A colorimetric sensor array for the detection of toxic industry chemical (TICs)

Chen Zhang and Kenneth S. Suslick

Department of Chemistry, University of Illinois at Urbana-Champaign,

600 S. Mathews Ave., Urbana, Illinois 61801, USA

Array-based vapor sensing derives from the biomimetic concept of using many cross-responsive sensor elements, rather than specific lock-and-key receptors. As with the mammalian olfactory system, it is the composite response of the array that that identifies an odorant or mixture of odorants.[1] Electronic nose technologies of this type generally use sensors based on weak chemical interactions (e.g., physisorption, absorption, etc.), including conductive polymers and polymer composites, fluorescent dye doped polymer systems, metal oxide sensors, and polymer coated surface acoustic wave (SAW) devices.[2,3] Most prior electronic nose technology suffers from some severe limitations, however: the detection of compounds at low concentrations relative to their vapor pressures is difficult; the discrimination between compounds within a similar chemical class has been limited; and perhaps most importantly, interference from the large environmental changes in humidity remains problematic. We report here the use of a colorimetric sensor array (which overcomes these problems) for the identification and semi-quantitative analysis of a wide range of toxic industrial chemicals (TICs).
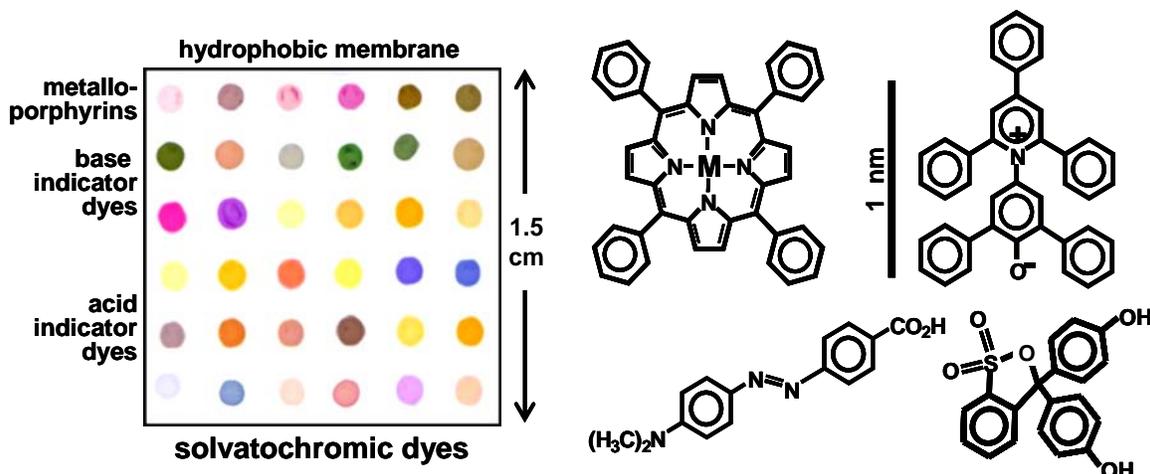
Fig. 1. The colorimetric sensor array (CSA) consists of a hydrophobic membrane on which 36 different chemically responsive dyes have been printed.

In recent years, we have developed a rather different, but quite simple, approach to an "optoelectronic nose" based on a colorimetric array initially using metalloporphyrins and more generally chemically-responsive dyes.[4-8] The array has also been applied in aqueous analysis.[9,10] The design of a colorimetric sensor array (CSA) is based on stronger dye-analyte interactions than those that cause simple physical adsorption. More specifically, we choose chemically-responsive dyes in three classes (Fig. 1): (i.) metal ion containing dyes that respond to Lewis basicity (i.e., electron pair donation, metal ion ligation), (ii.) pH indicators that respond to Brønsted acidity/basicity (i.e., proton acidity and hydrogen bonding), and (iii.) dyes with large permanent dipoles (e.g., zwitterionic solvatochromic dyes) that respond to local polarity.

We have extensively tested our CSAs against a matrix of ten TICs and nine interferents. Excellent detection limits (generally below the permissible exposure limits (PEL)) are demonstrated, as well as clear differentiation among 10 TICs (Fig. 2), 9 common chemical interferents, and binary mixtures thereof.
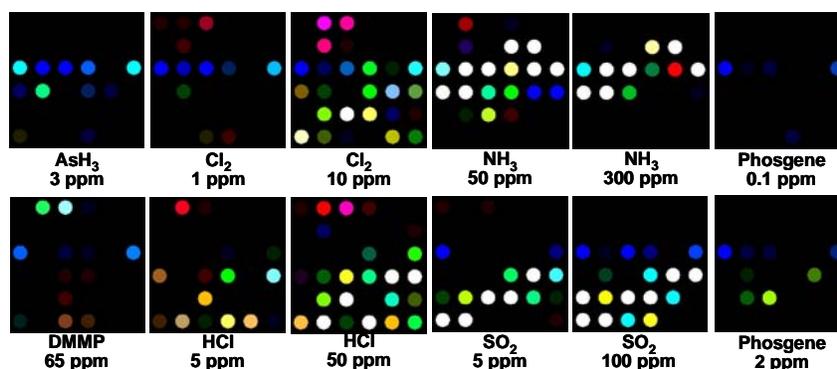
Fig. 2. Color difference maps of representative TICs at their PEL (permissible exposure level, i.e., the lower concentration) and IDLH (immediately dangerous to life or health) concentrations after full equilibration (i.e., 2 min of exposure). Arsine is shown at its IDLH, DMMP at PEL. For purposes of display, the color range of these difference maps are expanded from 3 to 8 bits per color (RGB range of 4-11 expanded to 0-255).

