

Fabrication and Optimization of a Conducting Polymer Sensor Array Using Stored Grain Model Volatiles

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ABSTRACT: During storage, grain can experience significant degradation in quality due to a variety of physical, chemical, and biological interactions. Most commonly, these losses are associated with insects or fungi. Continuous monitoring and an ability to differentiate between sources of spoilage are critical for rapid and effective intervention to minimize deterioration or losses. Therefore, there is a keen interest in developing a straightforward, cost-effective, and efficient method for monitoring of stored grain. Sensor arrays are currently used for classifying liquors, perfumes, and the quality of food products by mimicking the mammalian olfactory system. The use of this technology for monitoring of stored grain and identification of the source of spoilage is a new application, which has the potential for broad impact. The main focus of the work described herein is on the fabrication and optimization of a carbon black (CB) polymer sensor array to monitor stored grain model volatiles associated with insect secretions (benzene derivatives) and fungi (aliphatic hydrocarbon derivatives). Various methods of statistical analysis (RSD, PCA, LDA, *t* test) were used to select polymers for the array that were optimum for distinguishing between important compound classes (quinones, alcohols) and to minimize the sensitivity for other parameters such as humidity. The performance of the developed sensor array was satisfactory to demonstrate identification and separation of stored grain model volatiles at ambient conditions.

KEYWORDS: grain spoilage, conducting polymer sensors, sensor arrays, odor volatiles

■ INTRODUCTION

Most stored products have their own characteristic smell: fruity, minty, pungent, and other aromas. The volatiles that make up these odors can be used as indicator volatiles for healthy grain (e.g., sweet odor due to long chain aliphatic alcohol from wheat with certain moisture content; esteric fruity smell from some rice species). Any deviation from this characteristic odor could give an indication of grain spoilage.

Characteristic smells of stored grains do not change much under proper storage conditions; however, an increase in moisture content (MC), relative humidity (RH), temperature (T), or foreign agents (insects, fungi, mites, etc.) changes characteristic smells, which can in turn be used as an indicator volatile. For example, red flour beetles, *Tribolium castaneum* (Herbst), usually produce quinones in storage environments.^{1–3} The reported levels of defensive secretions are variable, depending not only on age and gender of adults but also on strain, food availability, photoperiod, beetle density, and health.⁴ Fungal volatiles, mostly alcohols and ketones, are another example of indicator volatiles which have been studied by several authors.^{5–7} These volatiles were identified by gas chromatography–mass spectrometry (GC–MS).

There are various instrumental methods for monitoring of insect volatiles.^{3,4,8–10} These methods include ultraviolet–visible spectroscopy (UV–vis), polarography, thin-layer chromatography, and gas chromatography. Each method qualitatively detects the presence of particular volatiles; however, quantitative detection of those volatiles is cumbersome and involves a number

of steps. In many cases no quantitative information is available for these studies. In addition, many of these techniques are also time-consuming, expensive, or not sensitive enough for the early detection of fungal and insect activity. A consistent biomarker with adequate reproducibility to detect incipient spoilage could help prevent major losses as a result of fungal infection or insect infestation of stored grain due to poor storage management.

In situ measurement or chemical analysis of any grain bin volatile sample has many advantages over ex situ techniques because it avoids excessive sampling and analysis steps. The development of an electronic nose using sensor arrays combined with pattern recognition techniques offers interesting alternatives. Instruments of this type have already proven useful in a number of practical applications such as to classify various liquors, perfumes, tobacco brands, and beers.^{11–13} An electronic nose has been tested for quality estimation of shrimp¹⁴ and bakery products.¹⁵

For odor classification, metal oxide, intrinsically conducting polymer, and conducting polymer composite sensors are usually used. Depending upon volatile characteristics, an array of sensing materials are selected for odor identification and discrimination. Carbon black conducting polymer sensors have

Received: July 8, 2011

Revised: February 12, 2012

Accepted: February 14, 2012

Published: February 14, 2012

been employed to identify a wide variety of organic volatiles.^{16,17} Freund and Lewis¹⁸ prepared conducting polymer composite sensors, which are sensitive to the identity, and determine concentrations of various organic vapors in air. An array of such sensing elements produced a chemically reversible diagnostic pattern of electrical resistance changes upon exposure to different odorants. They described that such a sensor array can be used as a signature of organic vapors for identification using principal component analysis. The sensor array also could provide information on the components of gas mixtures.

The primary objective of this research was to develop a sensor array which could efficiently recognize and differentiate the presence of stored grain model volatiles (e.g., anisole, benzoquinone, tetrahydrofuran, ketones, and aliphatic alcohols). The developed sensor array can be used for detection of insect infestation and fungal infection in stored grain.

EXPERIMENTAL PROCEDURES

Materials. The carbon black (CB) used in the composites was Black Pearls 2000 (BP2000), a furnace black material from Cabot Co. (Billerica, MA, USA). The polymers used in the composites are listed in Table 1. All polymers were purchased from Polysciences Inc.

Table 1. Polymers Used in the Sensor Arrays

ID ^a	symbol	polymer
1	P4VP	poly(4-vinylphenol)
2	PSAA	poly(styrene-co-allyl alcohol)
3	PMS	poly(alpha-methylstyrene) ^b
4	PVP	poly(N-vinylpyrrolidone)
5	PVA	poly(vinyl acetate) ^b
6	PMVE	poly(methyl vinyl ether-co-maleic anhydride)
7	PBAC	poly(bisphenol A-carbonate) ^b
11	PS	poly(styrene) ^b
12	PSMA	poly(styrene-co-maleic anhydride)
13	PVB	poly(vinyl butyral) ^b
14	PSu	poly(sulfone) ^b
15	PMMA	poly(methyl methacrylate) ^b
16	PVCA	poly(vinylidene chloride-co-acrylonitrile)
17	PEO	poly(ethylene oxide)

^aID: identification number. ^bSelected polymers.

(Warrington, PA, USA) or Aldrich Chemical Co. (Madison, WI, USA) and were used as received. These polymers can be classified as hydrogen bond acidic (HBA), hydrogen bond basic (HBB), dipolar and hydrogen bond basic (DBB), moderately dipolar (MD), and weakly dipolar (WD). Analytes will interact with these polymers based on their structure and intrinsic properties.¹⁹ The model volatiles (analytes) used in this study were toluene (To), anisole (Ani), methanol (Me), water (H₂O), 2-propanol (Pro), 1-octanol (Oc), acetone (Ac), 1,4-benzoquinone (BQ), and tetrahydrofuran (THF); all were reagent grade and were used as received from EM Scientific (Carson, NV, USA) or Aldrich Chemical Co. (Madison, WI, USA).

Instrumentation and Apparatus. Standard glassware was used to construct a bubbler apparatus (to provide known partial pressures of various vapors) and a flow chamber to control the resulting gas stream. The bubblers were 500 mL Pyrex bottles with two armed 29/34 ground joint (24 cm long with a 5 cm inside diameter) from Lasalle Scientific Inc. (Guelph, ON, Canada). To provide a pathway for gas flow, a glass tube terminated by a coarse filter frit was inserted into a glass stopper and then placed into the top of each bubbler. The carrier gas was oil free ultrahigh purity (99.99%) compressed nitrogen from Praxair Inc. (Calgary, AB, Canada). The measurements were performed at a temperature of 25 °C ± 1 °C, which was maintained through a microprocessor controlled water bath (model no. 28L,

Cole-Parmer, Montreal, QC, Canada). The carrier gas was introduced into the solvent through the porous ceramic frit, and the solvent-saturated gas mixture exited the bubbler via the side arm of the glass tube. Saturation of the gas streams in the experimental apparatus was verified for the highest flow rates (1000 sccm) used in this work through measurement of the rate of mass loss of liquid in the bubbler; thus saturation conditions were assumed to have been obtained for the lower flow rates used in other experiments. The vapor pressures of model volatiles and associated concentration derived from elsewhere²⁰ at 25 °C temperature are shown in Table 2.

