A Paper-based Cantilever Array Sensor: Monitoring Volatile Organic Compounds with Naked Eye

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Abstract: Volatile organic compound (VOC) detection is critical for controlling industrial and commercial emissions, environmental monitoring, and public health. Simple, portable, rapid and low-cost VOC sensing platforms offer the benefits of on-site and real-time monitoring anytime and anywhere. The best and most practically useful approaches to monitoring would include equipment-free and power-free detection by the naked eye. In this work, we created a novel, paper-based cantilever sensor array that allows simple and rapid naked-eye VOC detection without the need for power, electronics or readout interface/equipment. This simple VOC detection method was achieved using (i) low-cost paper materials as a substrate and (ii) swellable thin polymers adhered to the paper. Upon exposure to VOCs, the polymer swelling adhered to the paper-based cantilever, inducing mechanical deflection that generated a distinctive composite pattern of the deflection angles for a specific VOC. The angle is directly measured by the naked eye on a 3-D protractor printed on a paper facing the cantilevers. The generated angle patterns are subjected to statistical algorithms (linear discriminant analysis (LDA)) to classify each VOC sample and selectively detect a VOC. We classified four VOC samples with 100% accuracy using LDA.

1 Introduction

Driven by increasing concerns over environmental protection and public safety, the detection of volatile organic compounds (VOCs) has been a major focus of sensor research in recent years.¹ VOCs are harmful air pollutants that contribute to global warming and climate change by interacting with nitrogen oxides in the presence of sunlight. When they do, they form ground-level ozone.^{2, 3} VOCs are also highly dangerous to humans; these chemicals, cause immediate damage or long term human health effects such as skin irritation, dizziness, headache, fatigue, kidney and liver damage, and cancer.^{4, 5} Sources for VOCs include various commercial/industrial activities and everyday products such as paints, pesticides, building materials, toys, and furniture.⁴⁻⁶ Despite considerable efforts to legislatively strengthen VOC requirements worldwide, recent studies have revealed increased levels of atmospheric VOCs.⁷ The VOC emissions have significantly increased in developing countries. In particular areas, the rise in VOCs has not been accompanied by effective monitoring programs due to inadequate lab facilities and a lack of resources.⁸ For these reasons, developing simple, low-cost, portable technologies capable of detecting VOCs is critically important for (i) stand-alone operation that is easily applicable to daily life, and (ii) real-time, on-site measurement even in resource-limited settings (as opposed to often-employed laboratory-based measurements like Fourier transform infrared spectroscopy, gas chromatography-mass spectrometry, nuclear magnetic resonance spectroscopy, and Raman spectroscopy, all of which are expensive, bulky, slow, and complicated).^{9, 10} Equipment- and power-free detection by the naked eye would therefore be among the best approaches for resource-constrained countries, as well as the most practical for daily life.

1 Recently, electronic nose systems have successfully demonstrated potential as portable
2 biosensors for detecting VOCs.¹¹⁻¹³ The electronic nose is composed of an array of
3 several sensing units and pattern-recognition algorithms to sensitively and selectively
4 detect target VOCs. The sensing units utilize an array of differentially responsive
5 receptors to create unique response patterns, or fingerprints, for specific VOCs. Since the
6 first gas sensor was developed using a metal oxide semiconductor (MOS), advanced
7 techniques based on various nanotechnologies have been proposed for the electronic nose
8 systems. These include metal oxide semiconducting field effect transistors (MOSFETs),
9 conducting polymer sensors, optical sensors, quartz crystal microbalance sensors
10 (QCMs), and surface acoustic wave sensors (SAWs).¹¹⁻¹³ Despite the vast potential of
11 sensing techniques, however, conventional electronic nose systems are still large, non-
12 portable, and laboratory-based instruments.¹⁰ Moreover, existing electronic noses require
13 a complicated, battery-powered interface circuit as well as external readout equipment to
14 quantify and display the output values.^{10, 14} In addition, the system requires large numbers
15 of sensing units to improve selectivity performance which, in turn, complicates device
16 circuitry and fabrication processes, thereby increasing the power consumption and cost. In
17 this work, we created a novel sensing platform for simple, naked-eye VOC detection
18 without electrode, power, or read-out interface/equipment. Simple, low-cost VOC
19 detection was achieved by developing a cantilevered sensor array on paper. A thin layer
20 of organic polymers was spin-coated on commercial tape which was then attached to the
21 surface of the paper cantilever. Upon exposure to VOCs, the polymer swelling induced
22 mechanical deflection of the cantilevers; this generated a distinctive composite pattern of
23 deflection angles from the eight cantilevers, producing a selective fingerprint for a VOC.

