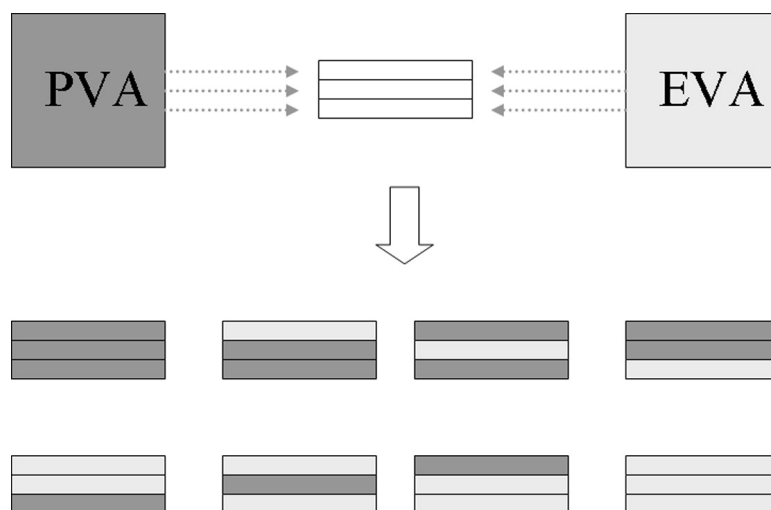Article

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Eight Combinatorial Stacks of Three Layers of Carbon Black/ PVA−Carbon Black/EVA Composite as a Vapor Detector Array

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Eight specimens of combinatorial stacking of 3 layers of carbon black/PVA−carbon black/EVA composite were prepared on substrate with interdigitated electrode. They were subjected to 15 solvent vapors with dielectric constants from 2−80,and their responses were processed for calculation of resolution factor (RF). If the detector responses are assumed to have a normal distribution, RF values of 1.0, 2.0, and 3.0 indicate the 76, 92, and 98% confidence, respectively, of correctly identifying one analyte from the other of a specific pair. Of the possible 105 pairs, 99 pairs have RF values of more than 3, 5 pairs have RF values of more than 1, and only one pair has an RF value of less than 1. The resolution factor was affected by both the dielectric constant and boiling point of tested solvents. Employing Fisher linear discrimination improves all RF values greater than 3, making confidence in resolving the pair reach almost 100%. Contributions from each combination were studied, and it was shown that diversity by combinatorial stacking is essential to the improvement of RF value. All of these capabilities are derived from combinatorial stacking of 3 layers of just two simple carbon black/polymer composites.

Introduction

Electronic noses are devices that mimic the olfactory sense. A set of differentially responsive detectors is employed to produce the specific pattern of response to a respective odor or chemical vapor. There are many classes of detectors that can be used for sensing odors, for example, chemiresistive, gravimetric, and optical detectors.[1] Chemiresistive detectors based on carbon black/polymer composites were introduced in 1990s.[2] They have been widely studied and used for electronic noses because of their low cost and simplicity.

Ability of electronic noses could be improved fundamentally by increasing the diversity of responses for a specific odor; therefore, a large number of detectors are required. For electronic noses with chemiresistive carbon black/ polymer detectors, a variety of polymers was used as the matrix to obtain a number of detectors with different characteristics.[2−5] However, the preparation of such a large number of polymers is laborious, time-consuming, and costly. It is tremendously advantageous to be able to produce an array of diverse detectors from a few feedstocks.

Several polymer−carbon black sensors were also made with the use of plasticizers.[6,7] Partial methanol elimination from the methoxy-precursor polymer of PTV led to new sensing materials with different selectivities.[8] Diversity of the detectors was achieved by variation of the chemical structure of monomers and chelating different heavy metal ions in the series of carbon black/poly(amidoamine)s detector.[9] However, these methods have their limits in chemistry compatibility and ease of production. In this work, an

innovative method, which is the combinatorial stacking of layers, was demonstrated by production of eight detectors with unique characteristics from poly(vinyl alcohol) or PVA and ethylene-co-vinyl acetate or EVA.

