures of the odorants.
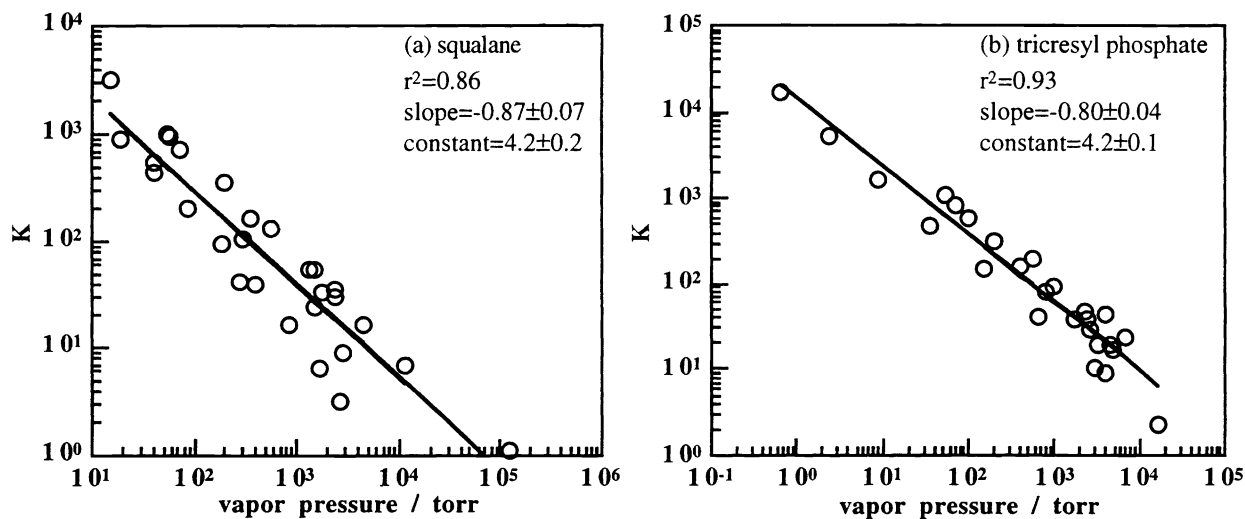

Figure 3. Plots of the partition coefficient, K, for an odorant sorbing into the stationary phases (a) squalane at 100 °C and (b) tricresyl phosphate at 120 °C, versus odorant vapor pressure. The values of K were computed from gas chromatography data.[13] The odorants plotted in (a) and (b) are: methanol, ethanol, acetone, dichloromethane, 1-propanol, ethyl acetate, 2,3-dimethylbutane, n-hexane, chloroform, 1-butanol, 2-chloroethanol, tetrachloromethane, benzene, 1-pentanol, cyclopentanone, toluene, n-octane, 1-hexanol, 1-heptanol, 2-octanol, n-decane, n-butane, 1-octanol and n-dodecane. Additional odorants plotted only in (a) are: ethane, m-diethylbenzene, o-diethylbenzene and o-xylene. Additional odorants plotted only in (b) are: ethylene glycol diacetate, n-hexadecane, n-tetradecane and n-octadecane. The solid lines represent the best line fits through the data points, with the fitting parameters given in the figures.

From these data, it can be seen that the polymer-based electronic nose clearly exhibits a characteristic displayed by the human olfactory system in that it discriminates against ambient background gases in air such as O_2, N_2, and CO_2, and is more sensitive, based on the partial pressure of odorant in the gas phase, to odorants having lower vapor pressures (Figure 2). A similar trend has also been noted previously in a qualitative study of the response of a different, polypyrrole-based, electronic nose detector array to fixed partial pressures of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol, but no explanation was advanced for the origin of the variation in mean signal response of this system.[16]

The primary trends observed in Figures 2 and 3 can be explained using simple thermodynamic principles. At equilibrium, the chemical potential, μ, of an odorant must be equal in both the sorbed and vapor phases.[17] The equilibrium mole fraction, χ, of the odorant in the sorbed phase is therefore related to the fraction of the vapor pressure of the odorant and to the chemical potential, by the relationships:[17]

$$\mu = \mu^O + RT\ln\gamma\,\chi \tag{1}$$

and

$$P/P^0 = a = \gamma\,\chi, \tag{2}$$

where μ^0 is the chemical potential of the odorant in its saturated vapor standard state, R is the gas constant, T is the temperature, γ is the odorant activity coefficient, and a is the odorant activity. If the activity coefficients, which account for

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the specific solvation interactions between the sorbent phase and the odorant molecules, are similar for odorants within a homologous series being sorbed into a given polymer, then the concentration of any member of the homologous odorant series sorbed into a specific polymer will be primarily determined by the fraction of the vapor pressure of the odorant in the gas phase, as opposed to being determined primarily by the absolute concentration of the odorant in the vapor phase.

