"ELECTRONIC NOSE" CHIP MICROSENSORS FOR CHEMICAL AGENT AND EXPLOSIVES DETECTION

Nathan S. Lewis
Professor of Chemistry
Division of Chemistry and Chemical Engineering, 127-72
Noyes Laboratory
Pasadena, CA 91125

ABSTRACT

Arrays of conducting polymer composite vapor detectors have been evaluated for performance in the presence of the nerve agent simulants dimethylmethylphosphonate (DMMP) and diisopropylmethylphosponate (DIMP). 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 in a laboratory air background. In addition, DMMP at 27 mg m^{-3} could be detected and differentiated from the signatures of the other test analytes in the presence of backgrounds of potential interferents in the background.

1. INTRODUCTION

In this work, we have evaluated the detection and discrimination capabilities of an array of carbon black-organic polymer composite chemiresistors towards the nerve agent simulants dimethylmethylphosphonate (DMMP) and diisopropylmethylphosphonate (DIMP). 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.

2. EXPERIMENTAL

The solvents used in this study were tetrahydrofuran (THF), benzene, methanol, toluene, dimethyl methylphosphonate (DMMP) and diisopropyl methylphosponate (DIMP). These solvents were purchased from Aldrich and were used without further purification. The vinegar (Lucky Brand), lighter fluid, and diesel fuel (Local 76) were purchased from commercial consumer sources.

The apparatus used to generate known concentrations of organic vapors and to acquire resistance vs. time data from the detectors has been described previously, as were the procedures for detector fabrication (Lonergan et al., 1996; Severin et al., 2000).

Principal component analysis (PCA) was performed for visualization of clustering (Duda, 1973). Data were analyzed for pairwise discrimination between analytes using the Fisher linear discriminant algorithm (Duda, and Hart, 1973; Vaid, 2000).

3. RESULTS

The sensitivities, $S = (\Delta R/R_b)/(P/P^o)$, 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 ambient on each detector type in our experimental configuration. Values for 3σ detection values for the most responsive detectors are summarized in Tables 1 and 2. These limits of detection are below the EC_{50} limits for the nerve agents sarin and soman, where EC_{50} is the airborne concentration sufficient to induce severe effects in 50% of those exposed for 30 minutes. The EC_{50} value for each gas is 0.8 mg m^{-3} (Institute of Medicine…,1999).

Table 1. Calculated Detection Limit of DMMP in mg m^{-3} For Various Carbon Black-Polymer Composites

host material[a]	background analyte at $P/P^o = 0.010$ in air				
	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 2. Calculated Detection Limit of DIMP in mg m^{-3} For Various Carbon Black-Polymer Composites

host material[a]	background analyte at $P/P^o = 0.010$ in air				
	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

[a]PEO=poly(ethylene oxide), PEVA=poly(ethylene-co-vinyl acetate), PCL=poly(caprolactone), PBS=poly(butadiene-co-styrene)

Figure 1 shows data in principal component space for DMMP and other analytes of interest. Other than DMMP, the vapors were presented to the detectors as single component analytes at P/P^o=0.010 in a background of laboratory air. DMMP were presented at P/P^o = 0.0017, 0.0054, or 0.013 in the presence of various analytes that had been added at P/P^o =0.010 to a laboratory air background flow. 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 or was laboratory air with a significant concentration of any of these other analytes. Analogous behavior was observed for DIMP.

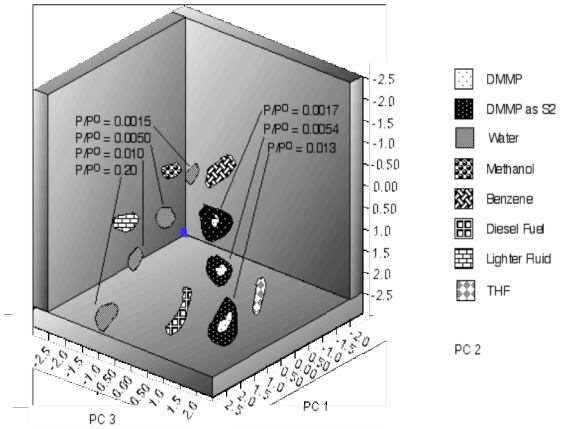

Fig. 1: Data in principal component space from an 8-detector array exposed to methanol, benzene, diesel fuel, lighter fluid, or tetrahydrofuran (THF) at P/P^o = 0.010, to water at P/P^o = 0.0015, 0.0050, 0.010, 0.020, or to DMMP at P/P^o = 0.0017, 0.0054 or 0.013 in a background. Using the above analytes (except DMMP) as the background, the detectors were also exposed to a foreground of DMMP at P/P^o = 0.0017, 0.0054 or 0.013. The data obtained when DMMP was the foreground solvent in the presence of an analyte in the background is indicated by the region labeled 'DMMP as S_2.'

Consistent with Figure 1, the data indicate that the pattern type for DIMP and for DMMP was preserved as the concentration of analyte increased. In addition, 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. DMMP and DIMP proved fully separable from all of the potential interferents tested. Resolution factors for each binary separation are given in Table 3. For reference, a resolution factor of 3 indicates 98 % correct classification ability for a binary separation.

4. CONCLUSION

In summary, generic, untailored arrays of carbon black/polymer chemiresistive vapor detectors can detect DMMP and DIMP at levels below the EC_{50} 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 ambient over the range of concentrations and ambients tested in this work.

Table 3. Resolution Factors For an 8-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[a,b,c]

	DM	DI	TH	BZ	ME	TO	W	LF	V
DM[b]	39	47	68	38	28	36	33	59	47
DI[b]		58	36	67	52	79	36	82	42
TH			89	82	250	49	83	32	109
BZ				186	128	234	49	81	37
ME					267	32	156	27	43
TO						211	29	89	25
W							264	28	34
LF								87	28
V									96

[a] The average and worst pairwise resolution factors are 82 and 28, respectively.

[b] $DMMP_{S2}$ and $DIMP_{S2}$ are the foreground solvents with THF, benzene, methanol, toluene, water, lighter fluid, vinegar or diesel fuel as background analytes.

[c] DM=$DMMP_{S2}$, DI=$DIMP_{S2}$, TH=THF, BZ=benzene, ME=methanol, TO=toluene, W=water, LF=lighter fluid, and V=vinegar.

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