Table 2. Vapor Pressure of Model Volatiles and Associated Concentration at 1% ($P/P_0 = 0.01$)

SI ^a	name	vapor pressure at 25 °C (mmHg)	concn (ppmv)
1	1-octanol	0.07	0.921
2	1,4-benzoquinone	0.10	1.316
3	anisole	3.54	46.57
4	water	23.8	313.2
5	toluene	28.4	373.7
6	2-propanol	44.1	578.9
7	methanol	123	1618
8	THF	155	2039
9	acetone	240	3157

^aSI: serial number.

Saturated vapor was carried out the side arm of the bubbler, blended with a controlled background flow of pure carrier gas, and then transferred into the rectangular sensing chamber made of Teflon (15.2 cm × 8.5 cm × 4.5 cm). The sensing elements were introduced into the chamber through open slot(s) and attached to a printed circuit board (PCB) connected through an edge connector (Figure 1). The chamber was sealed when connected to the PCB. The gas flow rates were controlled with mass flow controllers (model: FLO-9HL, Plasmionique Inc., St Hyacinthe, QC, Canada), three-way valves, and Teflon solenoid shut-off valves.

Measurements. To determine the response of the sensor elements to various vapors, the dc resistance of each sensor was determined as a function of time. Resistance measurements were performed using a simple two-point configuration. Sensors fabricated with the PCB supports were plugged directly into a 15- or 30-pin bus strip, which was then connected to a multiplexing ohmmeter via a ribbon cable. The resistances of the composite films on gold substrates were monitored through an Agilent data acquisition unit (model 34980A, Agilent Technologies, Inc., Santa Clara, CA, USA) using a personal computer (PC).

To initiate an experiment, the sensors were placed into the Teflon chamber and a background flow of compressed air was introduced until the resistance of the sensors stabilized. Solvent vapor streams of various concentrations and compositions were then passed over the sensors. The flow rates in the bubblers were controlled using mass flow controllers with the flow limit of 0.2 to 2000 sccm (standard cubic centimeter). Analyte gas flows were kept low enough (5 to 50 sccm) to ensure that the vapor was saturated with solvent prior to dilution with the background gas. In a typical experiment, resistance data from the sensor array elements were collected for 10 min (to serve as a baseline), followed by a 5 min collection during exposure to the solvent vapor stream, followed by a 5 min recovery time.

A blend of saturated vapor and ultrahigh purity nitrogen was used for the measurements. To achieve the required levels of volatile concentrations (ppmv), saturated vapor was diluted to appropriate concentrations by mixing and varying the gas flow rate from the nitrogen cylinder. For example, a flow rate (FR) of 1000 sccm of 3157 ppmv acetone and 990 sccm of nitrogen in the Teflon mixing chamber measured at the same pressure and temperature required 10 sccm of saturated acetone (Table 3). In a similar fashion, desired levels of

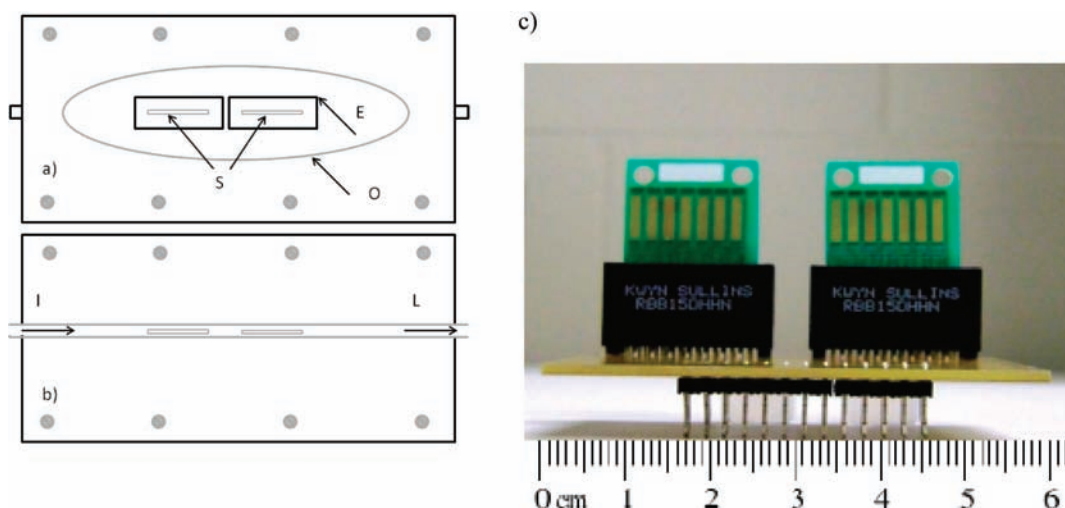


Figure 1. A schematic representation of a sensor chamber made of Teflon: (a) top view; O, O-ring; E, edge connector slot; S, sensor array slot; (b) inner chamber view; I, gas inlet; L, gas outlet; (c) sensor array connected with edge connector.

Table 3. Typical Example of Gas Flow and Their Concentration in Mixture

carrier gas (sccm)	analyte vapor (sccm)	mixture flow (sccm)	analyte concn (%)
1000	0000	1000	0
990.0	10.00	1000	1
980.0	20.00	1000	2

volatile concentrations were achieved by mixing various levels of nitrogen and saturated vapor from different bubblers in air.

Data Collection System. The data collection system used for characterization of the sensor array consisted of an Agilent 34980A Data Acquisition Switch Unit (Agilent Technologies, Inc., Santa Clara, CA, USA). The dc resistance of the sensor was read sequentially by the Agilent data acquisition unit. The control computer was interfaced with the data collection system through an IEEE general purpose interface board (GPIB). The resistance data were initially stored in the data acquisition unit, and once a complete set of data were recorded, the GPIB communications protocol sent the data to the control computer, where the data were stored in a tab-limited text file.

Sensor Construction. Gold interdigitated array electrodes (IDAs) to be used as the sensor substrate platform, deposited on a 1 mm thick printed circuit board (PCB), were custom designed in consultation with Nano Fabrication Lab, University of Manitoba, and Iders Inc., Winnipeg, MB. The sensor chip was fabricated by Dynamic & Proto Circuits Inc., Stoney Creek, ON. Each sensor chip had seven sensor elements (detectors) (Figure 2).

Carbon black polymer sensors were prepared on properly cleaned IDAs according to a previously reported procedure.¹⁷ In brief, to prepare the carbon black–polymer composites, 40 mg of carbon black and 160 mg of one of the insulating polymers (Table 1) were added to 20 mL of solvent. The solvents were tetrahydrofuran, dichloromethane, methanol, or acetone. The solutions were sonicated for 10 min to suspend the carbon black, and the films were cast by spray coating using an aluminum mask on the electrode area. The spraying procedure was repeated several times until a measurable film resistance (few kilohm) was obtained. Before use, the sensors were dried in open air for 1 day.

