

Correspondence

Differential Detection of Enantiomeric Gaseous Analytes Using Carbon Black–Chiral Polymer Composite, Chemically Sensitive Resistors

Erik J. Severin, Robert D. Sanner,[†] Brett J. Doleman, and Nathan S. Lewis*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Carbon black–chiral polymer composites were used to provide diagnostic differential resistance responses in the presence of enantiomers of chiral gaseous analytes. Vapors of (+)-2-butanol and (–)-2-butanol, (+)- α -pinene and (–)- α -pinene, (+)-epichlorohydrin and (–)-epichlorohydrin, and methyl (+)-2-chloropropionate and methyl (–)-2-chloropropionate were generated and passed over a chemically sensitive carbon black–poly((*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate) (77% butyrate) composite resistor. Each enantiomer of a pair produced a distinct relative differential resistance change on the chiral detector, whereas both enantiomers of a set produced identical signals on achiral carbon black–poly(ethylene-*co*-vinyl acetate) (82% ethylene) detectors.

We have previously reported the use of carbon black–polymer composites for array-based vapor sensing applications.¹ In such an array, no individual detector responds solely to a specific molecule, but the collective response of the entire array of detectors yields a unique fingerprint for the vapor of interest. Such arrays are often referred to as “electronic noses” and are not designed in advance to perform a specific task but are, instead, developed to classify, identify, and quantify vapors on the basis of pattern recognition algorithms.^{2–7} This approach to vapor sensing takes advantage of the collective output of an array of broadly responsive detectors. In the polymer composite array configuration, the signal transduction is extremely simple: swelling of the polymeric phase of the composite, in the presence of a vapor, leads to an increase in the electrical resistance of the composite, which is monitored using simple electronics.

An ideal detector array would produce a unique signature for every molecule to which it was exposed. To make progress

toward such a system, it is necessary to include detectors that probe important, but possibly subtle, molecular parameters such as chirality. None of the polymer-based conducting composite detectors reported to date are chiral, so enantiomers would not be differentiable on arrays of such detectors. We demonstrate herein the use of chiral polymers in carbon black–polymer composites to achieve the differential detection of enantiomers. The materials described represent additional detector elements that would be part of a larger detector array, thus broadening the discrimination ability of such arrays toward enantiomeric pairs of analytes.¹

EXPERIMENTAL SECTION

The carbon black used in the composites was Black Pearls 2000, a furnace black material donated by Cabot Co. (Billerica, MA). The polymer used in the chiral composites was poly((*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate) (77% butyrate) and was obtained from the Goodfellow Corp. (Berwyn, PA). The achiral polymer used for control experiments was poly(ethylene-*co*-vinyl acetate) (82% ethylene) (Polysciences Inc., Warrington, PA). The enantiomeric pairs examined were (+)-2-butanol and (–)-2-butanol (Aldrich, Milwaukee, WI), (+)- α -pinene and (–)- α -pinene (Fluka, Ronkonkoma, NY), (+)-epichlorohydrin and (–)-epichlorohydrin (Aldrich), and methyl (+)-2-chloropropionate and methyl (–)-2-chloropropionate (Aldrich).

An apparatus that provided known partial pressures of the vapors was constructed of general laboratory glassware. This consisted of a bubbler made from small, 12-mL centrifuge tubes with conical bottoms that were filled to a depth of 3 cm (~2 mL). Into the 1.5-cm-diameter mouth of the tube was affixed a two-hole rubber stopper. In each hole was a 5-mm-o.d. glass tube, one of which extended to the bottom of the bubbler and served as the gas inlet, and the other of which extended past the stopper by only a few millimeters and served as the gas exit. The carrier gas was nitrogen, obtained from a commercial gas supply tank. The measurements were performed at room temperature, which was 23 ± 1 °C.

The carrier gas was introduced through the glass tube which extended to the bottom of the bubbler apparatus and was bubbled through the solvent. The resulting vapor was carried out of the bubbler, diluted by blending with a controlled background flow of pure carrier gas, and then introduced into a sensing chamber.

