

# Detection and Classification Characteristics of Arrays of Carbon Black/Organic Polymer Composite Chemiresistive Vapor Detectors for the Nerve Agent Simulants Dimethylmethylphosphonate and Diisopropylmethylphosphonate

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**Arrays of conducting polymer composite vapor detectors have been evaluated for performance in the presence of the nerve agent simulants dimethylmethylphosphonate (DMMP) and diisopropylmethylphosphonate (DIMP). Limits of detection for DMMP on unoptimized carbon black/organic polymer composite vapor detectors in laboratory air were estimated to be 0.047–0.24 mg m<sup>-3</sup>. These values are lower than the EC<sub>50</sub> value (where EC<sub>50</sub> is the airborne concentration sufficient to induce severe effects in 50% of those exposed for 30 min) for the nerve agents sarin (methylphosphonofluoridic acid, 1-methylethyl ester) and soman (methylphosphonofluoridic acid, 1,2,2-trimethylpropyl ester), which has been established as ~0.8 mg m<sup>-3</sup>. Arrays of these vapor detectors were easily able to resolve signatures due to exposures to DMMP from those due to DIMP or due to a variety of other test analytes (including water, methanol, benzene, toluene, diesel fuel, lighter fluid, vinegar, and tetrahydrofuran) in a laboratory air background. In addition, DMMP at 27 mg m<sup>-3</sup> could be detected and differentiated from the signatures of the other test analytes in the presence of backgrounds of potential interferences, including water, methanol, benzene, toluene, diesel fuel, lighter fluid, vinegar, and tetrahydrofuran, even when these interferences were present in much higher concentrations than that of the DMMP or DIMP being detected.**

Arrays of chemically sensitive resistors fabricated from composites of carbon black with insulating organic polymers have received significant attention recently for use in detecting, quantifying, and discriminating among various organic vapors.<sup>1–4</sup>

One of the potential advantages of this approach to vapor sensing<sup>5–20</sup> is that it affords the possibility of fabricating very small size, low-power, and lightweight detector arrays that have hundreds of compositionally different detector pixels. For example, hundreds of such detectors have been deposited and read out in our laboratory on a Si chip having an area of 0.04 cm<sup>2</sup>,<sup>21,22</sup> thus, one could envision developing wearable badge-type detectors for personal environmental monitoring devices based on this technology.

In this work, we have evaluated the detection and discrimination capabilities of an array of carbon black/organic polymer composite chemiresistors toward the nerve agent simulants dimethylmethylphosphonate (DMMP)<sup>23,24</sup> and diisopropylmeth-

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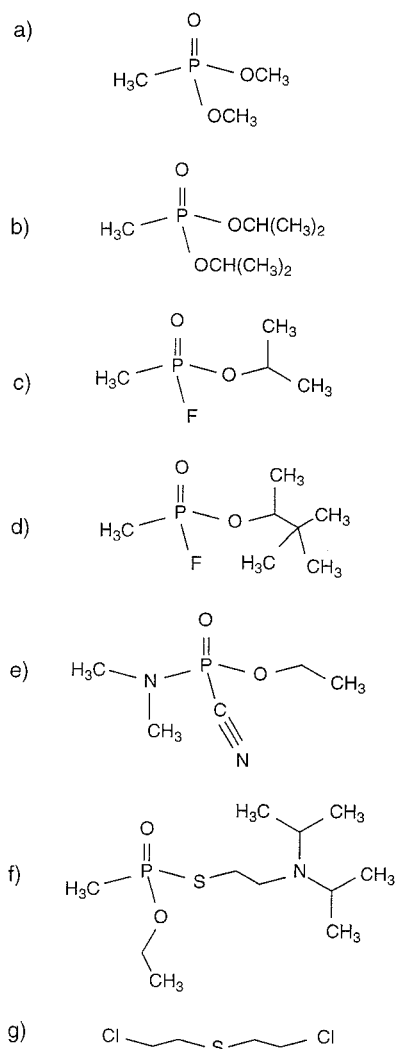


Figure 1. Structures of the chemical warfare simulants (a) dimethylmethylphosphonate (DMMP) and (b) diisopropylmethylphosphonate (DIMP) and of the nerve agents (c) sarin (methylphosphonofluoridic acid, 1-methylethyl ester), (d) soman (methylphosphonofluoridic acid, 1,2,2-trimethylpropyl ester), (e) tabun (dimethylphosphoramidocyanidic acid, ethyl ester), (f) VX (methylphosphonothioic acid, S-[2-[bis-(1-methylethyl)amino]ethyl]-O-methyl ester), and (g) sulfur mustard (1,1'-thiobis(2-chloroethane)).

ylphosphonate (DIMP) (Figure 1). Table 1 indicates some chemical warfare agents and concentrations of interest.<sup>25</sup> DMMP is often regarded as a simulant for sarin (methylphosphonofluoridic acid, 1-methylethyl ester) and DIMP as a simulant for soman (methylphosphonofluoridic acid, 1,2,2-trimethylpropyl ester), so DMMP and DIMP have been the focus of our initial efforts in this area. In this work, we report the detection limits of these detector arrays, under controlled laboratory conditions, for DMMP or DIMP in background air, as well as for DMMP or DIMP in the presence of a variety of different background analytes including water vapor, diesel fuel, organic solvent vapors, and other selected possible interferences. Additionally, we have evaluated the ability

Table 1. Human Exposure Guidelines for Selected Chemical Warfare Agents ( $\text{mg m}^{-3}$ )

agent	AEL <sup>a</sup>	EC <sub>50</sub> <sup>b</sup>	ED <sub>50</sub> <sup>c</sup>
sarin	0.0001	<0.8	1000
soman	0.00003	<0.8	200
tabun	0.0001	<1.7	<880
VX	0.00001	<0.3	<2.5
sulfur mustard	0.003	3.33	600

<sup>a</sup> AEL, the maximum airborne exposure concentration for an 8-h workday. <sup>b</sup> EC<sub>50</sub>, the airborne concentration sufficient to induce severe effects in 50% of those exposed for 30 min. <sup>c</sup> ED<sub>50</sub>, the amount of liquid agent on the skin sufficient to produce severe effects in 50% of the exposed population.