The performance in solvent differentiation by the eight combinations of stacking of 3 layers was studied. EVA and PVA were selected for their preferred absorption of solvents with differing polarities or dielectric constants (κ). PVA absorbs high-κ solvents well, while EVA prefers low-κ solvents. Combinatorial stacking of layers of these two materials is expected to provide a set of functional materials that prefer absorption of solvents with dielectric constants covering a wide range. The effects of stacking of 3 layers in different combinations were studied with their responses to 15 solvents. The ability to differentiate solvents using the set of detectors with combinatorial layer stacking will be presented using the resolution factor (RF). RF is the pairwise parameter, which represents the ability to resolve, pairwise, the responses to one analyte's vapors from those of the others. The details of the calculation can be found elsewhere.[6] If the detector responses are assumed to have a normal distribution, RF values of 1.0, 2.0, and 3.0 indicate the 76, 92, and 98% confidence, respectively, of correctly identifying one analyte from the other in a specific pair. RF could be used as a measure of performance of the detector array. Optimization of the resolution factor was performed with the Fisher linear discriminant method,[10] to determine the true performance in linear system. High-dimensional data were projected onto a line by a unit projection vector (V), with which the ratio of the distance between the means of the two classes and the variance within each class was maxi-

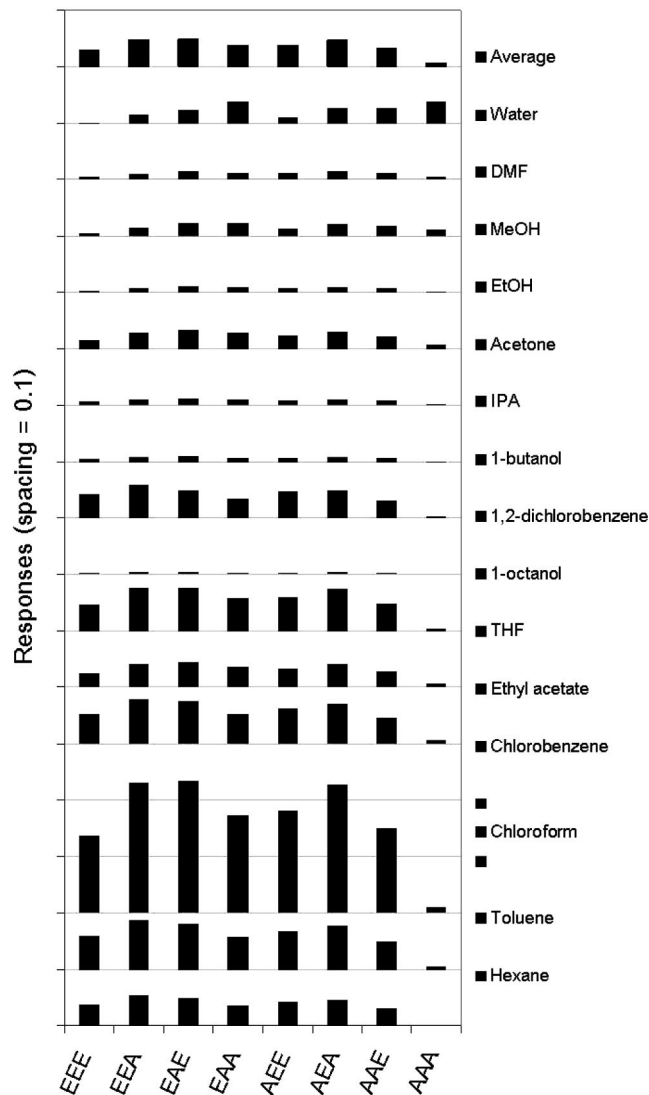* To whom correspondence should be addressed. E-mail: paisan@ mtec.or.th.

Figure 1. Response patterns for solvents with high to low κ (water−hexane).

mized. The contributions of detectors could be indicated by the square of the respective components of the unit projection vector.

Experimental Section

Poly(vinyl alcohol) (PVA) with MW. 30 000−70 000 was purchased from Aldrich, and ethylene-co-vinyl acetate (EVA), including 18% vinyl acetate, was purchased from the Thai Petrochemical Industry Public Co., Ltd. Electrical-conductive-grade carbon black powder was obtained from Degussa. The test set of solvents consisted of water, DMF, methanol, ethanol, acetone, isopropanol, 1-butanol, 1,2-dichlorobenzene, 1-octanol, THF, ethyl acetate, chlorobenzene, chloroform, toluene, and hexane. All solvents were obtained from Labscan, Fluka, and Merck. The boiling points and dielectric constants of these solvents are available.[11]

For fabrication as detectors, the solution of PVA in water of 30 mg/mL and EVA in toluene of 10 mg/mL were prepared. Carbon black was added at 20% and 25% for PVA and EVA, respectively. Interdigitated electrode with 200 μm spacing was prepared with primary coating of 50 nm chromium and top 200 nm gold on 10 × 15 mm glass