The angles were directly measured by the naked eye on a 3-D protractor printed on the same paper substrate. The generated angle patterns were subjected to statistical algorithms to selectively classify each VOC sample. This paper-based sensor array has an inexpensive and extremely simple design and fabrication parameters. These features enable the devices (i) to work independently and self-sustainably, which makes them usable even in resource-limited regions, and (ii) to ultimately improve human health, safety, and quality of life. The sensor platform could also find uses within U.S. military applications such as real-time sensing of soldiers' vitals in the battlefield.

2 Materials and methods

2.1 Materials

The polymers used in fabricating the sensor array were purchased from Sigma-Aldrich and used as received. The solvents used in this study are methanol, ethanol, acetone, and tetrahydrofuran (THF); all were reagent grade and were used as received from Fischer Scientific, Pharmco-AAPER, and Sigma-Aldrich. The tape used was 3MTM Scotch tape and was purchased from a local store. The paper substrate was Whatman[®] chromatography paper (200 mm × 200 mm × 0.18 mm) purchased from GE Healthcare Life Sciences.

2.2 Sensor Fabrication

The paper-based single- or eight-cantilever array was first designed using AutoCAD. We initially compared the performance of two paper substrates; regular A4 office paper (80 μm) thick and Whatman[®] chromatography paper, the results showed that the Whatman paper

promoted better adhesion for the tape, and the substrate was more suitable for the cutting and printing fabrication stages, and the cantilevers were more robust. Thus, the final version of the sensor array was printed onto the chromatography paper using a solid ink printer (Xerox ColorQube 8570). The design was then cut out to release the cantilevers and protractors and to remove excess paper edges (via laser machine) (Universal Laser Systems, VLS 3.5). The overall array dimensions were 140 mm $\times$ 160 mm. The eight-cantilever sensing arrays were split into two groups of four cantilevers, with total dimensions of 65 mm $\times$ 47 mm while each cantilever had 44 mm $\times$ 7 mm. The sensing layers extended across the length of the cantilevers to be 29 mm-long from the middle of the cantilever. For the sensing layers, the commercial tape (0.0625 mm-thick) was first attached to glass slides (25 mm $\times$ 75 mm) purchased from VWR Scientific. Then the polymer solutions were prepared by dissolving 200 mg of the polymer in 10 mL of solvent (THF or toluene). The polymer solutions were sonicated for 1 hr for complete dissolution of the polymers. After this, 0.8 ml of the resulting solutions were spin-coated for 18 s on the tape attached to the glass slides at a speed of 1500 rpm (Chemat Technology spin coater KW-4A).

2.3 Testing Setup

Standard glass was used to assemble a bubbler and flow chamber. The bubbler was a 500 mL Erlenmeyer flask with an exit sidearm. The carrier gas was ultra-high-purity nitrogen from the general lab source, neither filtered nor humidified. The gas was supplied to the flask inlet through a glass tube inserted into a rubber stopper via a flow meter; the gas flow was kept constant at 2 LPM.

