51.2: Vapor Detection, Classification, and Quantification Performance Using Arrays of Conducting Polymer Composite Chemically Sensitive Resistors

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ABSTRACT

We describe a method for generating a variety of chemically diverse, broadly responsive, low power vapor sensors. A key to our ability to fabricate chemically diverse sensing elements is the preparation of processable, air stable films of electrically conducting organic polymers. An array of such sensing elements produces a chemically reversible, diagnostic pattern of electrical resistance changes upon exposure to different odorants. Such conducting polymer elements are simply prepared and are readily modified chemically to respond to a broad range of analytes. In addition, these sensors yield a fairly rapid, low power, dc electrical signal in response to the vapor of interest, and their signals are readily integrated with software or hardware-based neural networks for purposes of analyte identification. Principle component analysis has demonstrated that such sensors can identify and quantify different airborne organic solvents, and can yield information on the components of gas mixtures.

Keywords: electronic nose, gas sensor,

conducting polymer

1. INTRODUCTION

Carbon black-polymer composites can be used 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, 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. RESULTS AND DISCUSSION

To quantify the ability of an array to discriminate between various odorants based on the different response patterns that each odorant produces, 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.

To analyze the data in a consistent fashion for different detectors and vapors, the responses for each individual detector were autoscaled[12] 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

$$A_{ij} = \frac{(\Delta R_{ij,max}/R_b) - \overline{}_j}{\beta_j} . \qquad (1)$$

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 1. 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.

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 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 2). 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.

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,

$$\vec{x}_a = (\overline{A}_{a1}, \overline{A}_{a2}, ..., \overline{A}_{an}) \qquad (2)$$

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

$$rf = \frac{|\vec{d}|}{\sqrt{\sigma_{a,\vec{d}}^2 + \sigma_{b,\vec{d}}^2}} . \qquad (3)$$

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[13] and recently used by Gardner and Bartlett[14] and is basically a multi-dimensional analogue to the separation factors used to quantify the resolving power of a column in gas chromatography.

Table 1 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.
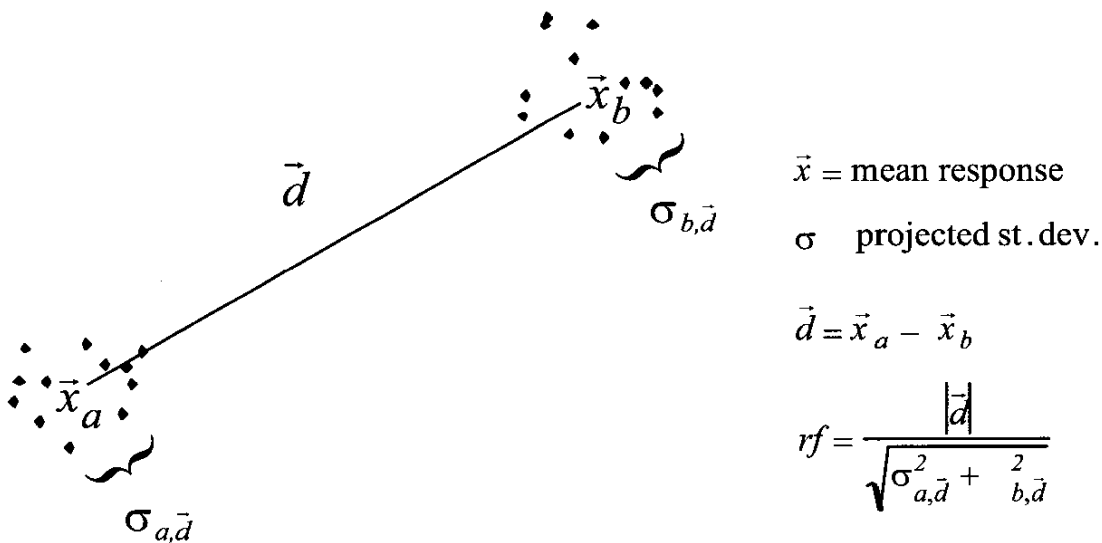
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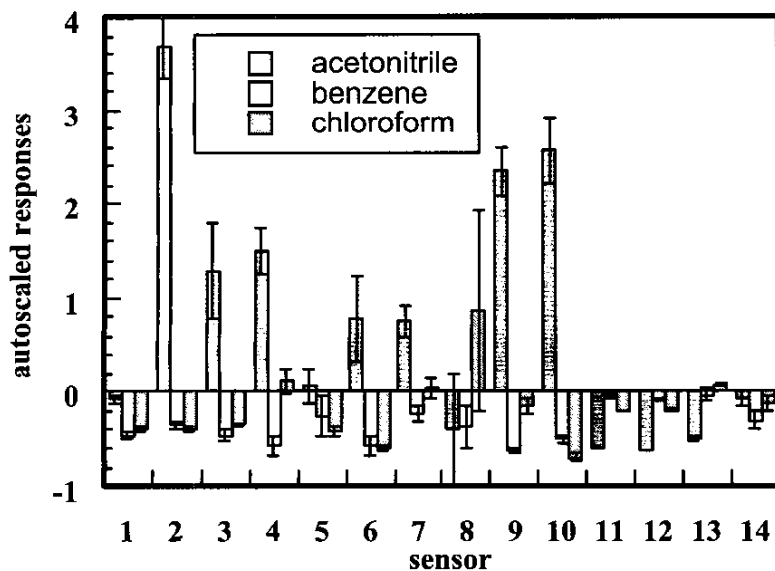
Figure 1. Autoscaled responses, A_{ij}, of the fourteen detectors in the carbon black-polymer composite array to approximately 6.7 ppth of benzene, chloroform and acetonitrile. Each bar represents the average autoscaled response over twelve exposures and the error bars represent the standard deviation in the responses.

$\vec{x}$ = mean response

σ projected st.dev.

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

$$rf = \frac{|\vec{d}|}{\sqrt{\sigma^2_{a,\vec{d}} + {}^2_{b,\vec{d}}}}$$

Figure 2. Mathematical definition of the resolution factor, rf, in multi-dimensional space.

Table 1. 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