Table 1. Resolution Factors for All Pairs of Solvents Presented in Order of Increasing Boiling Point (°C)[a]

	acetone (56.3)	chloroform (61.2)	MeOH (64..7)	THF (66.0)	hexane (68.7)	ethyl acetate (77.1)	EtOH (78.3)	IPA (82.3)	water (100.0)	toluene (110.6)	1-butanol (117.7)	chlorobenzene (131.7)	DMF (153.0)	1,2-dichlorobenzene (181.0)	1-octanol (194.5)
acetone	0.0	28.6	29.1	21.5	9.5	6.1	15.1	26.1	10.3	18.1	144.0	6.7	27.9	29.8	31.6
chloroform	28.6	0.0	30.0	21.5	26.5	26.0	31.9	32.0	30.5	20.4	32.5	14.8	31.4	23.5	33.3
MeOH	29.1	30.0	0.0	27.7	14.7	13.2	6.5	7.9	8.5	22.0	8.7	9.0	4.9	34.5	9.0
THF	21.5	21.5	27.7	0.0	13.1	11.7	27.8	28.6	18.8	3.3	32.4	8.8	28.9	6.0	34.5
hexane	9.5	26.5	14.7	13.1	0.0	4.7	32.1	34.2	12.5	14.2	63.7	3.2	26.6	**1.9**	64.2
ethyl acetate	6.1	26.0	13.2	11.7	4.7	0.0	15.2	17.5	11.6	11.6	21.1	4.9	15.2	11.3	21.5
EtOH	15.1	31.9	6.5	27.8	32.1	15.2	0.0	**2.3**	11.3	26.4	**2.0**	8.4	3.7	14.2	4.6
IPA	26.1	32.0	7.9	28.6	34.2	17.5	**2.3**	0.0	11.8	27.2	**1.8**	8.3	8.2	13.4	7.4
water	10.3	30.5	8.5	18.8	12.5	11.6	11.3	11.8	0.0	18.0	12.0	18.9	10.7	13.6	11.8
toluene	18.1	20.4	22.0	3.3	14.2	11.6	26.4	27.2	18.0	0.0	30.0	**0.8**	25.5	6.9	31.7
1-butanol	144.0	32.5	8.7	32.4	63.7	21.1	**2.0**	**1.8**	12.0	30.0	0.0	8.5	11.5	14.0	21.9
chlorobenzene	6.7	14.8	9.0	8.8	3.2	4.9	8.4	8.3	18.9	**0.8**	8.5	0.0	8.3	**2.6**	9.3
DMF	27.9	31.4	4.9	28.9	26.6	15.2	3.7	8.2	10.7	25.5	11.5	8.3	0.0	17.0	9.7
1,2-dichlorobenzene	29.8	23.5	34.5	6.0	**1.9**	11.3	14.2	13.4	13.6	6.9	14.0	**2.6**	17.0	0.0	16.1
1-octanol	31.6	33.3	9.0	34.5	64.2	21.5	4.6	7.4	11.8	31.7	21.9	9.3	9.7	16.1	0.0

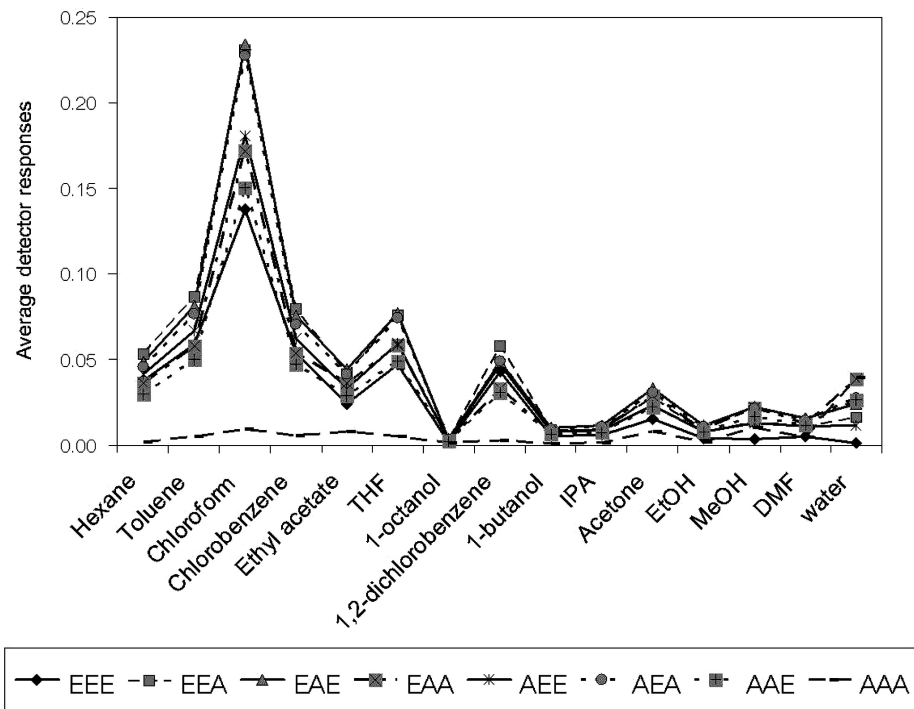[a] Boiling point (bp) indicated in parentheses.