This situation is consistent with observed response trends of the electronic nose detectors to the homologous series of alkane and alcohol odorants. The data in Table 1 suggest that the variation in the activity coefficients, within our two homologous series of odorants sorbing into the polymers used the electronic nose, is small relative to the variation in the vapor pressures across the homologous series. The data thus indicate that the relative changes in the signals produced by the polymer composite detectors in response to exposures to members of each homologous series of odorants studied herein are, to first order, independent of specific binding features of the odorant into the polymer phase and instead depend primarily on the equilibrium concentration of the odorant that is attained in the polymeric detector material.

Table 1. Activity coefficients for infinitely-dilute straight chain alkanes and 1-alcohols in specific gas chromatography stationary phases[13,15]

odorant	squalane[a]	tricresyl phosphate[b]	poly(vinyl acetate)[c]	poly(ethylene oxide)[d]	poly(ethylene glycol)[e]	odorant	squalane[a]	tricresyl phosphate[b]	poly(vinyl acetate)[c]	poly(ethylene oxide)[d]	poly(ethylene glycol)[e]
ethane	0.33					methanol	5.4	1.0	0.0049		0.63
butane	0.58	2.0			6.1	ethanol	4.1	1.3	0.0058	0.31	0.81
pentane				2.1		propanol	3.2	1.2	0.0081	0.29	0.93
hexane	0.73	2.6	0.030	2.6	12	butanol	2.9	1.2	0.0093	0.41	1.1
heptane			0.040	3.3		pentanol	2.5	1.2	0.011		1.2
octane	0.80	2.9	0.050	4.1	18	hexanol	2.5	1.2	0.013		1.5
nonane			0.082	5.2		heptanol	2.5	1.3	0.015		1.8
decane	0.88	3.6	0.095	6.5	27	octanol	2.6	1.3	0.018		2.2
unedecane			0.12	8.0		decanol			0.026		
dodecane	0.93	4.3	0.15	8.8	42						
tetradecane		5.1	0.23		66						
hexadecane		6.0	0.34		83						
octadecane		7.3			124						

[a]Temperature = 373 K, molecular weight = 422.8 g/mol. [b]Temperature = 393 K, molecular weight = 368.4 g/mol. [c]Temperature = 417 K, molecular weight ≈ 500000 g/mol. [d]Temperature = 352 K, molecular weight ≈ 1000 g/mol. [e]Temperature = 373 K, molecular weight ≈ 300 g/mol.

At a given odorant activity in the polymeric films, there must of course be some variation in sorbed odorant concentration, and in the resulting signal response, for different polymer types, otherwise it would be impossible to obtain odor quality information from the output of an array of sensing elements. In the electronic nose, differential sorption of odorants, with varying activity coefficients, into the various polymers produces a differential swelling, and therefore produces the differential $\Delta R_{max}/R_b$ output pattern of signals that can be used to identify odorants (Figures 1a and 1b). These differences in signal intensity are clearly due to specific chemical interactions between the odorant and polymer molecules, as reflected in the variation in activity coefficients, that act in conjunction with the sorption effects expected for an ideal sorbent/solute system to determine the response of an individual detector in the array to the odorant of concern. The data presented herein clearly show, however, that for the odorants studied in this work, the response intensity of the electronic nose detectors is determined, to first order, by the thermodynamic activity effects that dictate the concentration of odorant into the film, while the (smaller) deviations from the mean response intensity exhibited by the various individual detectors produce the outputs that can be used to extract odor quality information from the array. This behavior is critically important

for demining operations because the background is naturally rejected and the signal is enhanced for low vapor pressure compounds like TNT.

