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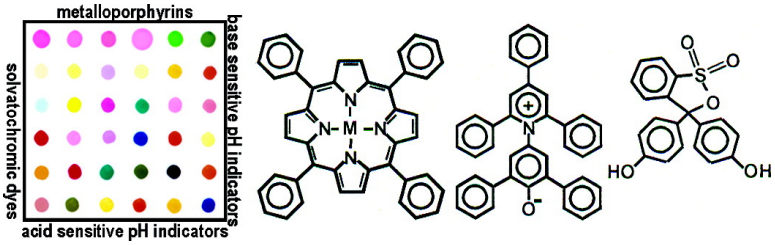

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A Colorimetric Sensor Array for Organics in Water

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Molecular recognition of organic compounds in aqueous solutions is inherently challenging, due to potential interference from the very high concentration of water. General purpose electronic analysis of aqueous solutions often consists of an array of cross-responsive sensors, inspired by the mammalian gustatory and olfactory systems,[1,2] i.e. semi-selective receptors whose composite responses determine smell and taste. In the past decade, a variety of array detectors have been explored,[3,4] most often based on conductive polymers or electrochemical sensors;[3] a common limitation of such arrays, however, is their general lack of chemical selectivity, which makes differentiation among similar compounds problematic. We report here the development of a simple and inexpensive colorimetric sensor array capable of distinguishing a wide range of organic compounds in aqueous solutions at concentrations as low as 1 μM.

Molecular recognition is, of course, a function of intermolecular interactions of the analyte. Recognizing that human beings are visual creatures and that our imaging technology is highly advanced yet inexpensive, we have developed a colorimetric approach to molecular recognition,[5,6] using a cross-responsive array containing a diverse family of chemically responsive dyes; the design of a colorimetric sensor array is based on stronger dye−analyte interactions than those that cause simple physical adsorption. More specifically, we chose chemoresponsive dyes in three classes: (1) metal ion-containing dyes that respond to Lewis basicity (i.e., electron pair donation, metal ion ligation), (2) pH indicators that respond to Brønsted acidity/basicity (i.e., proton acidity and hydrogen bonding), and (3) dyes with large permanent dipoles (e.g., zwitterionic solvatochromic dyes) that respond to local polarity. In previous work, we have established that an array of cross-responsive chemoresponsive dyes is a powerful vapor-sensing device, an "optoelectronic nose" with high sensitivity and enormous selectivity for volatile organic compounds (VOCs).[5,6]

For aqueous analyses, we need to make the array hydrophobic to avoid interference from the 55 M water. Representing the Lewis acid dyes, metalloporphyrins are a natural choice for sensor applications: they are very stable; they have open coordination sites for axial ligation to the metal ions; and they are easily modified (e.g., different metals for control over hard/soft acid−base interactions or peripheral substitution for shape and size selectivity). Derivatives of or precursors to traditional pH indicator dyes[7] selected for low water solubility serve as the arrays' probes for Brønsted acidity/basicity. Conventional solvatochromic dyes[8] round out the array and provide a measure of analyte polarity. The dyes are printed on a hydrophobic surface;[9] an image of the array is shown in Figure 1.

In use, the array is first saturated in an aqueous liquid without dissolved organics (i.e., phosphate buffer) and imaged by an ordinary flatbed scanner (cf. Supporting Information for details). After exposure to an analyte solution, rapid (seconds) color changes in the dyes are readily observed and digitally imaged. Simply

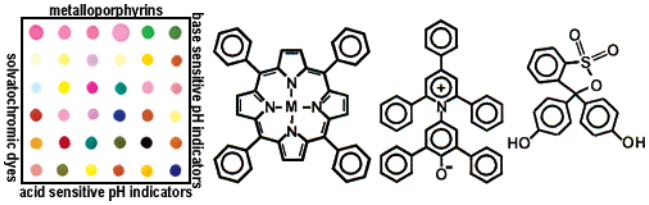

Figure 1. Disposable colorimetric sensor array printed on a hydrophobic surface, 25 mm × 25 mm.[9] Examples of Lewis base (metalloporphyrin), solvatochromic (Reichert's), and pH indicator (phenol red) dyes are illustrated.