Figure 2. Detector responses to solvents with low to high κ (hexane−water).

substrate by thermal evaporator. Three consecutive layers were built by applied the respective solution layer by layer, using the spincoater at the same speed of 3000 rpm. Eight specimens were the result of all combinations for three layers of two different species: EEE, EEA, EAE, EAA, AAE, AEA, AEE, and AAA (E and A stand for EVA and PVA, respectively). The first letter indicates the first applied layer and so on.

The testing system includes of a gas flow system, a test chamber, an analyte vaporizing chamber, and a digital multimeter (Keithly 2700) connected to a computer. Electrical resistance (R) of each detectors was measured and recorded. Nitrogen gas (99.99%) was used as a carrier gas. The temperature of analyte was maintained by immersion in ice bath for 30 min before testing and during the test. The typical testing procedure composed of 8 cycles for each analyte, but the data of the first cycle were discarded. Each cycle started by flowing nitrogen gas at the flow rate of 2 L/min into the test chamber for 60 s to obtain a baseline resistance (R_b). Then nitrogen gas was redirected to pass through the analyte vaporizing chamber before entering into the test chamber for 15 s, causing resistance change (dR). After that, pure nitrogen gas was redirected back to the test chamber for 120 s without passing through the analyte vaporizing chamber. Detecter response was defined as dR/R_b, the ratio of the change of electrical resistance in the analyte-containing atmosphere to the baseline resistance.

Results and Discussion

Patterns of response of detectors with three layers of PVA and EVA interlaid in combinations were shown in Figure 1. The patterns were arranged with solvents of decreasing dielectric constants (κ), that is, water (80.0), DMF (38.3), methanol (33.0), ethanol (24.3), acetone (20.7), isopropanol (20.0), 1-butanol (17.8), 1,2-dichlorobenzene (14.0), 1-oc-

tanol (10.3), THF (7.5), ethyl acetate (6.0), chlorobenzene (5.8), chloroform (4.8), toluene (2.4), and hexane (2.0); the number in parentheses is the dielectric constant.[8] The pattern of response is clearly differentiable by average magnitudes. Although the employed testing method was convenient and repeatable, it should be emphasized that the concentration of solvent vapors were not equal, depending on its vapor pressure or boiling point. Therefore, the magnitude of responses was affected not only by the intrinsic properties of solvents such as polarity but also the vapor concentration. However, despite the high boiling point of chlorobenzene (132 °C), the average response was higher than that to methanol with the boiling point of just 65 °C.

Generally, the responses to low-κ solvents were higher than those to high-κ ones (Figure 2.). For low-κ solvents, the particularly low responses to 1-octanol are probably because of the high boiling point of ∼195 °C. Chloroform, with combination of the low boiling point. (∼ 61 °C) and low-κ (∼5), had the highest responses, easy to differentiate from the rest.

With regard to magnitude, the responses to solvents could be divided into three groups. First group contains, chloroform, with very high responses; the second group contains 1,2-dichlorobenzene, THF, ethyl acetate, chlorobenzene, toluene, and hexane with fair responses (all solvents in this group have low-κ value of <15). The last group with mostly high-κ solvents is water, DMF, methanol, ethanol, acetone, isopropanol, butanol, and low-κ 1-octanol with rather low responses. Therefore, low- and high- solvents could be classified by the magnitude of response. Identification of a solvent within the group would require the differing response patterns. Confidence in resolving one in a pair of solvents could be indicated by the "resolution factor".