[†] Current address: Mail Code L-325, Lawrence Livermore National Laboratory, Livermore, CA 94550.

- (1) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298.
- (2) Zaromb, S.; Stetter, J. R. *Sens. Actuators* **1984**, *6*, 225.
- (3) Lundstrom, I.; Erlandsson, R.; Frykman, U.; Hedborg, E.; Spetz, A.; Sundgren, H.; Welin, S.; Winquist, F. *Nature* **1991**, *352*, 47.
- (4) Shurmer, H. V.; Gardner, J. W. *Sens. Actuators B* **1992**, *8*, 1.
- (5) Gardner, J. W.; Bartlett, P. N. *Sens. Actuators B* **1994**, *18*, 211.
- (6) Gardner, J. W.; Hines, E. L.; Tang, H. C. *Sens. Actuators B* **1992**, *9*, 9.
- (7) Nakamoto, T.; Fukuda, A.; Morizumi, T. *Sens. Actuators B* **1993**, *10*, 85.

This chamber consisted of a glass tube (22 cm long with a 2.6-cm inner diameter), to which inlet and outlet sidearms had been attached. The detectors were introduced into the chamber through a 24/40 standard taper ground-glass opening attached at one end of the chamber. The chamber was then sealed with a ground-glass stopper through which electrical lead wires for the detectors had been sealed. The gas flow rates were controlled using needle valves and stopcocks.

To prepare the detector substrates, two parallel bands of gold, 50–100 nm thick and separated by 5 mm, were deposited onto conventional 7.5-cm \times 2.5-cm glass slides. The slides were then cut into strips to produce 0.7-cm \times 2.5-cm pieces of glass, with each strip of glass having one pair of Au leads.

The detectors were made from a solution of the polymer into which carbon black had been suspended. Here 125 mg of the polymer was dissolved in 10 mL of tetrahydrofuran, and carbon black (42 mg) was added to produce a composition of 75% polymer and 25% carbon black by weight of solids. 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. Detectors used to analyze pinene vapors were fabricated slightly differently, having films made from a suspension with a carbon black loading of 30 wt % of solids. In both cases, an aliquot of the suspension was spin-coated, at 1000 rpm, onto a glass substrate using a Headway (Garland, TX) spin-coater, and the resulting film was allowed to dry in air. One coating of the suspension was applied to each substrate, yielding a film thickness of $\sim 1\ \mu\text{m}$, as determined by atomic force microscopy, except for pinene detectors, for which six coats of suspension were applied, producing films $\sim 6\ \mu\text{m}$ in thickness. The detectors with extra coatings gave higher signal-to-noise ratios when used for pinene.

The dc resistance of each detector was determined as a function of time using a simple two-point resistance configuration. Contacts were made to the gold lines by pressure-contacting electrical leads using flat-jawed alligator clips. Resistance data were acquired using a Hydra 2620A data acquisition unit (John Fluke Mfg. Co., Everett, WA) which was interfaced to a personal computer. All of the films had resistance values below the 10 M Ω limit of the Hydra 2620A.

To initiate an experiment, five copies of a given detector type were placed into the glass chamber, and a background flow of nitrogen was introduced until the resistance of the detectors stabilized. Solvent vapor streams were then passed over the detectors. The background and analyte flow rates were monitored using two flow meters (Gilmont Instruments, Inc.), which had ranges of 0.2–15.0 and 0.0015–0.310 L min⁻¹, respectively. In a typical experiment, resistance data on the detectors were collected for 150 s, with the background gas flowing (typically about 1–2 L min⁻¹) to serve as a baseline. This was followed by a 150-s data collection while the detectors were exposed to the diluted analyte vapor stream (typically about 200–300 mL min⁻¹). The detectors were then given 200–300 s to recover, during which time pure background gas was passed through the chamber. The exposure times varied somewhat, but steady-state values of resistance change were always reached for any given exposure time. Resistances for all detectors in a given trial were monitored contemporaneously through the use of the multiplexing capabilities of the Hydra multimeter. Results were obtained by running