3 Results and discussion

Fig. 1 presents photo images of a single-cantilever paper sensor and a schematic illustration of an eight-cantilever sensor array on paper. First, we demonstrated the validity of our concept, where the swelling polymer scotch tape (62.5 μm thick) adhered to the paper-based cantilever to induce mechanical deflection (Fig. 1a). The sensor unit was capable of selectively responding to three distinct VOCs by producing three different bending angles: methanol (23°), ethanol (52°), and isopropanol (7°) after 10-minute exposure. However, the process was not reversible because the VOCs could not be completely removed from the polymer. Based on this proof-of-concept experiment, we hypothesized that eight different swellable polymer matrices in the paper-based cantilever array would lead to the desired sensitivity/selectivity and provide fingerprint patterns for specific VOCs. Our sensor array consisted of two sets of four-cantilever arrays facing a printed protractor on chromatography paper. The design was first printed on the paper using a commercially-available solid-wax printer (Fig. 1b). Using a laser machine, the cantilevers and the protractors were then cut out to allow for motion. The protractor was folded into a 3-D structure to measure the degree of cantilever bending. The sensing layer was fabricated by spin-coating an organic polymer on a commercial tape (3MTM Magic Tape), which was subsequently transferred and adhered to the surfaces of the paper cantilevers (Fig. 1b). The eight polymers used in the array were poly(caprolactone) (PCL), poly(4-vinylphenol) (P4), poly(styrene) (PS), poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB), cellulose acetate (CA), poly(vinylidene chloride-co-acrylonitrile) (PVC), poly(dimethylsiloxane) (PDMS) and bare scotch tape (mainly made of methyl methacrylate). The structures of the polymers used are provided by Severin *et al.*¹⁶ In order to ensure that the polymers used as the sensing layers in the cantilever array would react to the presence of the four VOCs tested in this study, we selected

1 polymers to have high affinities with the solvent VOCs. The selection was based on Hansen
2 solubility parameters, as it is established that polymers dissolve in solvents that possess similar
3 solubility parameters.¹⁷ Tables 1 and 2 list the solubility parameters of the polymers,
4 respectively. The polymer layers with the scotch tape were designed to extend halfway across the
5 cantilever and an additional 0.7 cm beyond its root. This allowed for better adhesion on the paper
6 surface and provided for the greatest force to be exerted on the cantilever in response to the
7 swelling of the polymer layers (Fig. 1b).

8 We exposed the paper sensor array to the vapors above four different solvents (methanol,
9 ethanol, acetone, and tetrahydrofuran (THF)) using a 250 mL flask as a head space chamber (Fig.
10 2). To ensure saturation of the chamber environment with the VOC vapor, the nitrogen flowed
11 steadily at a rate of two liters per minute (2 LPM). The fastest response was in the case of
12 acetone while all cantilevers experienced maximum deflection within seven minutes of the start
13 of the exposure. On the other hand it required 10 and 20 minutes to produce response to ethanol
14 and methanol, respectively. Tetrahydrofuran produced the slowest response after 25 minutes of
15 exposure. All bending responses from the eight cantilevers were collected three times for each
16 VOC, and linear discriminant analysis (LDA) was used to differentiate, quantitatively, the type
17 of VOC. LDA is a statistical method for maximizing the ratio of between-class variance to
18 within-class variance, ensuring maximum separation between classes.^{18, 19} In the case of K
19 classes, LDA generates K-1 canonical factors that are linear combinations of the features in the
20 dataset. In our experiment, the different VOCs constituted different classes, whereas deflection
21 angles were the features in the eight cantilevers covered with different polymers. The
22 classification accuracy of LDA was computed using the jackknife method, also known as leave-

one-out method. In this method, one case was left out from the LDA and treated as an unknown, then later classified based on the model generated from the remaining cases in the dataset. The classification accuracy was calculated as the percentage of cases that were correctly classified. In addition, LDA computed the posterior probability of a case in its own class, which was a measure of the confidence for correctly classifying each case. A confidence value close to “1” results in higher classification accuracy. The various polymers possess different gas-solid partition coefficient, which will result in differences in the binding of a given vapour into a given polymer film. Consequently, different films will exhibit different volumetric and dimensional changes resulting in varying deflections of the corresponding cantilevers¹⁶.