Resolution factors (RF) for all pairs were shown in Table 1, with the first in the pair listed as column header. Solvents

Table 2. Resolution Factors for All Pairs of Solvents with Low to High κ Presented in Order of Increasing Dielectric Constant[a]

	hexane (2.0)	toluene (2.4)	chloroform (4.8)	chlorobenzene (5.8)	ethyl acetate (6.0)	THF (7.5)	1-octanol (10.3)	1,2-dichlorobenzene (14.0)	1-butanol (17.8)	IPA (20.0)	acetone (20.7)	EtOH (24.3)	MeOH (33.0)	DMF (38.3)	water (80.0)
hexane	0.0	14.2	26.5	3.2	4.7	13.1	64.2	**1.9**	63.7	34.2	9.5	32.1	14.7	26.6	12.5
toluene	14.2	0.0	20.4	**0.8**	11.6	3.3	31.7	6.9	30.0	27.2	18.1	26.4	22.0	25.5	18.0
chloroform	26.5	20.4	0.0	14.8	26.0	21.5	33.3	23.5	32.5	32.0	28.6	31.9	30.0	31.4	30.5
chlorobenzene	3.2	0.8	14.8	0.0	4.9	8.8	9.3	**2.6**	8.5	8.3	6.7	8.4	9.0	8.3	18.9
ethyl acetate	4.7	11.6	26.0	4.9	0.0	11.7	21.5	11.3	21.1	17.5	6.1	15.2	13.2	15.2	11.6
THF	13.1	3.3	21.5	8.8	11.7	0.0	34.5	6.0	32.4	28.6	21.5	27.8	27.7	28.9	18.8
1-octanol	64.2	31.7	33.3	9.3	21.5	34.5	0.0	16.1	21.9	7.4	31.6	4.6	9.0	9.7	11.8
1,2-dichlorobenzene	1.9	6.9	23.5	2.6	11.3	6.0	16.1	0.0	14.0	13.4	29.8	14.2	34.5	17.0	13.6
1-butanol	63.7	30.0	32.5	8.5	21.1	32.4	21.9	14.0	0.0	**1.8**	144.0	**2.0**	8.7	11.5	12.0
IPA	34.2	27.2	32.0	8.3	17.5	28.6	7.4	13.4	**1.8**	0.0	26.1	**2.3**	7.9	8.2	11.8
acetone	9.5	18.1	28.6	6.7	6.1	21.5	31.6	29.8	144.0	26.1	0.0	15.1	29.1	27.9	10.3
EtOH	32.1	26.4	31.9	8.4	15.2	27.8	4.6	14.2	2.0	2.3	15.1	0.0	6.5	3.7	11.3
MeOH	14.7	22.0	30.0	9.0	13.2	27.7	9.0	34.5	8.7	7.9	29.1	6.5	0.0	4.9	8.5
DMF	26.6	25.5	31.4	8.3	15.2	28.9	9.7	17.0	11.5	8.2	27.9	3.7	4.9	0.0	10.7
water	12.5	18.0	30.5	18.9	11.6	18.8	11.8	13.6	12.0	11.8	10.3	11.3	8.5	10.7	0.0

[a] κ indicated in parentheses.

Table 3. Optimized Resolution Factors for All Pairs of Solvents with Low to High κ Presented in Order of Increasing Dielectric Constant[a]

|	hexane (2.0)	toluene (2.4)	chloroform (4.8)	chlorobenzene (5.8)	ethyl acetate (6.0)	THF (7.5)	1-octanol (10.3)	1,2-dichlorobenzene (14.0)	1-butanol (17.8)	IPA (20.0)	acetone (20.7)	EtOH (24.3)	MeOH (33.0)	DMF (38.3)	water (80.0)
hexane	0.0	27.5	67.8	21.6	32.8	26.0	123.9	10.5	212.6	71.1	91.8	95.2	75.8	68.3	70.4
toluene	27.5	0.0	43.7	**3.3**	30.8	28.5	81.0	9.9	82.5	76.9	59.2	76.8	74.3	60.7	82.8
chloroform	67.8	43.7	0.0	41.9	145.9	147.1	114.2	49.6	157.3	116.4	273.4	164.2	136.7	119.2	84.4
chlorobenzene	21.6	3.3	41.9	0.0	29.4	12.5	59.4	6.4	56.1	52.1	42.5	69.4	65.8	45.7	64.2
ethyl acetate	32.8	30.8	145.9	29.4	0.0	25.1	29.2	17.6	43.4	35.7	13.0	40.8	33.6	23.0	33.9
THF	26.0	28.5	147.1	12.5	25.1	0.0	52.9	13.8	69.6	44.8	88.2	50.1	54.2	42.7	52.7
1-octanol	123.9	81.0	114.2	59.4	29.2	52.9	0.0	77.2	50.4	13.4	186.9	11.7	103.2	29.2	33.5
1,2-dichlorobenzene	10.5	9.9	49.6	6.4	17.6	13.8	77.2	0.0	125.1	69.6	204.1	165.7	76.9	163.2	192.9
1-butanol	212.6	82.5	157.3	56.1	43.4	69.6	50.4	125.1	0.0	5.2	321.6	16.2	37.1	19.7	84.2
IPA	71.1	76.9	116.4	52.1	35.7	44.8	13.4	69.6	5.2	0.0	46.5	12.5	65.1	16.2	30.5
acetone	91.8	59.2	273.4	42.5	13.0	88.2	186.9	204.1	321.6	46.5	0.0	97.9	109.9	76.4	109.9
EtOH	95.2	76.8	164.2	69.4	40.8	50.1	11.7	165.7	16.2	12.5	97.9	0.0	26.2	9.4	50.5
MeOH	75.8	74.3	136.7	65.8	33.6	54.2	103.2	76.9	37.1	65.1	109.9	26.2	0.0	19.7	77.0
DMF	68.3	60.7	119.2	45.7	23.0	42.7	29.2	163.2	19.7	16.2	76.4	9.4	19.7	0.0	54.1
water	70.4	82.8	84.4	64.2	33.9	52.7	33.5	192.9	84.2	30.5	109.9	50.5	77.0	54.1	0.0