Table 2. Polymers Used in the Carbon Black-Polymer Composite Detector Array

detector no.	polymer
1	poly(ethylene oxide), PEO
2	poly(ethylene-co-vinyl acetate), 45% vinyl acetate, PEVA
3	poly(butadiene-co-styrene), 72% butadiene, PBS
4	poly(vinylcarbazole), PVC
5	poly(vinyl acetate), PVA
6	poly(caprolactone), PCL
7	polysulfone
8	poly(vinylpyrrolidone), PVP
9	poly(4-vinylphenol), PVPH
10	poly(methyloctadecylsiloxane), PMODS

of these detectors to discriminate among DMMP, DIMP, and a collection of other selected organic vapors under the measured test conditions.

## EXPERIMENTAL SECTION

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 polymer used in the composites (Table 2) was (detector number, polymer, manufacturer): 1, poly(ethylene oxide), Polysciences; 2, poly(55% ethylene-co-45% vinyl acetate), Polysciences; 3, poly(72% butadiene-co-28% styrene), Scientific Polymer Products; 4, poly(vinylcarbazole), Polysciences; 5, poly(vinyl acetate), Scientific Polymer Products; 6, poly(caprolactone), Polysciences; 7, polysulfone, Polysciences; 8 poly(vinylpyrrolidone), Scientific Polymer Products; 9, poly(4-vinylphenol), Polysciences; 10, poly(methyloctadecylsiloxane), Polysciences. To form contacts on the substrate, two parallel bands of gold, 50–100 nm thick and separated by 1 mm, were deposited onto conventional 7.5 cm × 2.5 cm glass slides (Corning Inc.). The slides were then cut into strips to produce 0.7 cm × 2.5 cm pieces of glass. The detector films were made from a solution of the polymer into which carbon black had been suspended. A 160-mg sample of one of the insulating polymers was dissolved in 20 mL of solvent and 40 mg of carbon black was then suspended in this solution, to produce a composition of 80% polymer and 20% carbon black by weight of solids. The solvent was either toluene or tetrahydrofuran (THF), depending on the solubility of the polymer. The solutions were sonicated for 5 min to suspend the carbon black. A single solution that contained the polymer and the carbon black was used to prepare all the detectors of a given composition that were used in this work. An aliquot of the

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suspension was spin coated, at 1500 rpm, onto a glass substrate using a Headway (Garland, TX) spin coater, and the resulting film was allowed to dry in air for 24 h. Multiple coatings of the suspension were applied to each substrate to yield detectors having resistance values of approximately a few hundred kilohms.

The solvents used in this study were THF, benzene, methanol, toluene, DMMP, and DIMP. These solvents were purchased from Aldrich and were used without further purification. The vinegar (Lucky Brand), lighter fluid (butane and other low molecular weight hydrocarbons), and diesel fuel (Unocal 76) were purchased from commercial consumer sources.

The apparatus used to generate known concentrations of organic vapors and to acquire resistance versus time data from the detectors has been described previously.<sup>1,2,26</sup> Briefly, solvents were saturated with a background of laboratory air and the resultant flowing gas stream was mixed with an independently controlled flow of air to produce the desired diluted flow of analyte vapor. The gas flow rates were controlled with calibrated mass flow controllers, and analyte saturation of the flow stream that passed through the solvent bubblers was verified by measurement of the rate of mass loss of the solvent in the bubbler.<sup>27</sup> Solenoids and one-way valves were used to mix the gases and to direct them to a Teflon chamber that contained the conducting polymer composite detectors.<sup>28</sup> The performance of the entire vapor generation system was validated using a flame ionization detector to determine the concentration of a series of standard mixtures of toluene in air that were delivered to the detector chamber. These values were within 90% of the values expected based on the vapor pressure of the analyte and the dilution ratio expected from the settings of the mass flow controllers. The flame ionization detector was calibrated using standard gas calibration mixtures obtained from commercial suppliers.

The carrier gas for all experiments was oil-free air, obtained from the general compressed laboratory source which contained  $1.10 \pm 0.15$  parts per thousand (ppth) of water vapor. The air was filtered to remove particulates but deliberately was not dehumidified or otherwise purified. When water was used as the background analyte, the carrier gas was ultrazero air. Fluctuations in laboratory temperature,  $21.5 \pm 1.5$  °C, could cause a ~10% error in setting and controlling the vapor concentrations between nominally identical exposures over the course of the data collection analyzed in this work. No temperature control of the apparatus or of the carbon black/polymer composite detectors was performed. The flow rate of the vapor stream entering the exposure chamber (~1 L in total volume) was maintained at  $15 \text{ L min}^{-1}$ .