Gas–Sensor Interaction and Data Processing. The interaction between polymer sensor and gaseous analytes can be described by the sorption process¹⁶ and the solvation equation,²¹ where sorption is based on interactions between polymer composite (stationary phase) and gas (mobile phase) and is governed by a partition coefficient, which was mathematically described by Severin.¹⁶

When the interaction is of a complex nature, it can be explained by the solvation parameter model in a form suitable for characterizing the retention properties of sensing phases in gas–solid chromatography as given by eq 1, generally known as the linear solvation energy relationship (LSER) equation:^{21,22}

$$\log SP = c + rR_2 + s\pi^H_2 + a \sum \alpha^H_2 + b \sum \beta^H_2 + l \log L \quad (1)$$

where SP is some free energy related solute property such as a gas–solid partition coefficient, retention factor, specific retention volume,

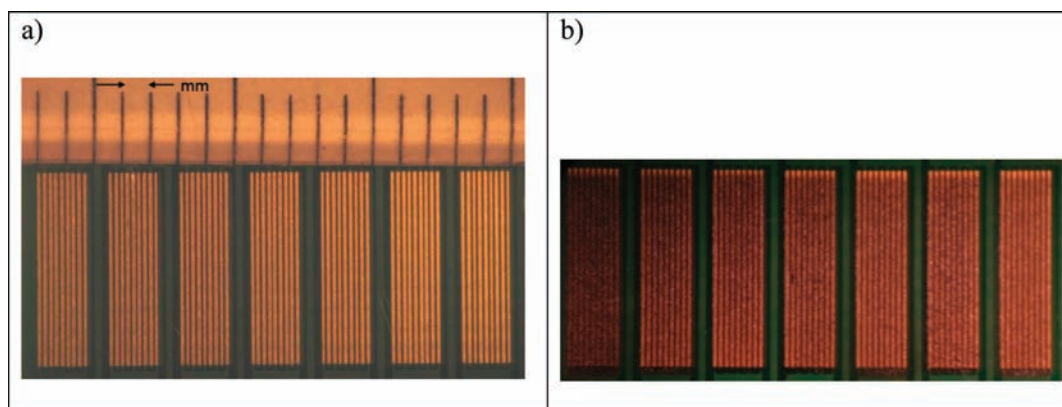


Figure 2. Sensor array (a) bare gold and (b) polymer on gold surface.

or relative adjusted retention time. The remainder of the equation is made up of product terms called system constants (r, s, a, b, l) and solute descriptors ($R_2, \pi^H, \sum\alpha^H, \sum\beta^H, \log L$). Each product term represents a contribution from a defined intermolecular interaction to the correlated solute property ($\log SP$). The $l \log L$ term represents the contribution from cavity formation and solute–stationary phase dispersion interactions; rR_2 the contribution from lone pair n- and π -electron interactions; π^H_2 the contribution from interactions of a dipole type; $a\sum\alpha^H_2$ the contribution from solute hydrogen-bond acid stationary phase hydrogen-bond base interactions; and $b\sum\beta^H_2$ the contribution from solute hydrogen-bond base stationary phase hydrogen-bond acid interactions. We applied Abraham's solvation equation (eq 1) during sensor array optimization.

Data preprocessing is an important tool for sensor study. It can be used to systematically modify the raw sensor signals from an array to provide more useful input to mathematical methods for data analysis (e.g., principal component analysis or linear discriminant analysis). There are no general guidelines to determine the appropriate data preprocessing technique for a particular type of sensor array, so it is beneficial to explore several preprocessing strategies to determine which is best suited for a particular sensor array/data analysis method. Likewise, there are a number of statistical techniques available for data analysis including both supervised and unsupervised techniques.

The overall objective of this work is to detect incipient spoilage of grain from various sources (e.g., insects, fungi) using a suitable sensor array. Fourteen different polymers with different structures and functional groups were available for this study. Backbone and functional groups provide the mechanisms of interaction with a particular analyte as described by eq 1, and an array of chemically diverse polymer base sensors will ultimately generate a response pattern unique to the various odors exposed to the array. To simplify the fabrication and function of the sensor array, the fourteen polymers were assessed and downselected to a seven sensor array on an inexpensive printed circuit board (PCB).

Downselection was achieved through a systematic statistical analysis of responses generated with the model volatiles of interest. Individual sensor performance was evaluated in terms of selectivity, reproducibility, and sensitivity with respect to model volatiles of interest. Scoring and ranking of sensors based on these figures of merit provides insight and a statistical basis for selecting sensor materials from each sensor set. Selectivity was assessed based on weighted contribution of the sensors to linear discriminant analysis (LDA), reproducibility from relative standard deviations (RSD) of repetitive exposures, and sensitivity through linearity and slope of responses as a function of concentration. These are all supervised methods for data analysis. Other methods such as principal component analysis (PCA), an unsupervised method, were also performed to gauge performance with multiple analytes; however, this method did not provide additional insight into individual sensor performance. Details of supervised and unsupervised techniques of data analysis were described by several authors.^{23–25}

RESULTS AND DISCUSSION

Selection of Model Volatiles. A few model volatiles (water, methanol, acetone, 2-propanol, anisole, 1,4-benzoquinone, toluene, 1-octanol, tetrahydrofuran) were selected to optimize sensor performance. The volatiles and their basic characteristics were discussed elsewhere.²⁰ These volatiles have some structural similarities with stored-grain volatiles. For example, benzoquinone derivatives (methyl benzoquinone (MBQ) and ethyl benzoquinone (EBQ)) are usually produced from red flour beetle as aggregation or sex pheromones.^{4,26} Long chain aliphatic alcohol and their derivatives evolve from wheat under certain physical (temperature, MC, RH) and biological conditions.^{7,27} Tetrahydrofuran (THF) and anisole were selected because their derivatives are produced when grain is severely damaged and produces a musty odor.^{7,28,29} All other low molecular weight alcohols and ketones are produced at different stages of degradation of stored grain.

Sensor Array Optimization. The optimization of a sensor array for incipient grain spoilage monitoring requires special attention to flow rate, linearity of sensor response, and random exposures of analytes to CB sensors (Figure 3 and Figure 4).

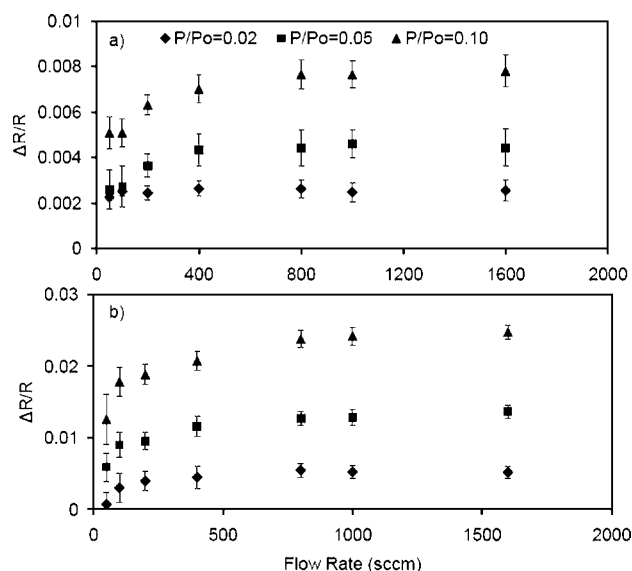


Figure 3. Effect of flow rate on carbon black polymer sensor poly(vinyl butyral). Analytes used here were (a) 1,4-benzoquinone and (b) 1-octanol at $P/P_0 = 0.02$ to 0.10 and 25 °C temperature. Error bar for 3 replicates.