The bending force (F) generated from the polymer swelling can be calculated using the beam equation:^{20, 21}

$$F = (E\delta WH^3)/(4L^3) \quad (1)$$

where E is the Young’s modulus of the paper material, δ is the cantilever deflection, and L , W , and H are length, width, and thickness of the paper cantilever beam with the polymer scotch tape. Based on the previous paper-based piezoresistive sensors with the similar dimension as our device,^{20, 21} approximately 2 GPa of Young’s modulus was calculated,¹⁵ and the cantilever deflection of our device was 0.77 mm per 1° on the protractor. The polymer swelling generated 0.90 μ N of the deflection force per 1° on the protractor for the total beam thickness with 0.305 mm (paper: 0.18mm, tape: 0.065mm, and polymer: ~ 0.06 mm).

Fig. 3a shows the deflection angle patterns for four VOC samples: methanol, ethanol, acetone, and THF. Upon exposure to VOCs, the swelling of the different polymers attached to the

cantilever array induced different mechanical bending, generating the selective angle patterns. As each polymer has a different chemical structure, each VOC reacted differently with each polymer film.^{22, 23} This collection of unique polymers allowed us to identify a more diverse set of VOC fingerprints. The analysis for angle measurements generated three canonical factors (95.0%, 3.7%, and 1.3%) representing linear combinations of the response matrices from the patterns (four samples $\times$ eight cantilevers $\times$ three replicates). The two most significant factors were plotted in 2-D, as depicted in Fig. 3b. Table 3 shows the classification accuracy of Fig. 3b using the jackknife method and indicates that the 12 training cases (four samples $\times$ three replicates) were separated into four respective groups with 91.7% average classification accuracy over the four VOC samples. Table 3 also demonstrates how the accuracy changes upon use of a different polymer. According to the type of the polymers, the classification accuracy for acetone is 100%, while the accuracy of the other VOCs varied from 33% to 100%. For each PCL, PS, PVB, and PDMS-based cantilever, the average classification accuracy is 100%. The average decreases slightly with a set of all polymers (91.7%), indicating that classification accuracies cannot be improved just by increasing the number of sensing units. In addition, the confidence of classifying each case as its true identity is shown in Table 4. The confidence is 1 for all cases that are correctly classified. Only one case can be misclassified (Observation 5). Observation 5, for instance, says that ethanol can be misclassified as THF. When LDA was applied to the partial data corresponding to the set of only three polymers, (PCL, PS, & PVB), all cases were correctly classified (Table 5). However, considering the other data from a different set of polymers or from a single polymer, classification accuracies decrease significantly, indicating that a set of different sensing surfaces is critical for VOC discrimination/classification.

4 Conclusions

In conclusion, we created a novel, paper-based cantilever sensor array that enabled four VOC samples to be detected with the naked eye. This simple VOC detection method was achieved using low-cost paper materials that monitored VOC-induced polymer swelling through the mechanical deflection of the cantilevers, thereby generating a selective angle pattern for a specific VOC. This work was for realizing a stand-alone VOC sensor without external equipment or interface electronics for readout. However, further study is required for an in-depth understanding of the relationship between the degree of swelling and the polymers and deflection angles of the paper cantilevers, which provide strategies to improve sensor selectivity/sensitivity and optimize the number of sensing units in the array. In addition, further investigation of the effect of relative humidity, temperature and storage conditions on the overall performance of the sensor will be conducted. Our future work will also focus on improving the sensor array to detect different concentrations of the VOCs other than the saturation level in addition to the detection and classification of the components in more complex solvent mixtures e.g., binary and ternary mixtures. The effort towards achieving this will involve increasing the number of sensing units, and incorporating the response time as an additional classification criteria to resolve the different solvent components present in the mixture as well as their corresponding concentrations.