The 20-detector array studied in this work had 2 nominally identical copies of each of 10 different polymer composites (Table 2). To initiate an experiment, the detectors were placed into the flow chamber and a background flow of laboratory air was introduced until the resistance of the detectors stabilized. Each exposure consisted of a three-step process that began with 180 s of air flow to achieve a smooth baseline resistance. After this period, the detectors were exposed for 300 s to analyte vapor at a controlled concentration in flowing air. The analyte exposure

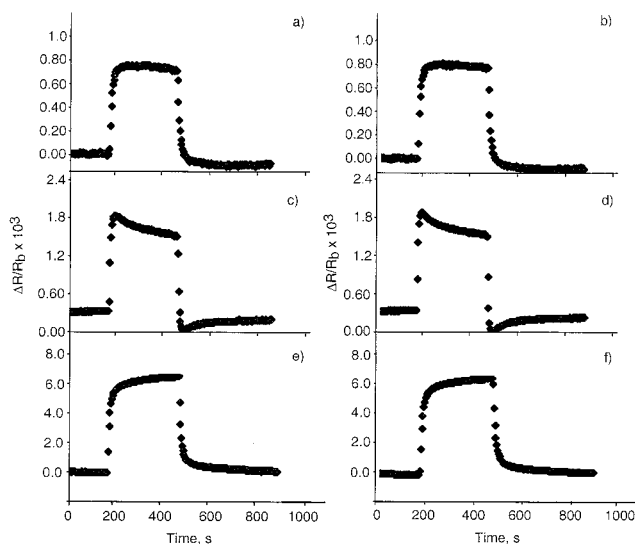


Figure 2. Relative differential resistance responses vs time for carbon black/polymer composite detectors exposed to DMMP at  $P/P^0 = 0.013$  in laboratory air. Replicate entries of the polymeric component of the carbon black composite indicate the responses of two different detectors of that were fabricated together and were exposed together to analyte. Each exposure consisted of 180 s of air, 300 s of analyte, and then 420 s of laboratory air. The polymer used to form the carbon black composite was (a) PEO, (b) PEO, (c) PEVA, (d) PEVA, (e) PCL, and (f) PCL.

was then followed by a 420-s flow of clean air to restore the baseline resistance values. Within each experiment, every exposure was assigned a randomly generated index number using the Microsoft Excel random number generator. The exposures were then presented to the detector array in ascending order of the assigned index values.

To obtain signatures for the different analytes of interest, each analyte was exposed to the vapor detector array in random order at a fixed value of  $P/P^0$ , where  $P^0$  is the vapor pressure of the analyte at room temperature and  $P$  is the partial pressure of the analyte. In this study, the 180-s baseline period was followed by 300 s of exposure to the test analyte at  $P/P^0 = 0.010$ . Representative resistance versus time response signatures of selected detectors, and a summary of the output data for different carbon black/polymer detectors exposed to DMMP in background air, are presented in Figure 2 and Table 3, respectively.

A separate run was performed to probe the detector response to a test analyte in the presence of various background compounds. In this run, the exposure phase consisted of two parts. The background analyte was exposed at  $P/P^0 = 0.010$  for 150 s, at which time the test analyte was introduced and exposed for an additional 150 s. During the exposure of the second (test) analyte, the first (background) analyte was continually flowing. The foreground test analytes DMMP and DIMP were presented to the array at  $P/P^0 = 0.0017$ ,  $0.0054$ , or  $0.013$ . Each unique foreground/background combination was replicated 8 times. The total experiment thus contained 192 total exposures (2 foreground solvents each at 3 different concentrations in the presence of a selected member of the 4 background solvents, with 8 replicates of each unique exposure combination).

Although the resistance of each detector was sampled once every 3–5 s during each exposure, only the relative differential

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Table 3.  $\Delta R/R_b$  Responses of Carbon Black/Polymer Detectors to DMMP in Background Air<sup>a</sup>

host material	activity, $P/P^0$ of DMMP		
	0.0017	0.0054	0.013
PEO	$(13.2 \pm 6.7) \times 10^{-5}$	$(4.35 \pm 5.6) \times 10^{-4}$	$(9.20 \pm 3.4) \times 10^{-4}$
PEO	$(12.6 \pm 3.1) \times 10^{-5}$	$(4.56 \pm 1.2) \times 10^{-4}$	$(9.03 \pm 2.3) \times 10^{-4}$
PEVA	$(28.7 \pm 9.8) \times 10^{-5}$	$(9.44 \pm 1.7) \times 10^{-4}$	$(0.188 \pm 4.9) \times 10^{-4}$
PEVA	$(24.1 \pm 7.8) \times 10^{-5}$	$(9.38 \pm 2.0) \times 10^{-4}$	$(0.190 \pm 5.1) \times 10^{-4}$
PCL	$(8.77 \pm 1.3) \times 10^{-4}$	$(0.239 \pm 4.9) \times 10^{-4}$	$(0.675 \pm 9.8) \times 10^{-4}$
PCL	$(8.81 \pm 1.0) \times 10^{-4}$	$(0.242 \pm 1.8) \times 10^{-4}$	$(0.671 \pm 4.7) \times 10^{-4}$

<sup>a</sup> Values are means and standard deviations for eight exposures of a carbon black/polymer composite detector to DMMP. Replicate entries of the host material denote the results for two detectors that were fabricated together and were exposed together to analyte.

resistance change,  $\Delta R/R_b$ , where  $\Delta R$  is the steady-state resistance change of the detector during exposure to the analyte and  $R_b$  is the baseline resistance of the detector during the initial 180-s period of exposure to background air, was used in analysis of the data. The value of  $R_b$  was calculated by taking the average of the last 30 s (~10 data points) of the initial 180-s air exposure, while  $\Delta R$  was calculated by averaging the last 30 s of data obtained during exposure of the detectors to the analyte of interest. In studies when a background analyte was introduced to the detectors prior to introduction of a foreground analyte, two separate  $\Delta R/R_b$  values, one for the background analyte relative to clean air and the other for the foreground analyte relative to the steady-state response of the background analyte, were calculated from the data. The value of  $R_b$  for exposure to a foreground analyte was determined using the last 30 s of data recorded during exposure of the detectors to the background analyte. The  $\Delta R/R_b$  values were then averaged for each set of detectors over the eight replicate exposures for each unique detector/analyte combination. The  $\Delta R/R_b$  values for both members of each pair of nominally identical carbon black/polymer detectors in the array were then combined to form a single average  $\Delta R/R_b$  value for that type of polymeric detector/carbon black composite in response to the particular analyte of interest. Because only four detector compositions responded well to DMMP and DIMP, for consistency, all plots and detector performance data were evaluated using only this subset of detectors. This eight-detector array consisted of two copies of carbon black/polymer composite detectors formed using poly(ethylene oxide) (PEO), poly(ethylene-co-vinyl acetate) (PEVA), poly(butadiene-co-styrene) (PBS), and poly(caprolactone) (PCL), respectively.