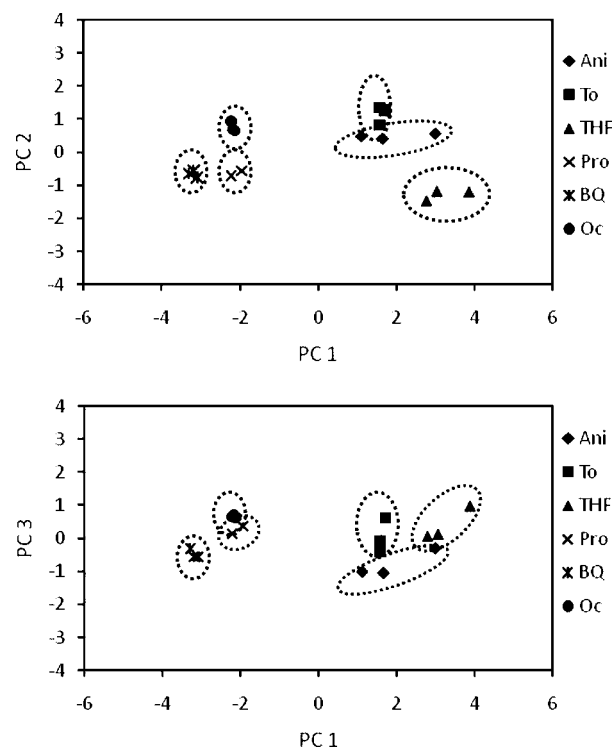


Figure 4. Principal component analysis using CB polymer composite sensors upon random exposure of various analytes: (◆) anisole, (■) toluene, (▲) tetrahydrofuran, (×) 2-propanol, (*) 1,4-benzoquinone, (●) 1-octanol.

Effect of Flow Rate on Sensor Response. Gas flow rate in a grain bin is typically very low unless it is purged for drying or cooling the grain. The gas circulation in a grain bulk

proceeds predominantly through diffusion although additional mass transport through intergranular space can be caused by temperature gradients in the grain bin. Other factors, such as external wind flow and pressure, internal moisture, and CO₂ by respiration of grain, insects, mites, and fungi, can also impact the process. As a result, the evolution of sensor array response patterns is expected to be slow, thus assumed to be in equilibrium with its surroundings. To efficiently test the sensor arrays, a relatively high flow rate (1000 sccm) was chosen in designing and performing most of the experiments. Care was taken to allow sufficient time for the array to reach equilibrium with the exposed volatiles to ensure that the response would be similar to that obtained for a similar concentration at a low flow rate. For 1,4-benzoquinone, it was not possible to generate constant vapor pressure over the entire duration of the experiment with this vapor delivery instrument. Therefore, sensor response dropped slightly, which is reflected in Figure 3. But it was possible to generate consistent 1,4-benzoquinone vapor pressure at low flow rate.

Linearity of Sensor Response. The linearity and slope of calibration curves are a measure of sensor performance. Large slopes indicate good or better sensitivity of a sensor compared to low slopes for a particular analyte. Table 4 shows the sensitivity of all sensors for the various analytes. Regression coefficients varied within the limit of 0.9996 to 0.7802. For some sensor–analyte combinations, correlation coefficients were low because the sensor exhibited only a very small response to the analyte. Poly(*N*-vinylpyrrolidone) and poly(4-vinylphenol) showed high level of interaction with 1-octanol and 1,4-benzoquinone, whereas anisole showed strong interaction with poly(4-vinylphenol), poly(vinyl butyral), poly(bisphenol A-carbonate), and poly(sulfone). Tetrahydrofuran showed the greatest interaction with poly(vinyl butyral).

Random Exposures of Analytes to CB Sensors. Random exposures of analytes to CB sensors were performed to check possible interference from new volatiles and sufficiency of recovery time. Figure 5 shows a typical sensor response to analytes when exposed randomly at certain partial pressure. The order of odor volatiles did not influence the sensor response after a 5 min recovery time. Figure 4 also confirms the ability of the sensor array to classify volatiles with random exposure of analytes.

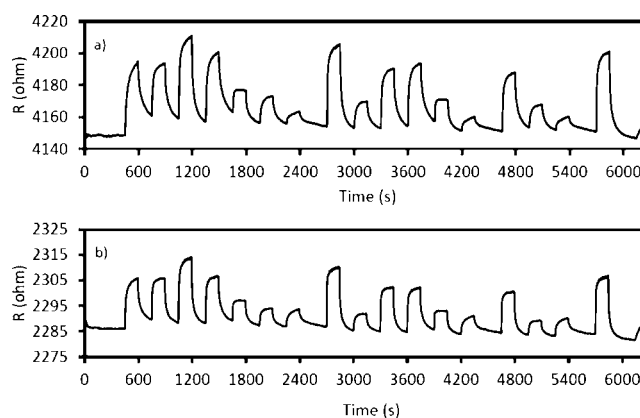


Figure 5. Random exposure of analytes to (a) poly(bisphenol A-carbonate) and (b) polystyrene sensor at fixed partial pressure (0.02) and 25 °C. The analytes are water vapor, methanol, acetone, tetrahydrofuran, 2-propanol, toluene, and 1-octanol. Flow rate was 1000 sccm.

Sensor Selection. The analysis of sensor arrays involves fabrication, testing and exposing the arrays to a set of target analytes at the concentration of interest. Most of the experimental concentration range is low, and it was within 1–5% of the analyte's vapor pressure by volume. Initially sensors were evaluated based on polymer types and functional groups, and how the polymers were predicted to respond to analytes based on bonding or nature of interaction. For example, in a stationary phase, hydrogen bonding base groups may show stronger interaction with alcohol containing volatiles than the one containing hydrogen bonding acid groups. A nonpolar stationary phase should show enhanced interaction with a nonpolar volatile compared to a polar one. The arrays were selected based on experimental data developed in the laboratory, using a combination of statistical and experimental techniques.

To determine the seven best polymers for detecting benzoquinone derivatives (MBQ, EBQ, and 1,4-benzoquinone), benzene derivatives (anisole, phenol), and long chain aliphatic alcohols (1-octanol, 1-butanol, methanol), we developed a protocol that is discussed in the following sections.