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References

- 1 H. Yamagiwa, S. Sato, T. Fukawa, T. Ikehara, R. Maeda, T. Mihara, M. Kimura, *Sci. Rep.*, 2014, **4**, 6247.
- 2 G.F. Fine, L.M. Cavanagh, A. Afonja, R. Binions, *Sensors*, 2010, **10**, 5469.
- 3 B. Li, G. Sauve, M.C. Iovu, M. Jeffries-EL, R. Zhang, J. Cooper, S. Santhanam, L. Schultz, J.C. Revelli, A.G. Kusne, T. Kowalewski, J.L. Snyder, L.E. Weiss, G.K. Fedder, R.D. McCullough, D.N. Lambeth, *Nano Letters*, 2006, **6**, 1598.
- 4 A.N. Mallya, R. Kottokkaran, P.C. Ramamurthy, *Sens. Actuators B*, 2014, **201**, 308.
- 5 M. Castro, B. Kumar, J.F. Feller, Z. Haddi, A. Amari, B. Bouchikhi, *Sens. Actuators B*, 2011, **159**, 213.
- 6 S. Fanget, S. Hentz, P. Puget, J. Arcamone, M. Matheron, E. Colinet, P. Andreucci, L. Duraffourg, Ed. Myers, M.L. Roukes, *Sens. Actuators B*, 2011, **160**, 804.
- 7 D. Helmig, C.R. Thompson, J. Evans, P. Boylan, J. Hueber, J.H. Park, *Environ. Sci. Technol.*, 2014, **48**, 4707.
- 8 D.K.W. Wang, C.C. Austin, *Anal. Bioanal. Chem.*, 2006, **386**, 1089.
- 9 K.M. Frazier, K.A. Mirica, J.J. Walish, T.M. Swager, *Lab Chip*, 2014, **14**, 4059.
- 10 S. Chiu, K. Tang, *Sensors*, 2013, **13**, 14214.
- 11 S. Chen, Y. Wang, S. Choi, *Open J. Appl. Biosens.*, 2013, **2**, 39.
- 12 L. Capelli, S. Sironi, R. Del Rosso, *Sensors*, 2014, **14**, 19979.
- 13 J. Gutierrez, M.C. Horrillo, *Talanta*, 2014, **124**, 95.
- 14 F. Tian, S.X. Yang, K. Dong, *Sensors*, 2005, **5**, 85.
- 15 P. Pasini, N. Powar, R. Gutierrez-Osuna, S. Daunert, A. Roda, *Anal. Bioanal. Chem.*, 2004, **378**, 76.

- 1 E.J. Severin, B.J. Doleman, N.S. Lewis, *Anal. Chem.* 2000, **72**, 658.
- 2 16 C.M. Hansen, Hansen solubility parameters: A user's handbook, 2nd ed. ; CRC press;
- 3 2007.
- 4 17 P. Pasini, N. Powar, R. Gutierrez-Osuna, S. Daunert, A. Roda, *Anal. Bioanal. Chem.*
- 5 2004, **378** (1), 76.
- 6 18 S. Choi, S. Huang, J. Li, J. Chae, *Lab Chip* 2011, **11** (21), 3681.
- 7 19 X. Liu, M. Mwangi, X. Li, M. O'Brien, G.M. Whitesides, *Lab Chip* 2011, **11** (13), 2189.
- 8 20 T. Ren, H. Tian, D. Xie, Y. Yang, *Sensors*, **12**, 6685.
- 9 21 M.C. Lonergan, E.J. Severin, B.J. Doleman, S.A. Beaber, R.H. Grubbs, N.S. Lewis,
- 10 *Chem. Mater.* 1996, **8**, 2298.
- 11 22 H. Lei, W.G. Pitt, L.K. McGrath, C.K. Ho, *Sens. Actuators B* 2007, **125** (2), 396.
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Figures and Tables

Figure 1. (a) Demonstrated paper-based VOC sensor unit selectively responding to three VOCs by producing three different bending angles. A protractor and cantilever were patterned on a paper. (b) Proposed paper-based VOC sensor array with eight different swellable polymer matrices.