Principal component analysis (PCA) was performed using macros written in Excel, and the data were plotted using Delta Graph and Claris Works. Data were normalized over the eight-detector array for a given exposure rather than over a collection of exposures for a given detector. This normalization procedure corrects for different analyte concentrations that are a consequence of the differing vapor pressures of the test analytes. The data were not autoscaled prior to use in principal component analysis.

Data were analyzed for pairwise discrimination between analytes using the Fisher linear discriminant algorithm.<sup>29,30</sup> In this statistical approach, the resolution factor (rf) for any solvent pair

is obtained along any vector,  $\bar{w}$ , from the vector projection onto  $\bar{w}$  of the distance between the cluster centroids,  $d_{\bar{w}}$ , divided by the sum of the projected standard deviations,  $\sigma_{a,\bar{w}}$  and  $\sigma_{b,\bar{w}}$ , for data arising from repeated exposures for two different analytes,  $a$  and  $b$ . The resulting numerical resolution factor along  $\bar{w}$  is defined as

$$\text{rf} = d_{\bar{w}} / \sqrt{\sigma_{a,\bar{w}}^2 + \sigma_{b,\bar{w}}^2}$$

The Fisher linear discriminant operates by searching for the vector,  $\bar{w}$ , such that the rf value is maximized along this optimal discriminant vector. Assuming a Gaussian distribution relative to the mean value of the data points in a given cluster, the probabilities of correctly identifying an analyte as  $a$  or  $b$  are approximately 72, 92, and 98% from a single presentation when analytes  $a$  and  $b$  are separated with resolution factors of 1.0, 2.0, or 3.0, respectively. Data extracted from multiple exposures to an analyte estimate the statistical distributions of the clustered data, although extremely high rf factors might overestimate the actual array discrimination performance based on the analysis of a relatively small number of presentations (10–20) of the detectors to each analyte.

## RESULTS

**A. Differentiation of DMMP from DIMP and Other Analytes of Interest in an Air Sample.** Figure 3 shows data in principal component space for DMMP, DIMP, and other analytes of interest. The vapors were presented to the detectors as single-component analytes at  $P/P^0 = 0.010$  in a background of laboratory air. The data indicate that, under such conditions, DMMP can be clearly resolved from the other analytes based on their distinct  $\Delta R/R_b$  response patterns on the detector array. As indicated in Table 4, resolution factors for pairwise differentiation between these pure analytes produced an average resolution factor of  $\approx 90$ , indicating robust resolution of DMMP from any of these other analytes under such conditions.

Table 5 shows the  $\Delta R/R_b$  response for DMMP at  $P/P^0 = 0.0017$ , 0.0054, and 0.013 to four detectors, PEO, PEVA, PBS, and PCL, that responded well to the DMMP analyte. The data displayed in this table have been normalized by the value of  $P/P^0$  and thus indicate that the pattern of response was, within experimental error, independent of the DMMP concentration. A

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Table 4. Resolution Factors for an Eight-Detector Array of Carbon Black Composites To Resolve Pairwise Each of the 10 Vapors, at Fixed Concentration, from Any Other Vapor in the Test Set<sup>a</sup>

	DIMP	THF	benzene	methanol	toluene	water	lighter fluid	vinegar	diesel fuel
DMMP	56	65	47	84	32	71	46	87	34
DIMP		60	33	78	56	84	29	79	40
THF			89	82	250	49	83	32	109
benzene				186	128	234	49	81	37
methanol					267	32	156	27	43
toluene						211	29	89	25
water							264	28	34
lighter fluid								87	28
vinegar									96

<sup>a</sup> The average and worst pairwise resolution factors are 91 and 25, respectively.

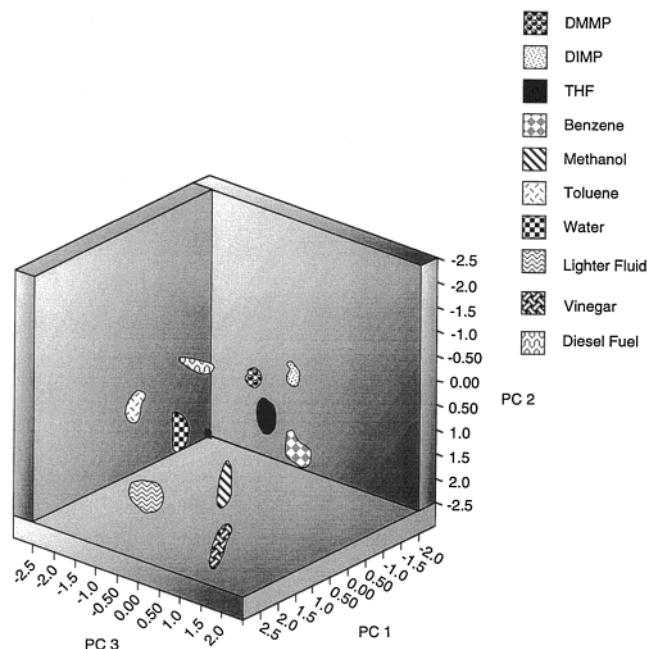


Figure 3. Data in principal component space of  $\Delta R/R_b$  values produced when an eight-detector carbon black/polymer composite array was exposed to DMMP, DIMP, THF, benzene, methanol, toluene, water, lighter fluid, vinegar, or diesel fuel, each at  $P/P^0 = 0.010$ , in an air background. The first three principal components contain 97% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte. Each analyte was presented eight times to the array with the order of presentation randomized over all repetitions of all exposure types.