To select the best sensor array from fourteen polymers, and eight selected model volatiles, individual sensor performance was evaluated in each sensor set using both supervised and

Table 4. Sensitivity^a of CB Polymer Sensors toward Model Volatiles (atm⁻¹)

sensor	Me	Ac	THF	BQ	Ani	Pro	To	Oc
1	0.3013	1.0000	0.7126	0.7146	1.0000	1.0000	0.5718	0.4105
2	0.0783	0.2277	0.2780	0.3149	0.4354	0.7899	0.5634	0.1017
3	0.0180	0.0564	0.0556	0.0947	0.2706	0.1592	0.3087	0.1226
4	1.0000	0.3150	0.0347	1.0000	0.0518	0.5158	0.3782	1.0000
5	0.0285	0.0537	0.0413	0.1187	0.3121	0.1779	0.1911	0.1906
6	0.0567	0.0643	0.0279	0.4232	0.5597	0.0743	0.2987	0.2946
7	0.0280	0.1589	0.1401	0.1771	0.7258	0.3103	0.8345	0.1752
11	0.0204	0.1000	0.1092	0.1393	0.5555	0.2654	0.6465	0.2105
12	0.0219	0.4448	0.3434	0.1034	0.2017	0.2309	0.2667	0.0757
13	0.1158	0.3864	1.0000	0.1256	0.8624	0.4788	1.0156	0.1916
14	0.0380	0.1908	0.1592	0.2081	0.7498	0.4497	0.8860	0.2320
15	0.0323	0.1569	0.1144	0.0651	0.2519	0.1894	0.1931	0.1547
16	0.0263	0.1853	0.1683	0.0463	0.1567	0.0644	0.2027	0.2619
17	0.0180	0.0382	0.0360	0.0531	0.3888	0.1522	1.0000	0.1868

^aFor simplicity all data are represented compared to highest slope for respective volatile; To, toluene; Ani, anisole; Me, methanol; Pro, 2-propanol; Oc, 1-octanol; Ac, acetone; BQ, 1,4-benzoquinone; and THF, tetrahydrofuran.

unsupervised techniques. Supervised techniques involved sensors' reproducibility, sensitivity, and selectivity and unsupervised principal component analysis. It was then scored i to xiv for each sensor's performance using these metrics individually and overall (i = best, xiv = poor) (Table 5).

Reproducibility. Figure 6 shows a typical example of reproducibility of carbon black polymer sensor response at 25 °C. Reproducibility of an individual sensor was calculated from relative standard deviations (RSD) for benzoquinone and 1-octanol at $P/P_0 = 0.02$. Large RSD indicates a noisy sensor, and as a result is not suitable for the sensor array. From the analysis it was observed that sensor 15, 7, 3, 17, 11, 13, and 14 performed relatively well for 1-octanol, whereas sensor 7, 11, 14, 5, 13, 17, and 3 performed well for 1,4-benzoquinone and their derivatives (Table 5).

Sensitivity. Sensitivity was also evaluated from the slope of calibration curves for volatiles of interest for P/P_0 in the range of 0.01 to 0.05 as shown in Figure 7. Poly(*N*-vinylpyrrolidone) shows the highest sensitivity for both 1-octanol and 1,4-benzoquinone and second highest for poly(4-vinylphenol). These two polymers presumably interact with those analytes through hydrogen bonding, much stronger interaction compared to other polymers.

The comparison of slope of poly(4-vinylphenol) for 1-octanol (0.128 atm^{-1}) and 1,4-benzoquinone (0.741 atm^{-1}) demonstrates that sensitivity was higher for the poly(4-vinylphenol) sensor toward 1-octanol compared to quinone. The increased sensitivity presumably comes from pi- π interactions and polarizability. As BQ does not have any acidic hydrogen, the contribution toward hydrogen bonding is expected to be negligible. In contrast, 1-octanol does have a hydrogen bonding contribution.

Using eq 1 and solving for regression coefficients using data from Table 6 and Table 7, values could be determined as shown in Table 8. The regression coefficients (i.e., r , s , a , b , and l) show the importance of the contribution of the corresponding chemical forces to the partition coefficient between a given vapor/sorbent pair. The regression constant, c , is a residual product of multiple linear regressions that has no significance in relation to the chemical forces.

Sensor 13 showed the highest tendency to interact through pi and n electron pairs among the sensors. Sensors 13 and 15 had a considerable amount of polarity compared to the others. Hydrogen-bond basicity was low for most of the sensors except 13, indicating that the acidic phase of sensor 13 will interact with a basic solute or vapor. Indeed the structure of sensor 13 has the greatest capacity for hydrogen-bond basicity. From the values of b , it was observed that almost all sensors have the capacity to interact with solute through hydrogen-bond acidity. To measure the ability of the phase to distinguish between or to separate homologues in any homologous series, sensor 13 contributed remarkably more than other sensors.

For example, from Table 7, interaction between sensor 13 and methanol (0.6294 atm^{-1}) is much higher compared to that of 2-propanol (0.1696 atm^{-1}). In this case, 1-octanol showed least interaction with sensor 13. This is how sensor 13 efficiently contributes to separation of homologous series of alcohols.

Selectivity. Selectivity is the ability of the array to distinguish one analyte from another. This ability is one of the most important criteria in selecting a sensor array. Linear discriminant analysis (LDA) can be used to measure a sensor's ability to distinguish analytes by maximizing the variance

Table 5. Sensor Selection Using Reproducibility, Sensitivity, and Selectivity Criteria for 1-Octanol and 1,4-Benzoquinone

ranks	poorer sensors														analytes
	i	ii	iii	iv	v	vi	vii	viii	ix	x	xi	xii	xiii	xiv	
reproducibility	15 ^a	7	3	17	11	13	14	6	5	1	4	2	16	12	Oc
	PMMA	PBAC	PMS	PEO	PS	PVB	PSu	PMVE	PVA	P4VP	PVP	PSAA	PVCA	PSMA	
	7	11	14	5	13	17	3	15	6	2	12	16	4	1	BQ
	PBAC	PS	PSu	PVA	PVB	PEO	PMS	PMMA	PMVE	PSAA	PSMA	PVCA	PVP	P4VP	
sensitivity	4	1	6	16	14	11	13	5	17	7	15	3	2	12	Oc
	PVP	P4VP	PMVE	PVCA	PSu	PS	PVB	PVA	PEO	PBAC	PMMA	PMS	PSAA	PSMA	
	4	1	6	2	14	7	11	13	5	12	3	15	17	16	BQ
	PVP	P4VP	PMVE	PSAA	PSu	PBAC	PS	PVB	PVA	PSMA	PMS	PMMA	PEO	PVCA	
selectivity	11	5	13	7	3	12	14	6	15	17	2	16	4	1	Oc:BQ
	PS	PVA	PVB	PBAC	PMS	PSMA	PSu	PMVE	PMMA	PEO	PSAA	PVCA	PVP	P4VP	

^aBold font indicates selected sensors.

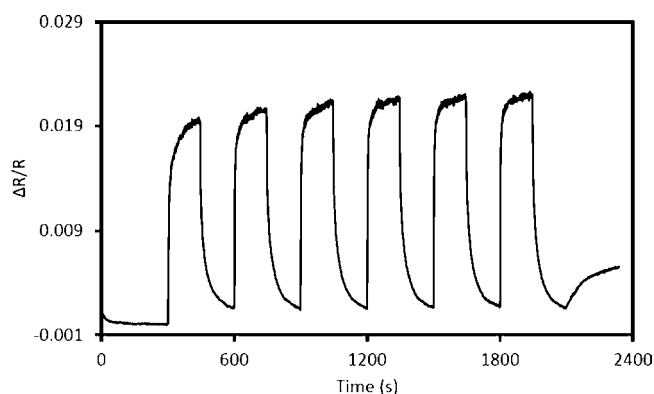


Figure 6. Reproducibility of carbon black polymer sensor (PBAC) to acetone at 0.02 partial pressure. $N = 6$, 1000 sccm flow rate and 25 °C.