While the CSAs are meant to be considered disposables, they are still re-usable. The CSA is best thought of as a "chemical fuse": just as with an electric fuse, as long as the concentration of the odorant (i.e., the current) fluctuates within some range, the CSA (fuse) is unaffected. But, if the concentration increases to too high a value, the CSA will

take too long to recover: i.e., the fuse is blown and the CSA should be replaced. As illustrated for one example in Fig. 3, the CSA will reproducibly cycle between the PEL and IDLH concentrations of many toxic industrial chemicals. After switching from one concentration to the other, equilibrium response is achieved within 2 minutes.
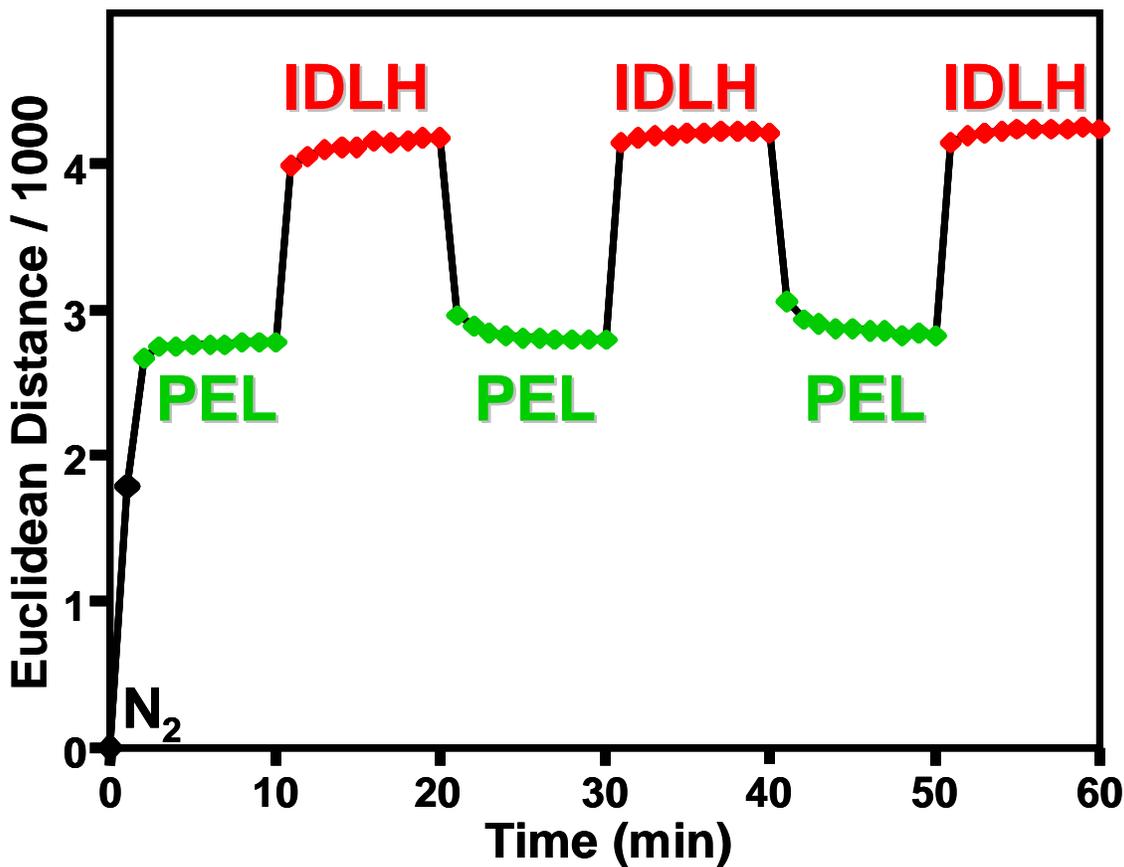
Fig. 3. Repeating cycling of SO_2 exposure of the array from N_2, to the permissible exposure level (PEL, 5 ppmv) and then from the PEL to the immediately dangerous to life or health (IDLH, 100 ppmv). Data acquired every min.; equilibrated response time is 2 min. The Euclidean distance is simply the total length of the 108-dimensional color difference vector, i.e., the total array response.

Reference

1. Wang, J.; Luthey-Schulten, Z. A.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3035-3039.

2. Gardner, J. W.; Bartlett, P. N. *Electronic Noses: Principles and Applications*; Oxford Univ Press: New York, 1999.

3. Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595-2626.

4. Rakow, N. A.; Suslick, K. S. *Nature* **2000**, *406*, 710-713.

5. Suslick, K. S.; Rakow, N. A.; Sen, A. *Tetrahedron* **2004**, *60*, 11133-11138.

6. Suslick, K. S. *MRS Bull.* **2004**, *29*, 720-725.

7. Janzen, M. C.; Ponder, J. B.; Bailey, D. P.; Ingison, C. K.; Suslick, K. S. *Anal. Chem.* **2006**, *78*, 3591-3600.

8. Rakow, N. A.; Sen, A.; Janzen, M. C.; Ponder, J. B.; Suslick, K. S. *Angew. Chem. Int. Ed.* **2005**, *44*, 4528-4532.

9. Zhang, C.; Suslick, K. S. *J. Am. Chem. Soc* **2005**, *127*, 11548-11549.

10. Zhang, C.; Bailey, D. P.; Suslick, K. S. *J. Agric. Food Chem.* **2006**, *54*, 4925-4931.