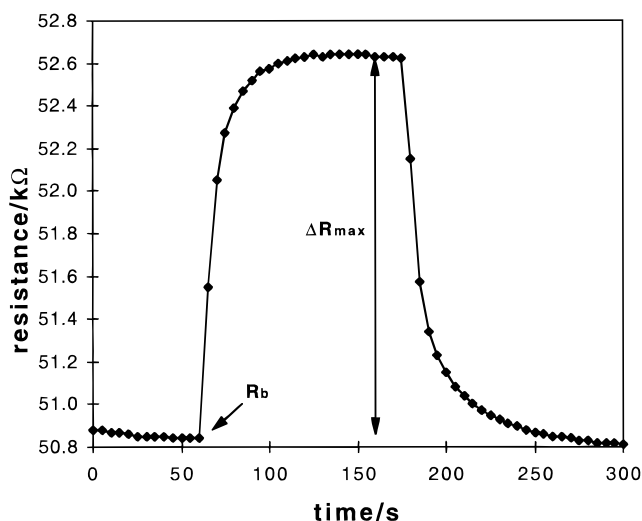


Figure 1. Typical chiral detector response upon exposure to 5 ppth of (+)-2-butanol.

two trials (except for epichlorohydrin for which three trials were run) of five exposures each, with the trials performed on different days. Each analyte was exposed to five copies of the detector simultaneously, and the results were averaged to obtain the reported data set. In the case of epichlorohydrin, a third trial was run using 300-s exposure and recovery times to investigate whether longer time cycles produced different response signals, but the data were essentially identical to those obtained using the shorter detector cycle times described above. The exposures were made at the following concentrations: epichlorohydrin, 3 parts per thousand (ppth); α -pinene, 1 ppth; methyl-2-chloropropionate, 2 ppth; and 2-butanol, 4 ppth. Concentrations were calculated by diluting gas streams to known volumes, and the analyte concentrations were determined from measurements of the flow rate of the gas and the rate of mass loss of the solvent.¹

The achiral control detectors were made from benzene solutions of poly(ethylene-co-vinyl acetate) (82% ethylene) into which carbon black had been suspended. Glass slides with gold contacts were coated by dipping the slide into the suspension. Three coatings were applied to each slide. The polymer concentration was 10 mg mL⁻¹, and the carbon black loading was 30 wt % of solids. Results were obtained by running one trial of four (for epichlorohydrin and methyl 2-chloropropionate) or five (for 2-butanol and α -pinene) exposures. Five detectors were exposed simultaneously to each analyte, and the results were averaged to obtain the reported data set. The control exposures were made at the following concentrations: epichlorohydrin, 4 ppth; α -pinene, 1 ppth; methyl 2-chloropropionate, 3 ppth; and 2-butanol, 4 ppth.

RESULTS AND DISCUSSION

Figure 1 represents a typical response of a chiral detector to 2-butanol. All the detectors displayed an increase in resistance upon exposure to the vapor and returned to their baseline values after the vapor was removed. In all of the experiments performed, the change in resistance was quite rapid, taking less than 20 s to reach 75% of the final resistance value (taken after 150 s). The responses were analyzed by calculating the maximum differential response value, ΔR_{max} , observed during the exposure period, dividing it by the baseline value of the resistance, R_b , (taken as