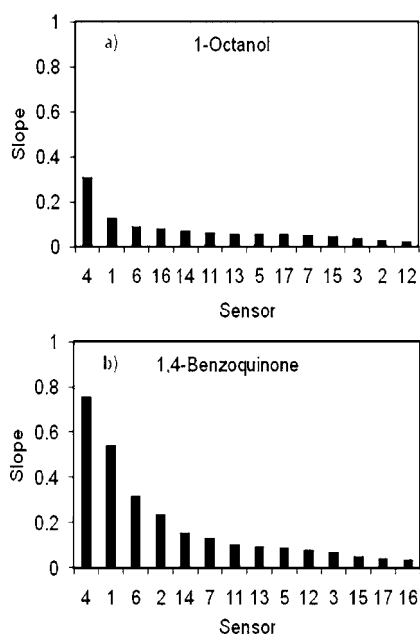


Figure 7. Sensitivity of various carbon black polymer sensors toward (a) 1-octanol and (b) 1,4-benzoquinone at low concentration range ($P/P_0 = 0.01$ to 0.05).

Table 6. Values of Solute Descriptors¹⁹

volatiles	R_2	π^H_2	$\sum\alpha^H_2$	$\sum\beta^H_2$	$\log L$
methanol	0.278	0.44	0.43	0.47	0.970
2-propanol	0.212	0.36	0.33	0.56	1.764
1-octanol	0.199	0.42	0.37	0.48	4.619
acetone	0.179	0.70	0.04	0.49	1.696
THF	0.289	0.52	0.00	0.48	2.636
toluene	0.601	0.52	0.00	0.14	3.325
anisole	0.708	0.75	0.00	0.29	3.890

between the clusters and minimizing variance within the clusters. In principle, small constants imply that it contributes relatively little to distinguishing between analytes, and large values suggest a large contribution. Figure 8 shows that the sensors poly(styrene) and poly(vinyl acetate) have the greatest contribution in distinguishing 1,4-benzoquinone and 1-octanol.

Principal Component Analysis. Another unsupervised technique was adopted to see whether sensors selected from

the methods mentioned above were still able to differentiate two analytes of interest. The principal component analysis (PCA) was performed using seven selected sensors responses.

During sensor array optimization, large amounts of data are dealt with in a very short time. A significant challenge exists in finding ways to extract information useful in solving the problem at hand from the data. Graphical analysis of the raw data is often not possible since the number of samples and sensors is typically greater than three. Therefore, methods for reducing the data to dimensions that can be accommodated graphically are often used. Visual examination of sensor array data in reduced dimensions can provide useful information about both samples and sensors. PCA (sometimes referred to as factor analysis) is a mathematical technique used to identify important factors or variables in multidimensional data matrix. The vectors consisting of most valuable information of a data matrix are eigenvectors (e_vs) and can be used for sensor data interpretation. Usually, the first few eigenvectors (e_{v1}, e_{v2}) contain most of the information of the sensor data set. Using PCA, e_{v1} and e_{v2} were obtained for ranking of all sensors. In terms of e_{v1}, the seven best sensors were 3, 15, 5, 13, 14, 11, and 7 while according to e_{v2} the best sensors were 17, 4, 1, 6, 2, 11, and 14. Again PCA was done with the seven best sensors based on ranking for e_{v1} (Figure 9a) and e_{v2} (Figure 9b). Sensor array according to e_{v1} showed better classifiability of model volatiles compared to that of e_{v2}. Sensor array selected according to e_{v2} was not able to distinguish between anisole and toluene. It also failed to distinguish benzoquinone from 1-octanol. Downselecting the seven best sensors in terms of classifiability of volatiles of interest both supervised and unsupervised techniques worked well.

In terms of reproducibility of the sensor for both 1-octanol and 1,4-benzoquinone, the best six sensors (PBAC, PMMA, PMS, PSu, PS, PVB) were found and poly(ethylene oxide) was the seventh sensor. Poly(ethylene oxide) was rejected from the sensor array as it had poor sensitivity and less selectivity toward Oc and BQ, though it was a moderately reproducible sensor.

When PCA was done with the seven sensors selected from reproducibility criteria, it showed poor distinguishability between Oc and BQ (Figure 10a). When poly(ethylene oxide) was excluded from the sensor array, the new sensor array was able to separate Oc and BQ (Figure 10b).

The best sensors (P4VP, PSAA, PVP, PVCA) in terms of sensitivity could not be kept in the sensor array. They were poorly selective and least reproducible toward the analytes of interest. Poly(methyl vinyl ether-*co*-malic anhydride) was excluded for its low selectivity and reproducibility, but moderate sensitivity. Moderately sensitive sensors were included in the sensor array.

Poly(vinyl acetate), poly(styrene), and poly(vinyl butyral) were the best sensors in terms of selectivity. These sensors were moderately reproducible and sensitive toward the analytes of interest. Poly(bisphenol A-carbonate), poly(sulfone), and poly(α -methylstyrene) were moderately selective. Poly(styrene-*co*-maleic anhydride) was excluded from the sensor array as it was moderately selective but poorly reproducible and less sensitive to volatiles of interest.

The seven good sensors which will be sufficient in pattern recognition of volatiles of interest were selected. These are poly(vinyl acetate), poly(styrene), poly(bisphenol A-carbonate), poly(sulfone), poly(α -methylstyrene), poly(methyl methacrylate),

Table 7. Slope/Sensitivity of Sensor to Various Gaseous Analytes (atm^{-1})

sensor	Me ^a	Ac	THF	Ani	Pro	To	Oc
3	0.0981	0.2364	0.2771	0.0836	0.0564	0.0772	0.0382
5	0.1550	0.2251	0.2058	0.0964	0.0630	0.0478	0.0594
7	0.1520	0.6663	0.6983	0.2242	0.1099	0.2087	0.0546
11	0.1107	0.4192	0.5441	0.1716	0.094	0.1617	0.0656
13	0.6294	1.6201	4.9836	0.2664	0.1696	0.2540	0.0597
14	0.2064	0.8000	0.7932	0.2316	0.1593	0.2216	0.0723
15	0.1755	0.6577	0.5699	0.0778	0.0671	0.0483	0.0482

^aTo, toluene; Ani, anisole; Me, methanol; Pro, 2-propanol; Oc, 1-octanol; Ac, acetone; and THF, tetrahydrofuran.