Figure 2. Schematic diagram of the test set-up. Saturated vapor streams were obtained by bubbling nitrogen into liquid solvents.

Figure 3. Selectivity characterization: Pattern generation of the four VOC samples to characterize selectivity of the sensor. (a) Mechanical bending response patterns of interaction between the VOC samples and eight polymer surfaces. The eight polymers are poly(caprolactone) (PCL), poly(4-vinylphenol) (P4), poly(styrene) (PS), poly(vinyl butryal-co-vinyl alcohol-co-vinyl acetate) (PVB), cellulose acetate (CA), poly(vinylidene chloride-co-acrylonitrile) (PVC), poly(dimethylsiloxane) (PDMS) and bare scotch tape (mainly made of methyl methacrylate). (b) Canonical score plot for the patterns as obtained from LDA with 100% confidence ellipses.

Table 1. The Hansen Solubility Parameters of the solvents used in the gas absorption

Solvent	δ_D (Dispersion)	δ_P (Polar)	δ_H (Hydrogen bonding)
Acetone	15.5	10.4	7.00
Methanol	15.1	12.3	22.3
Ethanol	15.8	8.8	19.4
Tetrahydrofuran	16.8	5.7	8.00

Table 2. The list of polymers used for the gas absorption and their Hansen Solubility Parameters

Polymer	δ_D (Dispersion)	δ_P (Polar)	δ_H (Hydrogen bonding)
Tape	15.8	6.5	5.4
PCL	17.7	5	8.4
P4	17.5	8	15
PS	22.28	5.75	4.3
PVB	18.6	4.4	13
CA	18.2	12.4	10.8
PVC	17.6	7.8	3.4
PDMS	N/A	N/A	N/A

Table 3. LDA classification accuracy of four samples by using a single and eight polymer-based cantilevers. The values are taken from the Jackknife classification matrix based on LDA analysis

	Methanol	Ethanol	Acetone	THF	Average
Tape	33%	100%	100%	100%	83.3%
PCL	100%	100%	100%	100%	100%
P4	66.7%	66.7%	100%	0%	58.3%
PS	100%	100%	100%	100%	100%
PVB	100%	100%	100%	100%	100%
CA	100%	100%	100%	0%	75%
PVC	100%	100%	100%	66.7%	91.7%
PDMS	100%	100%	100%	100%	100%
All polymers	100%	66.7%	100%	100%	91.7%

Table 4. Detection and identification of the four unknown VOC samples by applying LDA to the data of all eight polymer cantilevers.

Observation #	True VOC	Predicted VOC	Confidence of the Classification
1	Methanol	Methanol	1
2	Methanol	Methanol	1
3	Methanol	Methanol	1
4	Ethanol	Ethanol	1
5	<i>Ethanol</i>	<i>THF</i>	<i>1</i>
6	Ethanol	Ethanol	1
7	Acetone	Acetone	1
8	Acetone	Acetone	1
9	Acetone	Acetone	1
10	THF	THF	1
11	THF	THF	1
12	THF	THF	1

1 **Table 5.** Detection and identification of the four unknown VOC samples by applying LDA to the
 2 data of the set of three polymers only (PCL, PS, & PVB)

Observation #	True VOC	Predicted VOC	Confidence of the Classification
1	Methanol	Methanol	1
2	Methanol	Methanol	1
3	Methanol	Methanol	1
4	Ethanol	Ethanol	1
5	Ethanol	Ethanol	1
6	Ethanol	Ethanol	1
7	Acetone	Acetone	0.998
8	Acetone	Acetone	1
9	Acetone	Acetone	1
10	THF	THF	1
11	THF	THF	0.999
12	THF	THF	1

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