Table 1. Representative Data^a for the (+) and (−) Enantiomers of 2-Butanol

detector no.	$Q_{(-)}$ ^b	$Q_{(+)}$ ^b	$\Delta Q_{(+/-)}$	Q_{rel} , %	α	$\Delta_{1,2}(\Delta G)$, kJ/mol
Trial 1						
1	3.41 (0.01)	3.60 (0.03)	0.19	5.5	1.06	−0.133
2	3.29 (0.02)	3.52 (0.03)	0.23	7.0	1.07	−0.167
3	2.89 (0.02)	3.10 (0.02)	0.21	7.3	1.07	−0.174
4	2.96 (0.02)	3.17 (0.03)	0.21	7.0	1.07	−0.166
5	2.75 (0.03)	2.97 (0.04)	0.22	8.0	1.08	−0.189
average			0.21 (0.02)	7.0 (0.9)	1.07 (0.01)	−0.17 (0.02)
Trial 2						
1	2.71 (0.04)	2.97 (0.04)	0.26	9.5	1.10	−0.224
2	2.59 (0.02)	2.87 (0.04)	0.28	11	1.11	−0.253
3	2.55 (0.03)	2.79 (0.04)	0.24	9.5	1.10	−0.224
4	2.62 (0.03)	2.86 (0.04)	0.24	9.2	1.09	−0.216
5	2.49 (0.03)	2.73 (0.04)	0.24	9.6	1.10	−0.225
average			0.25 (0.02)	9.7 (0.6)	1.10 (0.01)	−0.23 (0.01)
control detector no.	$Q_{(-)}$ ^b	$Q_{(+)}$ ^b	$\Delta Q_{(+/-)}$			
1	2.71 (0.02)	2.73 (0.06)	0.02			
2	2.50 (0.01)	2.50 (0.01)	0.00			
3	2.58 (0.03)	2.56 (0.02)	−0.02			
4	3.02 (0.03)	3.04 (0.01)	0.02			
average			0.00 (0.02)			

^a The numbers in parentheses are estimated standard deviations.
^b $Q_{(+)}$ and $Q_{(-)}$ correspond to the percent relative differential resistance change averaged over five exposures for the (+) and (−) enantiomers, respectively. α is defined as K_1/K_2 , where K_1 is defined as the larger partition coefficient.

the resistance value just before the exposure began), and the result expressed as a percent change in resistance, Q :

$$Q = (\Delta R_{\text{max}}/R_b) \times 100 \quad (1)$$

$Q_{(+)}$ and $Q_{(-)}$ correspond to the percent relative differential resistance response for the (+) and (−) enantiomers, respectively. A representative data set, for the enantiomers of 2-butanol, is presented in Table 1, while Table 2 summarizes the data for all of the enantiomers studied in this work.

As reported in Tables 1 and 2, statistically significant differences in detector response were observed when enantiomers of a given analyte were exposed to the chiral carbon black-polymer composite detectors. In contrast, no statistically significant difference in response was observed when achiral detectors were exposed to these same pairs of enantiomers. The magnitude of the differentiation between enantiomers can be quantified by considering the relative difference in response, Q_{rel} , between the enantiomers:

$$Q_{\text{rel}} = [\Delta Q_{(+/-)}/Q_{(-)}] \quad (2)$$

where $\Delta Q_{(+/-)}$ is the difference in percent response of a detector when exposed to the (+) and (−) enantiomers of an analyte, respectively. As defined, $\Delta Q_{(+/-)}$ was always positive because, in our samples, $Q_{(+)}$ was always greater than $Q_{(-)}$.

In gas chromatography, the partition coefficient, K , is defined as $K = C_s/C_v$, where C_s is the concentration of solute in the sorbent phase and C_v is the concentration in the vapor phase, at

Table 2. Differences in Percent Response,^a $\Delta Q_{(+/-)}$, Observed for Chiral Detectors during Exposure to the (+) and (−) Enantiomers of Four Test Vapors