Table 8. Systems Constants for Sensor (s)

sensor	c	r	s	a	b	l
3	-37.5224	31.6794	18.2449	4.5511	33.8616	0.5094
5	-43.1466	35.4743	21.7236	7.6798	38.1557	0.6459
7	-29.3444	25.2999	14.8804	1.6734	27.3789	0.3012
11	-29.5175	25.0424	14.1696	1.8864	27.4249	0.4323
13	-91.4165	83.4684	44.1773	12.917	88.1347	1.3746
14	-25.8551	22.2209	13.1183	1.3005	24.5864	0.2195
15	-57.7764	48.2029	29.8219	8.5648	53.2104	0.8479

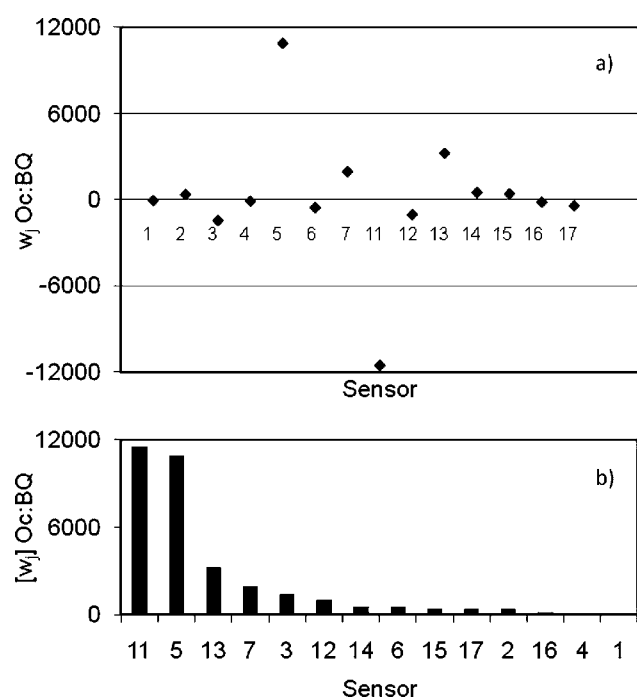


Figure 8. Linear discriminate analysis between 1-octanol and 1,4-benzoquinone: (a) ability to discriminate by fourteen different sensors; (b) absolute discriminate value against all sensors.

and poly(vinyl butyral). In this sensor array most RH sensitive sensors (PVP, P4VP) are absent, which resulted in the array having low RH sensitivity.

Linear Discrimination Analysis. Using PCA, the clusters from our target volatiles 1-octanol and 1,4-benzoquinone always appeared in the same region; but sometimes noticeable distance may not be observed at very low concentration. In practical application, it might be a challenging task to separate and identify them (1-octanol and 1,4-benzoquinone) from each other with this statistical tool at concentration below one part per million. So, further efficient analysis was needed to separate and identify the target volatiles. To achieve this goal LDA was carried out, because it is a useful method to find a linear

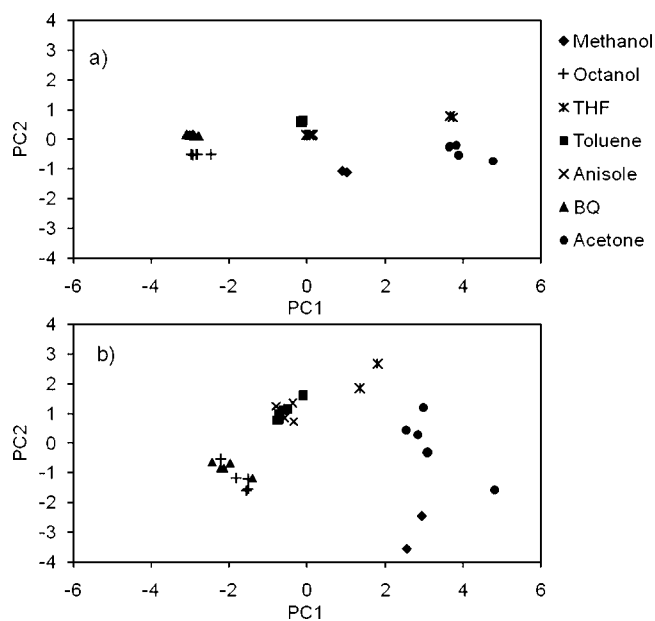


Figure 9. Distribution of model volatiles within principal component space according to sensor array selected by (a) ev1 and (b) ev2.

combination of features which characterizes or separates two or more classes of objects or events. Using PCA, 1-octanol and 1,4-benzoquinone form clusters very close to each other, but using LDA we can completely separate and identify them. In Figure 11, LDA is used to identify unknown volatiles from a group of volatiles. Three different sets of data from 1-octanol, anisole, and 1,4-benzoquinone were used here to separate and identify them from each other. Figure 11a shows that three different clusters are formed in different regions; and none of them overlapped or were close to each other. Figure 11b shows that two clusters overlapped with each other, where one cluster is for known 1-octanol and another represents unknown 1-octanol, while anisole forms a cluster far apart from the 1-octanol cluster. These data clearly indicate that 1-octanol can be separated and identified from anisole. Figure 11c shows that the clusters from known and unknown

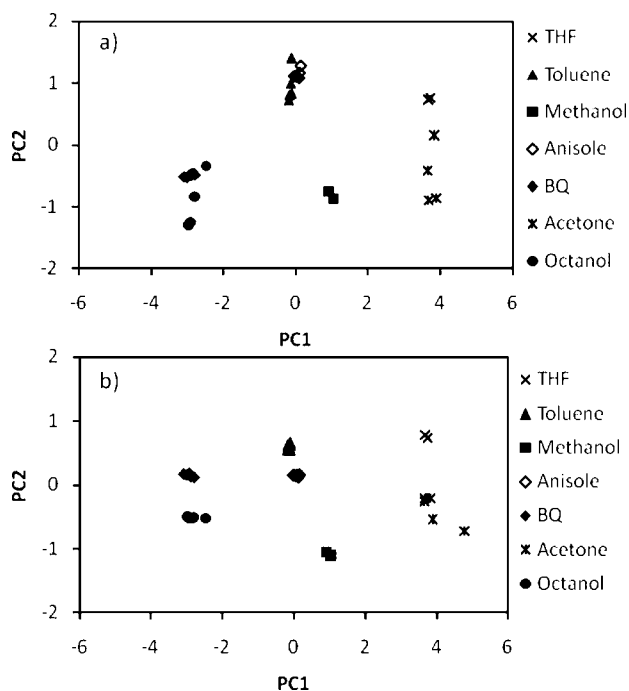


Figure 10. PCA using (a) the seven best sensors in terms of reproducibility and (b) the seven best sensors after eliminating faulty or poor one: poly(ethylene oxide).

1-octanol overlap with each other, while 1,4-benzoquinone forms a cluster in a different region. Although in PCA, 1-octanol and 1,4-benzoquinone form clusters very close to each other, in LDA we can completely separate and identify them. The separation and identification process is further advanced using LDA, where the concentration of both volatiles is gradually increased from 1 to 10% of vapor pressure and sufficient time is needed to reach their equilibrium states. Figure 12 shows that, with increasing the concentration of volatiles, 1,4-benzoquinone and 1-octanol move to positive and negative directions, respectively. In the case of 1-octanol the $\Delta R/R$ value constantly increased in the negative direction, while 1,4-benzoquinone moved in the positive direction up to 7% of its vapor pressure and then gradually declined. While generating continuous vapor, a high flow rate of nitrogen disturbs the solid–gas phase equilibrium of 1,4-benzoquinone. However, in real grain bin application, it may not happen because insect pheromones and fungal derived volatiles will always be in equilibrium with headspace gas at very low air flow. So, LDA can be used as an appropriate tool to separate and identify incipient grain spoilage along with PCA.

Validation of Sensor Selection. A couple of sensor arrays were made using the best seven sensing polymers in terms of reproducibility, sensitivity and selectivity. Then the array was exposed to those volatiles of interest and PCA was done using old eigenvectors. Those sensor arrays efficiently distinguished the analytes of interest along with other volatiles when they were exposed individually in the sensor arrays (Figure 13). The new exposures of volatiles to new sensor arrays fell within the same principal component space of previously determined using old sensor array.