similar dependence of the  $\Delta R/R_b$  detector response values versus analyte concentration has been obtained for carbon black/polymer composite chemiresistors in the presence of other vapors, for a comparable range of partial pressures of the organic vapors in a background of laboratory air.<sup>31</sup>

The sensitivities,  $S = (\Delta R/R_b)/(P/P^0)$ , of these detectors toward DMMP and DIMP, combined with the baseline noise values for the detectors, were used to obtain detection limits for DMMP and DIMP in an air sample on each detector type in our experimental configuration. Detection limits were taken as concentrations at which the signal/noise ratio (calculated from the

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Table 5. Normalized  $\Delta R/R_b$  Responses of an Eight-Detector Array for Various Carbon Black/Polymer Composites<sup>a</sup>

host material	activity, $P/P^0$ of DMMP		
	0.0017	0.0054	0.013
PEO	$0.0869 \pm 0.011$	$0.0964 \pm 0.024$	$0.0834 \pm 0.025$
PEVA	$0.188 \pm 0.034$	$0.209 \pm 0.023$	$0.170 \pm 0.029$
PCL	$0.577 \pm 0.053$	$0.531 \pm 0.031$	$0.612 \pm 0.035$
PBS	$0.146 \pm 0.034$	$0.163 \pm 0.045$	$0.133 \pm 0.021$

<sup>a</sup> Values represent means and standard deviations of  $(\Delta R/R_b)/(P/P^0)$  for carbon black/polymer composite detectors in laboratory air. Data from two detectors of each polymer type were averaged together for this analysis. The analyte was exposed to the detectors eight times at each concentration, with the concentrations randomized in the experiment.

Table 6. Calculated Detection Limit of DMMP (in  $\text{mg m}^{-3}$ ) for Various Carbon Black/Polymer Composites

host material	air	background analyte at $P/P^0 = 0.010$ in air			
		THF	water	methanol	benzene
PEO	0.14	0.18	0.20	0.15	0.13
PEVA	0.050	0.055	0.068	0.053	0.047
PCL	0.059	0.051	0.048	0.062	0.057
PBS	0.19	0.22	0.16	0.24	0.18

Table 7. Calculated Detection Limit of DIMP (in  $\text{mg m}^{-3}$ ) for Various Carbon Black/Polymer Composites

host material	air	background analyte at $P/P^0 = 0.010$ in air			
		THF	water	methanol	benzene
PEO	0.19	0.67	0.32	0.58	0.76
PEVA	0.074	0.055	0.053	0.062	0.082
PCL	0.049	0.039	0.088	0.051	0.057

sensitivity) was 3:1.<sup>32</sup> Values for these  $3\sigma$  detection values for the four most responsive detectors are summarized in Tables 6 and 7.

**B. Differentiation of DMMP from DIMP and Other Analytes of Interest in the Presence of Varying Background Analytes.** Parts a–c of Figure 4 show the  $\Delta R/R_b$  response for carbon black/polymer composite detectors that contained poly(ethylene oxide), poly(ethylene-co-vinyl acetate), and poly(caprolactone), respectively, to DMMP at  $P/P^0 = 0.0017$ , 0.0054, or 0.013 in the presence of various analytes that had been added at  $P/P^0 = 0.010$  to a laboratory air background flow. The data of Figure