analyte	trial	$\Delta Q_{(+/-)}$	Q_{rel} , %	avg α	avg $\Delta_{1,2}(\Delta G)$, kJ/mol
2-butanol	1	0.21 (0.02)	7.0 (0.9)	1.07 (0.01)	−0.17 (0.02)
	2	0.25 (0.02)	9.8 (0.6)	1.10 (0.01)	−0.23 (0.01)
α -pinene	control	0.02 (0.01)			
	1	0.15 (0.01)	7.6 (1.5)	1.08 (0.01)	−0.18 (0.03)
epichlorohydrin	2	0.15 (0.04)	8.0 (1.1)	1.08 (0.01)	−0.19 (0.02)
	control	0.02 (0.01)			
methyl 2-chloro-propionate	1	0.22 (0.01)	6.9 (0.6)	1.07 (0.01)	−0.16 (0.02)
	2	0.19 (0.03)	5.6 (0.6)	1.06 (0.01)	−0.13 (0.01)
	3	0.24 (0.03)	7.1 (1.2)	1.07 (0.01)	−0.17 (0.03)
	control	0.03 (0.03)			
	1	0.26 (0.03)	9.1 (1.2)	1.09 (0.01)	−0.21 (0.03)
	2	0.26 (0.01)	8.9 (0.6)	1.09 (0.01)	−0.21 (0.01)
	control	0.02 (0.01)			

^a The values tabulated are the percent response values that were averaged over five nominally identical detectors, each of which had been exposed four (for epichlorohydrin and methyl 2-chloropropionate) or five (for 2-butanol and α -pinene) times to the analyte vapor. The other quantities were calculated using the formulas and definitions given in the text.

equilibrium. In our experimental protocol, C_v is constant since the vapor stream is continuously being replenished by the vapor generation apparatus. Therefore, we can define a ratio, α , of the partition coefficients between the two enantiomers, as follows:

$$\alpha = K_1/K_2 = [C_s/C_v]_1/[C_s/C_v]_2 = [C_s]_1/[C_s]_2 \quad (3)$$

To remain consistent with the gas chromatography literature, K_1 is defined as the larger partition coefficient, ensuring that $\alpha > 1$.⁸ This corresponds to the analyte which gave the larger response, which, in this work, was always the (+) enantiomer.

The differences in steady-state response for each of the enantiomeric pairs can be attributed to the differences in the free energy, ΔG , of sorption for each enantiomer into the chiral carbon black-polymer composite (i.e., $(\Delta G_1 - \Delta G_2)$, or $\Delta_{1,2}(\Delta G)$). The difference in ΔG of sorption is related to the ratio of the partition coefficients, as expressed below:⁸

$$\Delta_{1,2}(\Delta G) = -RT \ln(\alpha) \quad (4)$$

We have shown that the composite chemiresistor detectors respond linearly to gaseous analyte concentrations over at least a factor of 10^2 in concentration; therefore, C_s is proportional to Q .^{1,9} And, since the vapor concentrations of each enantiomer of an analyte were identical, with only the amount sorbing into the polymer matrix being different, we can relate α to $Q_{(+)}$ and $Q_{(-)}$ as follows:

$$\alpha = [C_s]_1/[C_s]_2 = Q_{(+)}/Q_{(-)} \quad (5)$$

The values of $\Delta_{1,2}(\Delta G)$ calculated using the percent response data and the relationships of eqs 2–5 are given in Table 2. These

(8) Schurig, V. *J. Chromatogr. A* **1994**, 666, 111.

(9) Severin, E. J.; Doleman, B. J.; Lewis, N. S., to be submitted.

values are similar to the minimum $-\Delta_{1,2}(\Delta G)$ values (~ 0.1 kJ mol⁻¹) observed for enantiomers in chiral gas chromatography.⁸

In summary, we have shown that the resistance response of carbon black-polymer composite detectors can be extended to differentiate between enantiomers in the vapor phase. This behavior increases the number of molecular characteristics of a vapor-based analyte that can be probed by a carbon black-polymer composite sensor array. The enhancement in classification ability arising from the use of these chiral detectors in an array configuration will be highly task-dependent, and quantification of the separation ability of enantiomers in specific application scenarios will be reported separately.

ACKNOWLEDGMENT

R.D.S. thanks Lawrence Livermore National Laboratory for a Professional Research and Teaching leave. B.J.D. thanks the Natural Science and Engineering Research Council of Canada for a 1967 Centennial Fellowship. We gratefully acknowledge support for this work by DARPA, NASA, and the Army Research Office.

Received for review July 15, 1997. Accepted January 13, 1998.

AC970757H