Slight variation occurred for the distribution of benzoquinone response in the principal component space due to its inherent property of sublimation. Another possibility could be the inconsistency of saturated vapor pressure during gas

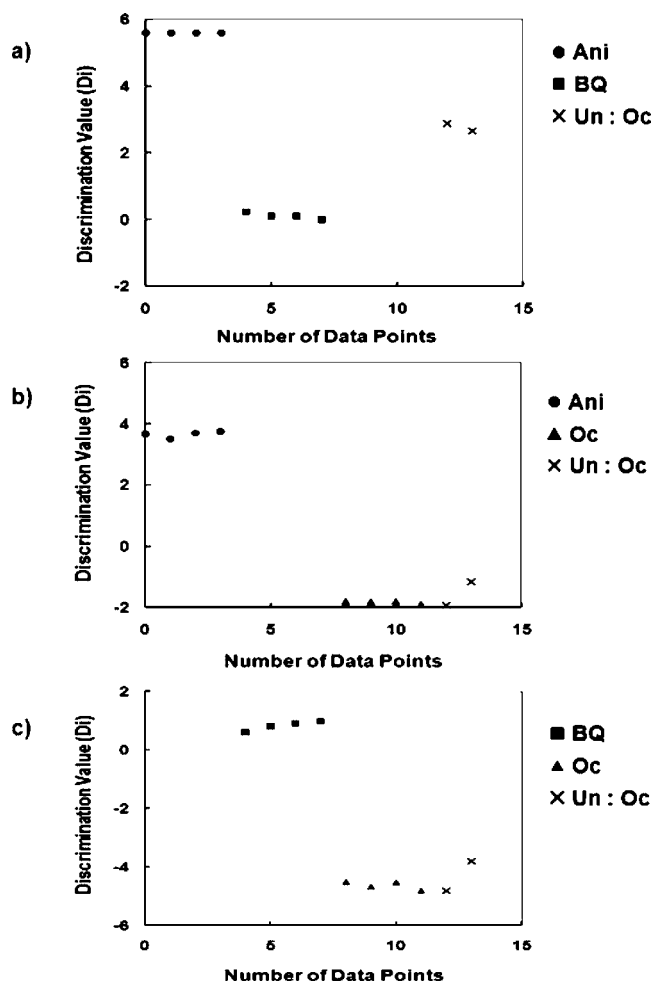


Figure 11. Linear discrimination analyses of selective volatiles obtain from sensor array. Data obtained from multiple exposures of 1-octanol (\blacktriangle), 1,4-benzoquinone (\blacksquare), and anisole (\bullet), in 10% of concentration on sensor arrays. The LDA can separate and identify the solvents of interest from each: (a) 1,4-benzoquinone (\blacksquare) and anisole (\bullet) are known volatiles, and 1-octanol (\times) is unknown; (b) anisole (\bullet) and 1-octanol (\blacktriangle) are known volatiles, and 1-octanol (\times) is unknown; (c) 1,4-benzoquinone (\blacksquare) and 1-octanol (\blacktriangle) are known volatiles, and 1-octanol (\times) is unknown.

delivery at the flow rate (20 sccm) for 5 to 10 min. Similar uncertainty was also observed while detecting quinone derivatives (MBQ and EBQ) from red flour beetle secretions on wheat using gas chromatography–mass spectrometry method.²⁶

Variation of Sensor Response within the PCB and among PCB. To check the variation of sensor response within the PCB and among PCB, t test was performed for equal variance. It was tested with two analytes, 1-octanol and methanol, and the obtained t test values were 0.4151 and 0.0141 for 1-octanol and methanol, respectively with equal variance (from t test table,^{30,31} the $t_{crit} = 2.179$ at $p = 0.025$ and $df = 12$). In both cases, t test(obs) < t_{crit} , which implies that both sets were from the same population (Figure 14).

The sensor array potentially classifies stored-grain model volatiles. This study illustrates the application of a carbon black polymer sensor array for the detection of stored grain model volatiles (insect pheromones and fungal odor) in the headspace with a one step process. The developed sensor array may help farmers in taking early preventive measures to save their

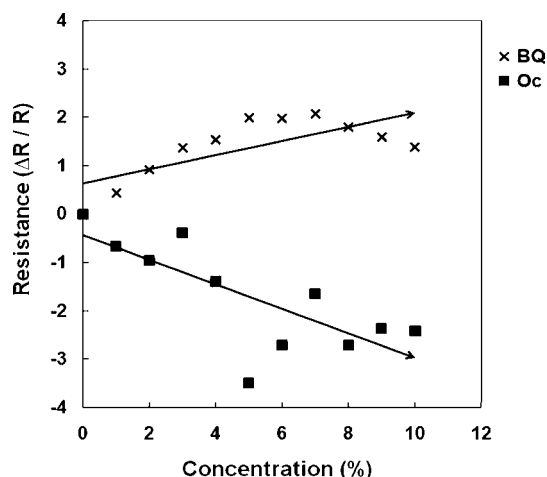


Figure 12. Linear discrimination analyses of 1-octanol (■) and 1,4-benzoquinone (×). Data were obtained from multiple exposures (1 to 10% of vapor pressure), and in each case volatiles were exposed for 8 h. Arrow indicates the movement of volatile response at elevated concentrations.

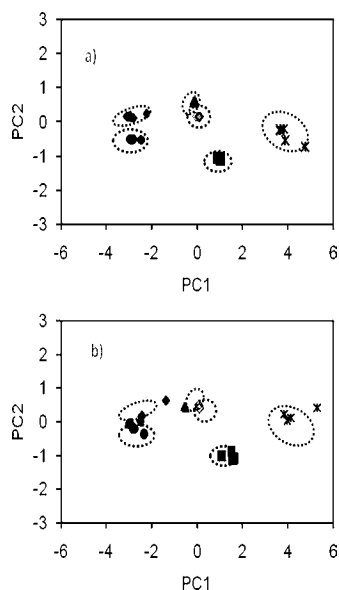


Figure 13. PCA (a) using old sensor array; (b) using old eigenvectors for new sensor array. Space within the ellipses was distributed using 3σ along both axes: (◇) anisole, (▲) toluene, (◆) 1,4-benzoquinone, (■) methanol, (*) acetone, (●) 1-octanol.

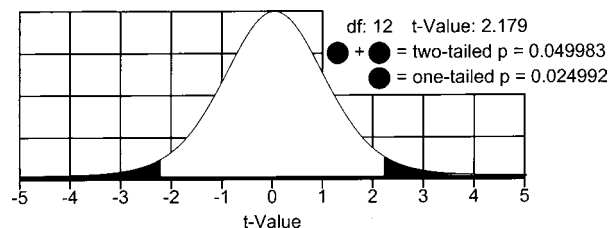


Figure 14. Probability distribution of various sensor responses within PCB and among PCB.

agricultural commodities like wheat, barley, rice, and other cereals from insects and fungi. Our future work is to verify the performance of the sensor array for detection of insect and fungal infestation of wheat in storage bins.

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Funding

The Canada Research Chairs (CRC) program and the Natural Sciences and Engineering Research Council (NSERC) of Canada are gratefully acknowledged for funding this project.

Notes

The authors declare no competing financial interest.

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