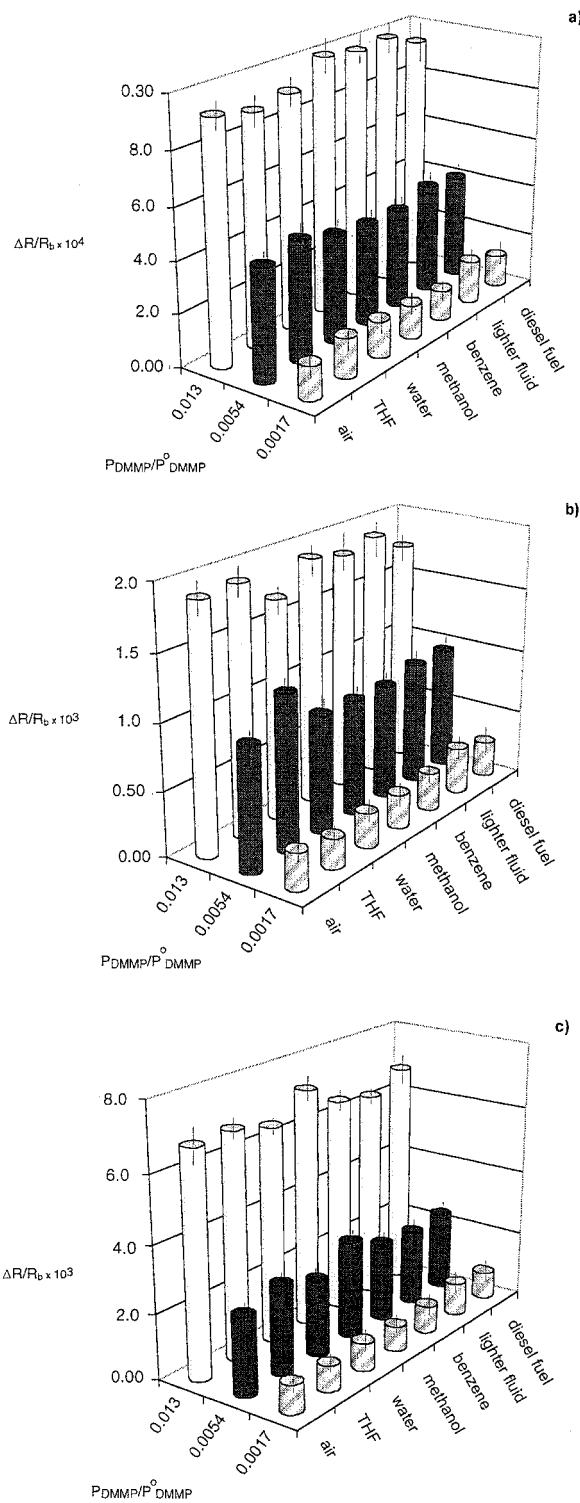


Figure 4.  $\Delta R/R_b$  responses of carbon black/polymer composite detectors containing (a) PEO, (b) PEVA, or (c) PCL to DMMP at  $P/P^\circ = 0.0017, 0.0054, \text{ or } 0.013$  with THF, water, methanol, benzene, lighter fluid, or diesel fuel as background analytes at  $P/P^\circ = 0.010$ . The height of the bars represent the average values, and the error bars represents the  $1\sigma$  standard deviation of the data.

4 support the data of Table 5 that the  $\Delta R/R_b$  response on these detectors is approximately a linear function of analyte partial pressure and furthermore indicate that the  $\Delta R/R_b$  values for this range of DMMP partial pressures are, within experimental error, independent of whether the background gas was laboratory air

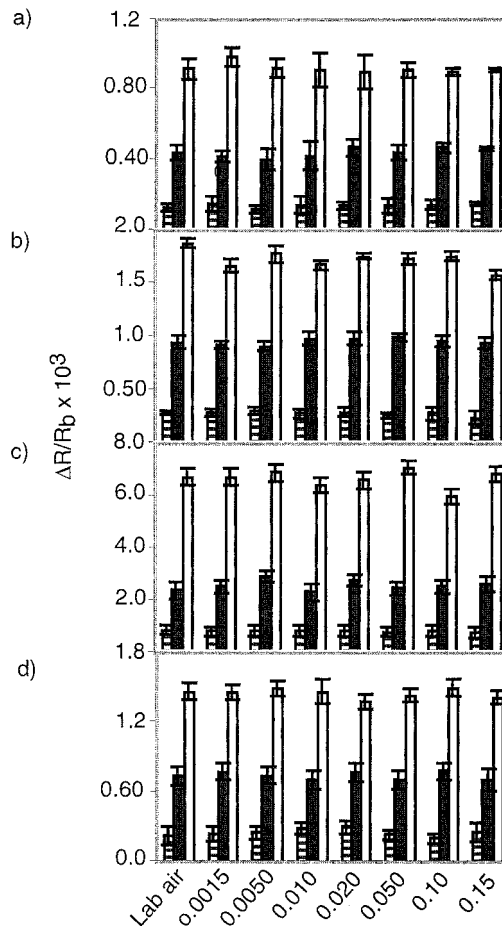


Figure 5.  $\Delta R/R_b$  responses of carbon black/polymer composite detectors containing (a) PEO, (b) PEVA, (c) PCL, and (d) PBS to DMMP at  $P/P^\circ = 0.010$  with  $P_{H_2O}/P^\circ_{H_2O} = 0.0015, 0.0050, 0.010, 0.020, 0.050, 0.10, \text{ or } 0.15$  in laboratory air as the background analyte.

or was laboratory air with a significant concentration of any of these other analytes. Analogous behavior was observed for DIMP. Similar behavior has also been observed previously in a general probe of the behavior of carbon black/polymer composite vapor detectors, in which  $\Delta R/R_b$  response patterns to various test organic vapors were observed to be essentially independent of the composition of the background ambient for a range of analyte concentrations and analyte types under laboratory test conditions.<sup>31</sup>

Figure 5 shows the  $\Delta R/R_b$  response of four detector types to DMMP as a function of the relative humidity of the background air, when  $P_{H_2O}/P^\circ_{H_2O}$  was varied from 0 to 0.15 at room temperature. These data are of interest for detection of DMMP and DIMP in environments in which the relative humidity is not fully controlled. The data clearly show that, within experimental error, the  $\Delta R/R_b$  response pattern for DMMP on carbon black composite detectors that contain either PEO, PEVA, PCL, or PBS was independent of the relative humidity over the range of values explored in this work.

Figures 6 and 7 summarize, in principal component space, the results of all experiments performed in this work involving exposures of DMMP and DIMP to an eight-detector array as a function of the composition of the background ambient gas in the flow stream. Consistent with Figures 3 and 4, the data indicate