[a] κ indicated in parentheses.
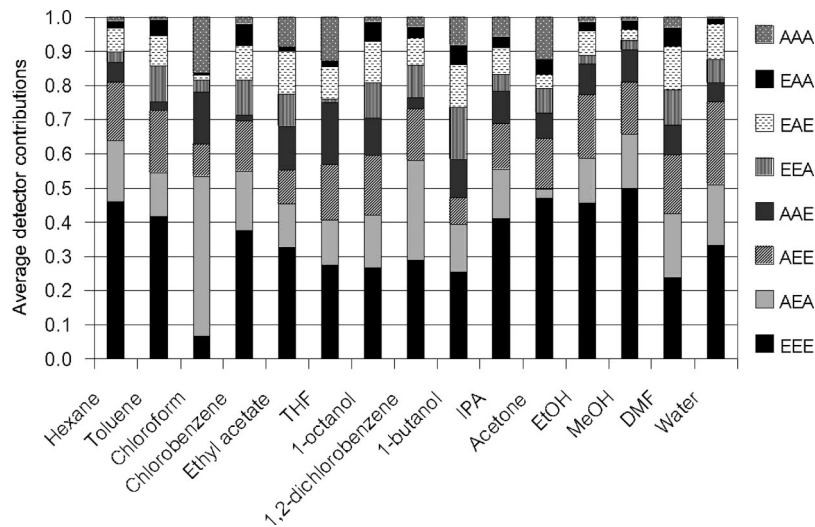
Figure 3. Average detector contributions for all pairs of individual solvents.
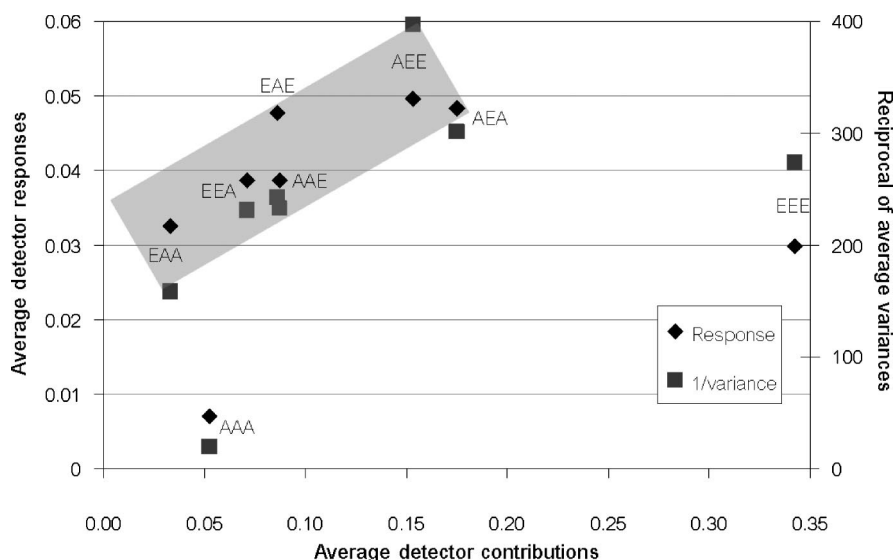