3.2. Quantifying Detector Array Performance

3.2.1. Data Processing

It is also important to quantify the ability of an array to discriminate between various odorants based on the different response patterns that each odorant produces. To do this, a series of odorants was presented to the detector array, and the responses were evaluated using conventional chemometric methods. In these experiments, although the resistance of each detector was sampled once every 3 seconds during each exposure, only the maximum relative differential resistance change, $\Delta R_{ij,max}/R_b$ where $\Delta R_{ij,max}$ is the maximum resistance change of the jth detector during the ith exposure and R_b is the baseline resistance of the detector prior to the exposure, was used in analysis of the data. A sample response for a carbon black-polymer composite detector is shown in Figure 4.
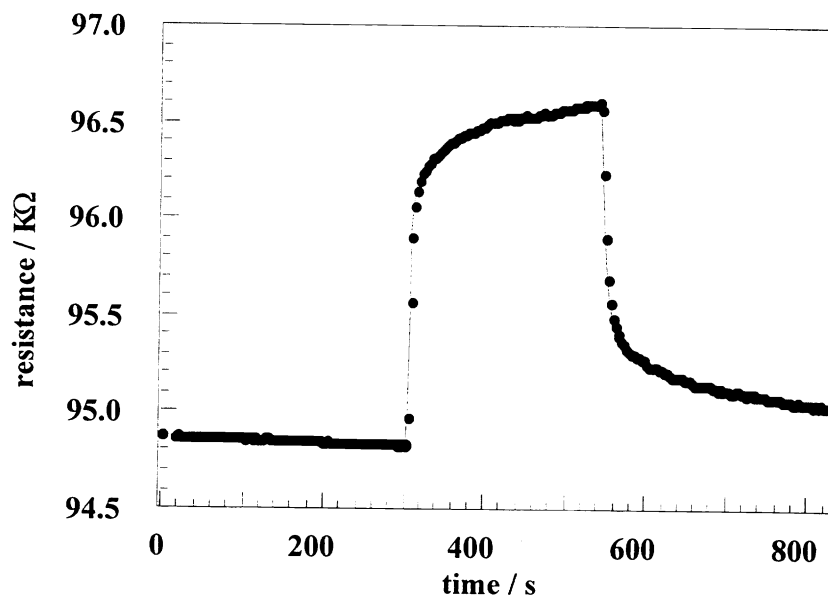

Figure 4. Resistances as a function of time during an exposure of a carbon black-poly(N-vinylpyrrolidone) composite detector to 6.7 ppth ethanol in air. The detectors were given 300 s before and after the exposure to achieve a stable baseline in air and 240 s to respond to the ethanol.

To analyze the data in a consistent fashion for different detectors and vapors, the responses for each individual detector were autoscaled[18] so that all detectors, regardless of their general response magnitudes, had the same operating range in the analysis of the data. The autoscaled response of the jth detector to the ith exposure, A_{ij}, was obtained from

$$A_{ij} = \frac{(\Delta R_{ij,max} / R_b) - \alpha_j}{\beta_j} .$$ (3)

The terms α_j and β_j represent the mean and standard deviation, respectively, of the maximum relative differential resistance response of the jth detector to the entire group of analytes.

The autoscaled patterns that resulted from exposure of fourteen carbon black-polymer composite chemiresistor detectors to acetonitrile, benzene or chloroform are depicted in Figure 5. Although these patterns are obviously different even to the untrained human eye, the goal of this work was to assess in a quantitative fashion the differences between such patterns.

3.2.2. Quantitative Statistical Metric

Neural networks were not used to analyze these differences because although the performance of neural networks in pattern classification can be superior to that of statistically based chemometric methods, the use of a neural network

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intimately couples the performance of a specific training/learning algorithm to the detector response data. A statistical measure of the differences between two clusters of patterns can be obtained by determining the distance between the centroids of the data arising from repeated exposures to a given vapor and dividing this distance by the sum of the standard deviations of the two different pattern clusters projected along the vector that connects these centroid points (Figure 6). It can be shown in a straightforward manner that this metric is independent of the coordinate system chosen to display the data and is instead an inherent, statistical property of the data set.
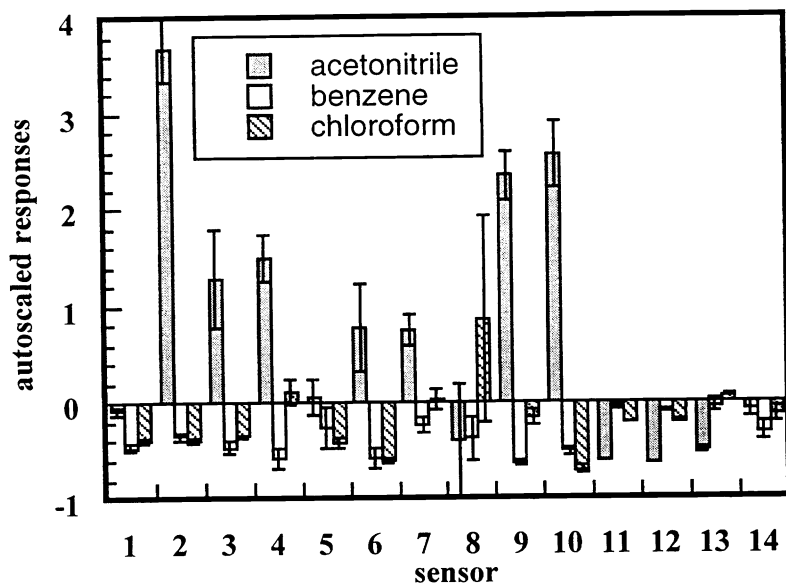

Figure 5. Autoscaled responses, A_{ij}, of the fourteen detectors in the carbon black-polymer composite array to approximately 6.7 ppth of benzene, chloroform and acetonitrile. Each bar represents the average autoscaled response over twelve exposures and the error bars represent the standard deviation in the responses.