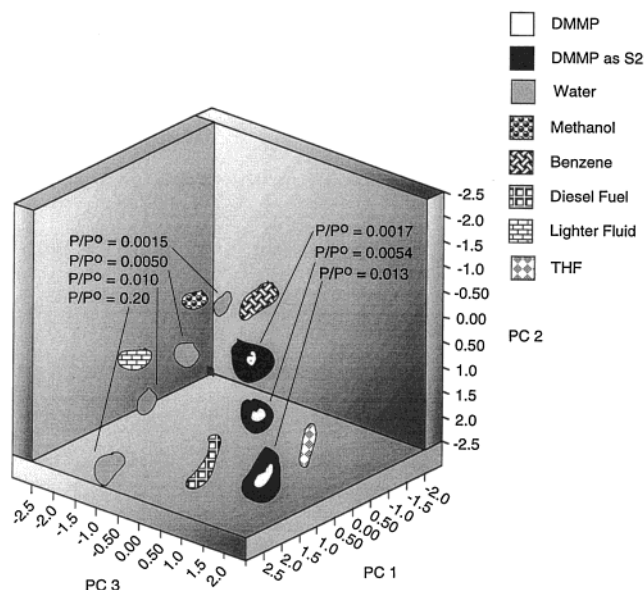


Figure 6. Data in principal component space from an eight-detector array exposed to methanol, benzene, diesel fuel, lighter fluid, or THF at  $P/P^0 = 0.010$ , to water at  $P/P^0 = 0.0015, 0.0050, 0.010, \text{ or } 0.020$ , or to DMMP at  $P/P^0 = 0.0017, 0.0054, \text{ or } 0.013$  in an background. Using the above analytes (except DMMP) as the background, the detectors were also exposed to a foreground of DMMP at  $P/P^0 = 0.0017, 0.0054, \text{ or } 0.013$ . Each pure analyte or unique foreground/background combination was presented eight times to the array with the order of presentation randomized over all repetitions of all exposure types. The data obtained when DIMP was the foreground solvent in the presence of an analyte in the background is indicated by the region labeled "DMMP as S<sub>2</sub>". The first three principal components contain 97% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte.

that the pattern type for DIMP and for DMMP was preserved as the concentration of analyte increased. In addition, Figures 6 and 7 demonstrate that all of the tested concentrations of DMMP and DIMP could be clearly differentiated from the patterns produced by exposure to the other pure analytes of interest. Finally, the data of Figures 6 and 7 indicate that the DMMP and DIMP patterns were essentially unchanged regardless of the composition of the background ambient gas flow evaluated in this work. Resolution factors for the eight-detector array under various conditions of interest are presented in Tables 4 and 8.

Sensitivities and detection limits were also calculated for DMMP and DIMP in the presence of variation in the composition of the background ambient. Values for the detection limits under the various conditions studied herein are presented in Tables 6 and 7. As expected from the results above, the detection limits were relatively insensitive to the composition of the background analyte.

## DISCUSSION

Under our experimental conditions, the detection limits for DMMP were lower than the EC<sub>50</sub> values for sarin (Table 1). The vapor pressures of sarin and DMMP are  $1.61 \times 10^4$  and  $1.45 \times 10^4$  mg m<sup>-3</sup> at 20 °C, respectively.<sup>33</sup> Because the equilibrium  $\Delta R/R_0$  response of carbon black/polymer composite sorption detectors depends primarily on the vapor pressure of the analyte,<sup>34</sup> the detection limits for DMMP are expected to be very similar to those for sarin.

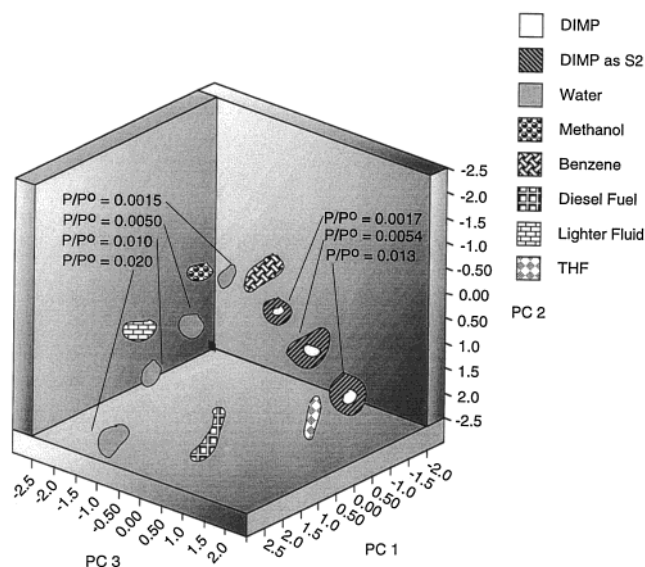


Figure 7. Data in principal component space from an eight-detector array exposed to methanol, benzene, diesel fuel, lighter fluid, or THF at  $P/P^0 = 0.010$ , to water at  $P/P^0 = 0.0015, 0.0050, 0.010, \text{ or } 0.020$ , or to DIMP at  $P/P^0 = 0.0017, 0.0054, \text{ or } 0.013$  in an background. Using the above analytes (except DIMP) as the background, the detectors were also exposed to a foreground of DIMP at  $P/P^0 = 0.0017, 0.0054, \text{ or } 0.013$ . Each pure analyte or unique foreground/background combination was presented eight times to the array with the order of presentation randomized over all repetitions of all exposure types. The data obtained when DIMP was the foreground solvent in the presence of an analyte in the background is indicated by the region labeled "DMMP as S<sub>2</sub>". The first three principal components contain 97% of the total variance in the data. The ellipsoids contain 95% of the data for each analyte.

The data clearly show that DMMP and DIMP were robustly detected and differentiated from each other at  $P/P^0 = 0.0017$  in the presence of various other potential "interferences" at partial pressures of  $P/P^0 = 0.010$ . Because of the significant differences in vapor pressures between DMMP and DIMP and the set of interferences, the observed behavior corresponds to detection of DMMP and DIMP at the levels of 0.047–0.24 and 0.049–0.76 mg m<sup>-3</sup>, respectively, in the presence of background concentrations of water, methanol, benzene, toluene, diesel fuel, lighter fluid, vinegar, and THF in the range 900– $1.6 \times 10^3$  mg m<sup>-3</sup>. The specific analyte concentrations for  $P/P^0 = 0.013$  of diesel fuel, vinegar, and lighter fluid have not been specified because these reagents are multicomponent mixtures of analytes; nevertheless, the primary component of these analytes was present at concentrations in excess of  $1.7 \times 10^4$  mg m<sup>-3</sup> under our test conditions. The ability to detect rather low concentrations of DMMP in the presence of much higher concentrations of these other analytes arises primarily from the underlying thermodynamics of sorption-based detectors, as shown in detail previously,<sup>34</sup> which favors detection of low vapor pressure analytes based on their higher partition coefficients into polymeric detector films.