Figure 4. Average responses and the reciprocal of average variances of responses versus average contributions of individual detectors for all solvent pairs.

were arranged with increasing boiling point from left to right and from top to bottom. All RF's on the diagonal were zero for the pair of the same solvent The table is symmetrical along the diagonal because RF is equal regardless of the order in the pair (A/B or B/A). The number of all possible pairs is the number of cells on either side of the diagonal, which is 105. The pair of 1-butanol and acetone has the highest RF of 144, while the lowest RF of 0.8 belongs to the pair of chlorobenzene and toluene. Of all 105 pairs, 99 pairs have RF > 3; 5 pairs have RF > 1, and only one pair has an RF < 1. Chloroform, water, DMF, methanol, acetone, THF, ethyl acetate, and 1-octanol are 8, out of 15 solvents, that could be confidently distinguished from the others.

Almost all pairs with RF < 3 are in proximity of the diagonal in the lower right corner. In respect to the distribution of RF values, Table 1 could be divided into four sections. The upper left section has all RF values > 3, and it is indicated that the solvents with low boiling points could be differentiated with high confidence. The upper right and lower left sections are equivalent with almost all RF values of > 3, except for the RF value of 1.9 between 1,2-

dichlorobenzene and hexane. Differentiation between low and high boiling point solvents can also be performed with high confidence. Five of the six RFs with values below 3 are in the lower right section. Therefore, it is more difficult to differentiate those solvents with high boiling points. It is likely that the low vapor concentrations from high boiling points resulted in poorer differentiability. The higher vapor concentrations from low boiling points increased absorption and hence the better differentiation. Good differentiation between solvents with low and high boiling points is probably caused by large differences in vapor concentrations. It should also be remarked that low-RF pairs are dispersed near the diagonal where the boiling points are similar. However, the boiling points of ethyl acetate (77 °C) and ethanol (78 °C) at the section boundary are very close. It is then uncertain whether boiling points are the main factor in enhancing differentiation.

Table 2 displays all RF's with solvents rearranged with increasing dielectric constant (κ) from left to right and from top to bottom. The distribution of solvent pairs with RF < 3 is clustered near the upper left and lower right corner. Table
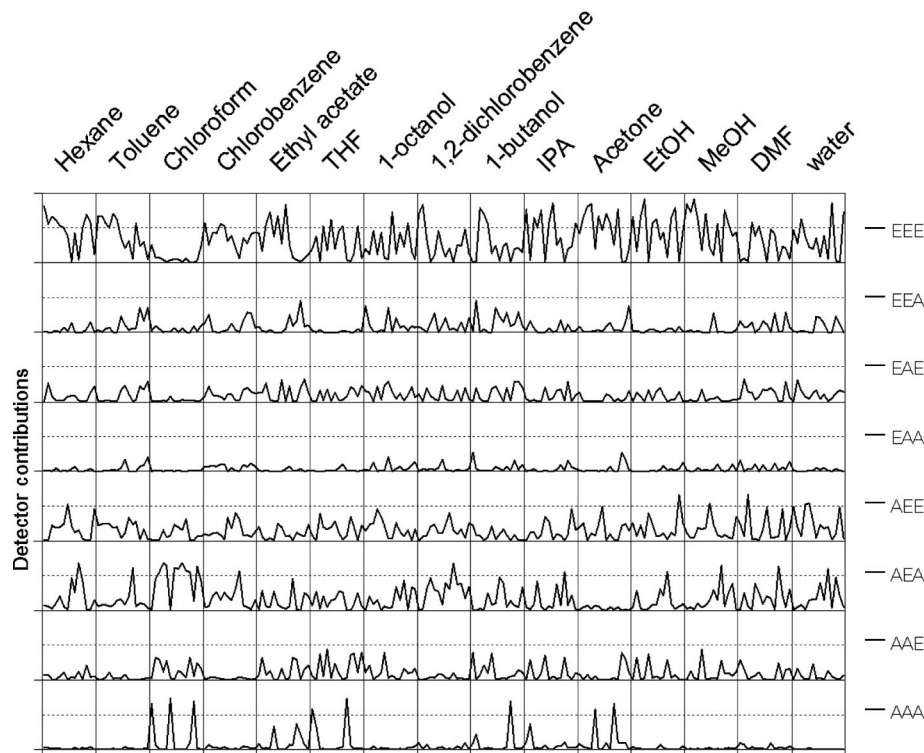
Figure 5. Detector contributions for all solvent pairs (including the reverses).