$\vec{x}$ = mean response

σ = projected st.dev.

$$\vec{d} = \vec{x}_a - \vec{x}_b$$

$$rf = \frac{|\vec{d}|}{\sqrt{\sigma^2_{a,\vec{d}} + \sigma^2_{b,\vec{d}}}}$$
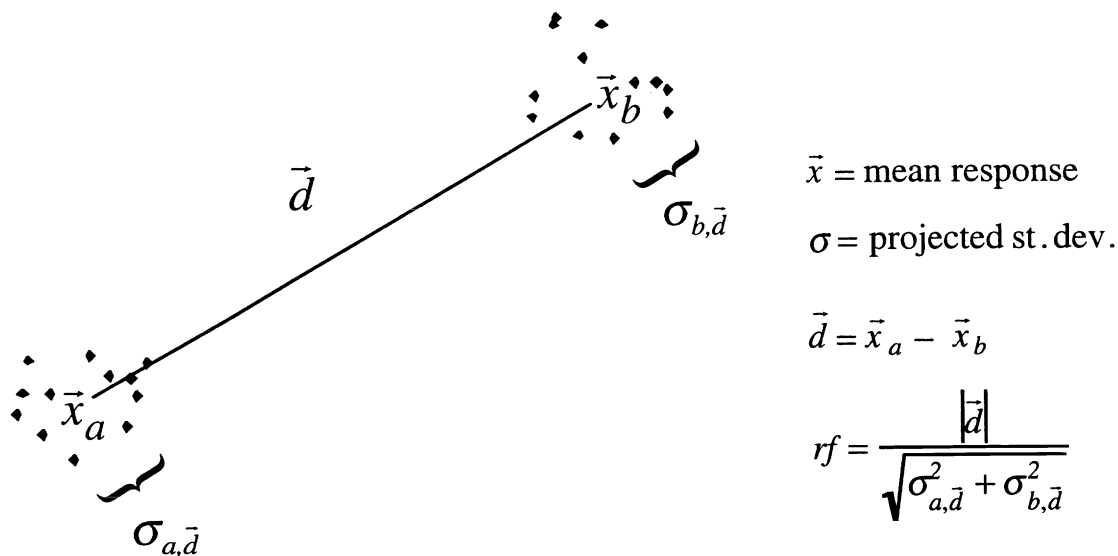
Figure 6. Mathematical definition of the resolution factor, rf, in multi-dimensional space.

From standard vector analysis, the mean response vector, $\vec{x}_a$, of an n-detector array to analyte a is given as the n-dimensional vector containing the mean autoscaled response of each detector, $\overline{A}_{aj}$, to the ath analyte as components such that,

$$\bar{x}_a = (\bar{A}_{a1}, \bar{A}_{a2}, ..., \bar{A}_{an}) . \tag{4}$$

The average separation, $|\bar{d}|$, between two analytes, a and b, in the Euclidean detector response space is then equal to the magnitude of the difference between $\bar{x}_a$ and $\bar{x}_b$. The noise of the detector responses is also important in quantifying the resolving power of the detector array. Thus the standard deviations, $\sigma_{a,\bar{d}}$ and $\sigma_{b,\bar{d}}$, obtained from all the individual array responses to each of a and b along vector $\bar{d}$, are used to describe the average separation and ultimately to define the pairwise resolution factor as

$$rf = \frac{|\bar{d}|}{\sqrt{\sigma_{a,\bar{d}}^2 + \sigma_{b,\bar{d}}^2}} . \tag{5}$$

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. This resolution factor is equivalent to that proposed by Müller[19] and recently used by Gardner and Bartlett[20] and is basically a multi-dimensional analogue to the separation factors used to quantify the resolving power of a column in gas chromatography.

3.2.3. Resolving Power of Detector Arrays at a Fixed Analyte Concentration

Table 2 presents the resolution factors obtained from an array of the fourteen carbon black-polymer composite detectors for all 171 pairs of the nineteen vapors. In general, the full array of carbon black-polymer detectors can easily resolve the odorant pairs presented at a fixed concentration.