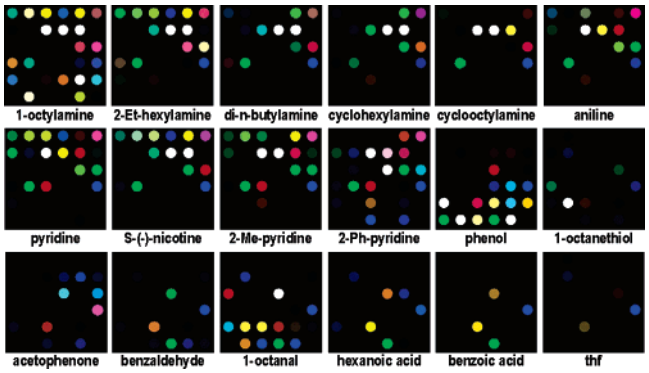

Figure 2. Color change profiles with the base-sensitive sensor array for representative aqueous solutions of organic compounds (all amines 10 mM, all others 50 mM, in pH 7 phosphate buffer). Further examples and complete digital data are provided as Supporting Information.

subtracting the original control image from the final sample image (red value after exposure minus red value before, green minus green, blue minus blue), provides a color change profile for the analyte solution. The center of each dye spot is averaged to avoid edge artifacts. The color change profile is, then, simply a 3N-dimensional vector (where N = number of dyes) that can be easily analyzed by standard statistical and chemometric[10] techniques. It is, moreover, convenient to visually represent these vectors as color change maps by representing each spot as the absolute value of its color change in RGB.

As shown in Figure 2, the color change profiles are unique fingerprints for each specific analyte mixture. Many of the dyes that make up the array are, of course, pH sensitive. For this reason, all analyte solutions in Figure 2 were made in a phosphate buffer with a measured pH value of 7.0 ± 0.2.[11] Thus, the color change profiles obtained are characteristic of dye interactions with the analytes, *not* simply changes in pH: *interestingly, we find that pH indicators indicate much more than just pH.*

We note that our array is not an "electronic tongue" because our sensor plate is not responsive to the more usual gustatory analytes (e.g. salt, sugar, MSG). Because the array is made from hydrophobic dyes on a hydrophobic membrane, it is *not* affected by salt concentration, ionic strength, or highly hydrophilic com-

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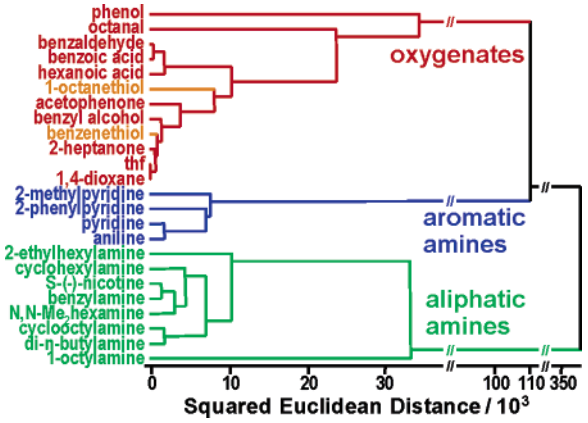

Figure 3. Hierarchical cluster analysis (HCA)[12] of aqueous solutions containing various organics using the color change profiles. The dendrogram shows quantitatively the pattern similarities of the color change profiles. All amines and thiols at 10 mM; all oxygenates at 50 mM.

pounds,[11] which can be highly advantageous for many uses. Of course, for many gustatory applications, salt-sensitive and sugar-sensitive chromophores would be essential and could be easily incorporated into a future array.