2 could again be divided into four sections with upper right and equivalent lower left sections having RF values of >3. The solvent pairs in these high-RF sections are between low-κ and high-κ solvents, in agreement with their substantial differences in magnitude of response. It is harder to differentiate between solvents with similar κ values as in the upper left and lower right sections. Chlorobenzene and toluene are particularly hard to differentiate with the lowest RF values of 0.8, possibly because of the similar κ values and high boiling points. From Tables 1 and 2, it could be concluded that RF was affected by both the dielectric constant and the boiling point.

However, simple RF employs responses from all detectors with equal weight. Resolution factor can be linearly maximized with Fisher linear discrimination technique[10] by optimized weighting of constituents.

When optimized, all RF values were greater than 3 (Table 3). Most RFs are very high, so that the confidence in differentiation reached almost 100%. The minimum is 3.3 for the pair of chlorobenzene and toluene. It is definitely proved that the set of combinatorial stacking of three layers of just two polymer composites could be employed as a detector array for a wide range of solvents with low to high κ (~2−80).

It is interesting to look at the components of the projection vector (V), on which the pair of analytes have the maximized RF value. V is a unit vector, the square of each component of V represents percentage of contribution of the individual detector to provide the best resolution for the pair of analytes. The detector contributions averaged for all pairs of individual solvents with the others are presented in Figure 3. It is obvious that EEE has very significant contributions for most solvents. Total contribution of four combinations, that is,

EEE, AEA, AEE, and AAE, could be approximately larger than 0.7 or 70% for most solvents.

For all pairs, average responses and the reciprocal of average response variances were plotted against average contributions of individual detectors (Figure 4). The scale of average responses was adjusted so that each point had the point of the corresponding reciprocal of average variances situated nearby. The gray band indicated the probable linear relationship with the average contribution, but AAA and EEE were excluded. It has shown that the characteristics of mixed-layer detectors seemed to be similar in the group, and, pure trilayers, AAA and EEE, had different characteristics. The characteristic responses of mixed layers were not the combination of those of pure trilayers, but as of a new kind of detector with its own characteristics. The average responses and variances could be tuned by the combination of interlayering.

For average contributions, EEE has the highest of 0.34, AEA and AEE have the next highest of 0.17 and 0.15, respectively. AAE, EEA, and EAE have the average contributions in the range of 0.07−0.09, while EAA and AAA have lowest values of less than 0.05. The contributions are not coincided with the magnitude of responses, where EEE and AAA have the lowest values. Instead, they have better relation to the reciprocal of average response variance: EEE, AEA, and AEE have the greatest values, AAE, EEA, and EAE have average values of near 0.004, and EAA and AAA have the lowest ones. Grouping of detectors by the reciprocal of average response variances is similar to that by average contributions. It is indicated that the reciprocal of response variance substantially determined contribution of detectors in optimization.

The high average variance gives AAA its low contribution in V. Severe agglomeration of carbon black particles in PVA layers was observed and is expected to be the source of large uncertainty in responses. It seems that EAA and AAA, with total contribution of just 0.1 or 10%, could be left out from the detector array without any significant deterioration in performance.

Figure 5 shows contributions of all individual detectors for all possible pairs of individual solvents including the same pairs with reverse order, providing the full spectrum of contribution in detailed perspectives. It can be seen that EEE, AEE, AEA, and AAA are the main contributors and have significant contributions of near or more than 0.5. The high contributions of EEE, AEE, and AEA are in agreement with high average values. Even though the average contribution of AAA is very low, but for some particular pairs, it becomes the most significant contributor with more than 50% contribution. They are among the group of chloroform, ethyl acetate, THF, 1-butanol, and acetone. Although those pairs have unoptimized RF's of more than 3, AAA responses could provide further enhancement through optimization. This demonstrates the advantage of the large number of detectors. Although EEA, EAE, and AAE have no major contributions, they improve the confidence with additional confirmation. However, the contributions of EAA are all low, making it dispensable.

Conclusions

For the employed testing procedure, the resolution factor (RF) was affected by both the dielectric constant and the boiling point. Of the possible 105 pairs, 99 pairs have RF > 3; 5 pairs have RF > 1, and only one pair with RF < 1. Fisher linear discrimination improved all RF's beyond 3.

Improvements were the result of selective contributions from individual detectors; some possessed more significant contributions than others in resolving of a particular pair. These illustrate the diversity created by the combinatorial stacking of layers. It is definitely proved that the set of combinatorial stacks of three layers of two polymer composites could be employed as an array of detectors for detection of solvents having low to high κ.

References and Notes

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