It is also of interest to study the array performance, at resolving analytes at a fixed concentration, as a function of the number of detectors in the array. For this purpose, the ability of all possible combinations of 1 through 14 detectors in the array to resolve the analytes was calculated. As a performance criterion, the average resolution factor over all analyte pairs, for all combinations of n detectors, $\overline{rf}(n)$, was chosen. The results, plotted in Figure 7, show an increasing performance in this task with an increasing number of detectors.
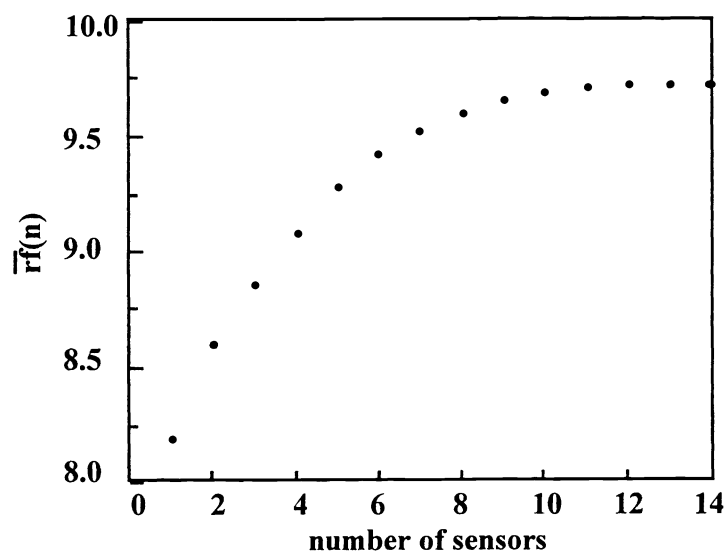

Figure 7. The average ability, of all array combinations of the specified number of carbon black-polymer composite detectors to resolve all 171 possible pairwise combinations of the nineteen analytes using autoscaled data.

The data therefore show that for a task where the clutter is variable or unknown in advance, such as land mine detection, in general increasing the number of detectors in the array will be beneficial in separating the target from the background. In addition, of course, an increase in the number of detectors will also result in improved signal/noise performance for the system as a whole, which will also produce an improvement in the resolving power of the array between the various odorants of concern. The exact functional form of the improvement in resolving power with increasing numbers

of detectors will be both task and detector dependent, and is the topic of ongoing work with respect to the land mine detection problem.

Table 2. Resolution factors quantifying the ability of the fourteen element carbon black-polymer composite detector array to resolve pairwise each of the nineteen vapors, at fixed concentration, from any other vapor in the test set. The average and worst pairwise resolution factors are 9.7 and 0.91, respectively.

	acetone	acetonitrile	anisole	benzene	butyl amine	chloroform	cyclohexane	dichloromethane	ethanol	ethyl acetate	isopropyl alcohol	methanol	n-heptane	n-pentane	thf	toluene	triethyl amine	trifluorotoluene
1,2-dimethoxy ethane	14	11	16	19	6.5	17	24	16	13	11	21	18	22	23	17	16	22	22
acetone		7.0	18	10	7.1	2.7	14	3.6	5.2	2.2	3.3	5.5	14	12	2.0	17	11	21
acetonitrile			11	8.7	9.3	8.4	11	7.1	12	7.5	8.6	13	10	11	8.6	19	10	11
anisole				9.0	5.6	11	14	16	7.6	11	15	9.3	13	15	19	7.6	12	5.2
benzene					7.1	1.8	21	15	5.8	3.8	2.8	5.6	19	16	2.2	12	4.9	12
butyl amine						6.8	9.1	7.5	7.1	6.5	7.3	8.5	8.4	9.3	7.1	6.4	7.9	6.9
chloroform							4.9	2.9	6.0	5.1	2.0	6.3	4.2	4.8	9.3	14	4.0	4.4
cyclohexane								21	7.5	6.5	5.2	6.2	20	0.91	3.8	14	4.5	19
dichloromethane									5.6	2.9	3.3	5.4	20	19	2.9	16	10	23
ethanol										6.2	5.6	3.5	7.1	7.5	6.2	12	6.1	6.4
ethyl acetate											4.2	7.1	5.6	6.0	4.4	25	6.1	7.2
isopropyl alcohol												5.6	4.8	4.4	1.6	13	7.5	8.4
methanol													6.1	6.1	6.4	13	5.5	6.6
n-heptane														11	3.5	12	3.8	13
n-pentane															3.7	14	4.4	18
thf																17	3.2	6.5
toluene																	11	7.0
triethyl amine																		10

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