Aqueous solutions of organic compounds having various functional groups have been examined. As shown in Figure 2, different organic compounds give radically different color change profiles and are easily distinguished by eye even without statistical analysis. There are also clear familial resemblances: e.g., amines have similar patterns, as do carboxylic acids, etc. A hierarchical cluster analysis (HCA)[10,12] provides a quantitative measure of the familial nature of the color change patterns in the form of a dendrogram, as shown in Figure 3. Remarkably, even subtle structural features are readily distinguished: e.g., the color change patterns of 1° vs 2° vs branched vs cyclic amines are easily distinguished, even for analytes with same number of carbons, as are substituted pyridines.

For these sensor arrays, every analyte at a different concentration may be considered a different analyte: i.e., some dyes change color at low analyte concentrations and then saturate, others turn on only at increasingly higher concentrations (cf. Supporting Information). The limits of detection of the sensor array depend on the analyte. Amines have both the lowest detection limits and recognition limits. The lower detection limits range from ~100 μM to ~1 μM (i.e. 2−0.02 ppm mole fraction) for amines (cf. Supporting Information).

The enormous discriminatory power of this colorimetric sensor comes from the chemical diversity of the 36 sensor dyes used in the array. Each analyte is represented as a 108-dimensional vector (36 red, green, and blue differences). Not all of the 108 dimensions are equally important, of course; from a principal component analysis of the patterns shown in Figure 2, 95% of all discriminatory information is contained in eight dimensions (and 17 dim. for 98%). The RGB vector components do not, of course, range over the full 256 possible values; in the database representing the cases in Figures 2, the average RGB change in the eight most important dimensions is ~34. This implies a "practical" limit of discrimination that is still extremely large: a very rough estimate of recognizably distinct patterns is $>1 \times 10^{12}$ (i.e., 34^8).

An absolute statistical measure of the reliability of hierarchical cluster analysis is complex and database dependent. The obvious empirical measure, however, is simply the number of misclassifications within a given database. For the analytes examined here, there were no misclassifications out of 144 cases (cf. Supporting Information).

Complex mixtures present no inherent difficulty for the colorimetric sensor array approach. As is true in any cross-reactive sensor system, no component-by-component analysis is possible. There are, however, multiple analytical goals with complex mixtures, only one of which is a full component-by component analysis. In many cases, the analytical goal is a comparison of identity between one complex mixture and another. In other cases, the goal is to monitor change in one or in a few components against a complex but constant background. The digital color-change profiles serve these functions very well. To demonstrate the potential of our colorimetric sensor array in the application of real-world cases, a series of common soft drinks have been tested as examples of readily available, well-controlled complex mixtures (Figure 4). In all cases, facile discrimination of one product from another is readily apparent.

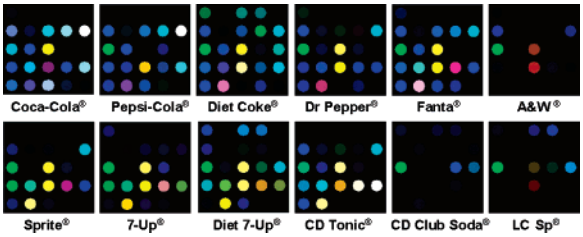

Figure 4. Color change profiles with the acid-sensitive array for a series of common soft drinks, chosen as readily available standards for comparisons among complex mixtures. CD: Canada Dry; LCSp: LaCroix Sparkling Water. Data analysis as in Figure 2 (cf. Supporting Information).

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Supporting Information Available: Full sets of digital data, difference maps, and dendrograms at different analyte concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Color changes due to small pH variations are negligible as shown by intentionally adjusting buffer solutions pH values from 6.5 to 7.5, which showed no significant array responses compared to pH 7.0 buffer. Neither varying the concentration of the phosphate buffer nor adding NaCl produced any array response compared to pure water at pH 7.0.
(12) HCA is based by the groupings of the analyte patterns, which are represented here by 108-dimensional vectors (i.e., 36 red, green, and blue differences). The difference between clusters of analytes is given quantitatively by the squared Euclidean distance between the centroids of the clusters (i.e. the sum of the squares of the differences in each dimension). The vectors with the smallest distances to each other are clustered first, and they are then clustered with other clusters with the smallest distances, etc. to establish the dendrogram.[10]

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