It has been shown previously that the steady-state  $\Delta R/R_0$  response of carbon black/organic polymer composite detectors

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Table 8. Resolution Factors for an Eight-Detector Array of Carbon Black Composites To Resolve Pairwise Each of the 10 Vapors at Fixed Concentration, from Any Other Vapor in the Test Set<sup>a,b</sup>

	DIMP <sub>S2</sub>	THF	benzene	methanol	toluene	water	lighter fluid	vinegar	diesel fuel
DMMP <sub>S2</sub>	39	47	68	38	28	36	33	59	47
DIMP <sub>S2</sub>		58	36	67	52	79	36	82	42
THF			89	82	250	49	83	32	109
benzene				186	128	234	49	81	37
methanol					267	32	156	27	43
toluene						211	29	89	25
water							264	28	34
lighter fluid								87	28
vinegar									96

<sup>a</sup> The average and worst pairwise resolution factors are 82 and 28, respectively. <sup>b</sup> DMMP<sub>S2</sub> and DIMP<sub>S2</sub> are the foreground solvents with THF, benzene, methanol, toluene, water, lighter fluid, vinegar, or diesel fuel as background analytes.

to binary mixtures of organic vapors is generally a linear combination of the steady-state  $\Delta R/R_b$  responses for the individual components of the mixture.<sup>31</sup> Thus, the presence of DMMP or DIMP could in principle be determined in a binary mixture of vapors exposed simultaneously to a carbon black/polymer composite detector array if there were some prior knowledge about the composition of the analyte. However, use of the steady-state  $\Delta R/R_b$  response patterns is best-suited for situations in which the detectors are to be utilized in change detection mode, as opposed to performing an analysis of a complex analyte mixture without any prior separation steps or temporal information on changes in vapor composition with time. In principle, an array having as many as five to six components can be analyzed using the equilibrium response data of a detector array containing six to seven detectors provided that the detectors are at most partially correlated with each other.<sup>35</sup> Additional information can be obtained, in principle, from use of the time dependence of the detector responses; however, such data are typically not independent of the analyte background composition or linear with changes in analyte concentration. The time response of the carbon black/polymer composite detectors is also more sensitive to variations in film thickness and carbon black content than are the steady-state  $\Delta R/R_b$  values used herein, so the exact performance of such a system must be evaluated for the particular task at hand and with respect to the specific implementation of the detection and sampling system used in such an application.

In this work, we have quoted limits of detection as opposed to limits of classification.<sup>35</sup> The former are fundamental quantities that are independent of the task of concern, while the latter are intimately linked to the nature and type of the interferences and background analytes and to how well-matched a particular algorithm is to the training and test sets of data being analyzed.<sup>35</sup> Under certain conditions and for certain tasks, limits of classification on polymer-coated surface acoustic wave detector arrays have been shown to be within a factor of 2–3 of the limits of detection,<sup>35</sup> so the values quoted herein provide a reasonable (order of magnitude) estimate of the performance that might be expected in certain tasks. We also note that the detection limits presented above are only approximate performance measures for such detectors. Signal/noise ratios, and thus limits of detection, for carbon black/polymer composite chemiresistors at equilibrium with an analyte of interest have been shown to decrease as the

detector area decreases,<sup>36</sup> so our detection limits must be scaled accordingly if the detector area is varied. In addition, the sensitivity of sorption detectors decreases with increasing temperature,<sup>35</sup> so the signal/noise ratio, and thus detection limits, will decrease if the detectors are heated. In comparing the performance of these chemiresistors to prior results on polymer-coated surface acoustic wave devices for detection of DMMP and other nerve agents and nerve agent simulants,<sup>23</sup> it is important to note that we have not used any preconcentration of the sampled analyte and have only used steady-state  $\Delta R/R_b$  amplitudes in an attempt to characterize the fundamental performance of the detectors toward the analytes of interest. Significant tradeoffs in sensitivity, time response, power, and other system properties would of course be involved in an engineering implementation of these detectors in a fielded device for nerve agent detection. Finally, we note that the detectors used in our study were not specifically designed to possess high partition coefficients toward phosphonate-containing analytes such as DMMP or DIMP. Work on polymeric coatings for surface acoustic wave devices has indicated that significant improvements in sensitivity are possible through use of detector films designed to have hydrogen-bonding acceptor groups that provide complementarity to the hydrogen-bonding donor groups in phosphonate-containing nerve agents.<sup>23,37</sup> Because the sensitivity improvements in the polymer-coated surface acoustic wave devices are directly related to increases in sorption of the analytes into the polymer films,<sup>38,39</sup> similar improvements in detection limits toward DMMP, DIMP, sarin, and soman would be expected if such polymers were incorporated into arrays of carbon black/polymer composite vapor detectors.

In summary, generic, untailed arrays of carbon black/polymer chemiresistive vapor detectors can detect DMMP and DIMP at levels below the EC<sub>50</sub> limits for the nerve agents sarin and soman. DMMP can be differentiated from DIMP and from a variety of other analytes either in laboratory air or in laboratory air that contains the presence of relatively high concentrations of various types of volatile organic vapors. Concentration-normalized response patterns for DMMP and DIMP are independent of concentration and of background analytes over the range of

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concentrations and analytes tested in this work. Further improvements in the fundamental performance parameters of these detectors toward the analytes of interest are likely to occur through the use of specially tailored polymers and better control over temperature and other system variables.

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