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# Colorimetric Sensor Arrays for the Analysis of Beers: A Feasibility Study

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Eighteen commercial beers have been analyzed in both liquid and gas phases using colorimetric sensor arrays made from selected chemically responsive dyes printed on a hydrophobic membrane. Digital imaging of the dye array before and after exposure to the complex analytes in either the liquid phase or the head-gas provides a color change profile as a unique fingerprint for the specific analyte. The digital data libraries generated were analyzed using statistical and chemometric methods, including principal component analysis (PCA) and hierarchical clustering analysis (HCA). In either liquid- or gas-phase experiments, facile identification of specific beers was achieved using comparison of the color change profiles; using HCA statistical analysis the error rate of identification was <3%. Differentiation between even very similar beers proved to be straightforward. In addition, differentiation of pristine beer from the effects of watering or decarbonation proved to be possible. These results suggest that colorimetric sensor arrays may prove to be useful for quality assurance/quality control applications of beers and perhaps other beverages.

**KEYWORDS: Colorimetric sensor array; cross-responsive dyes; chemometrics; food; beverages; beers**

## INTRODUCTION

Quality control of foods and beverages is obviously important for both industrial and personal concerns. In the past decade, a variety of sensor techniques have been developed (*1*−*11*) and various applications realized for the analyses of foods and beverages in both liquid and gas phases (*12*−*24*). Generally, the so-called electronic tongue (*4*) and electronic nose (*5*) devices consist of an array of cross-responsive sensors; these are inspired by the mammalian gustatory and olfactory systems (*25*−*27*), in which the composite responses of the array differentiate analytes from one another. Instead of the traditional component-by-component analyses via the combination of various chromatographic and spectroscopic techniques (*28*), electronic tongue and nose approaches are potentially less expensive. Most array detectors are based on conductive polymers or electrochemical sensors; a common limitation of such arrays, however, is their general lack of *chemical discrimination*, which makes differentiation among similar species problematic.

Recognizing that human beings are visual creatures and, consequently, that imaging technology is highly advanced yet extremely inexpensive, we have developed an optoelectronic approach. Over the past few years, we have developed a colorimetric sensor array for the general detection, identification, and quantification of volatile organic compounds in the gas phase (*29*−*31*). The colorimetric sensor arrays are inexpensive disposables; therefore, their reversibility is not an important issue. In fact, we have argued elsewhere (*31*) that a requirement of robust, nondisposable sensors has substantial disadvantages for the development of sensor technology, especially for electronic nose/tongue applications.

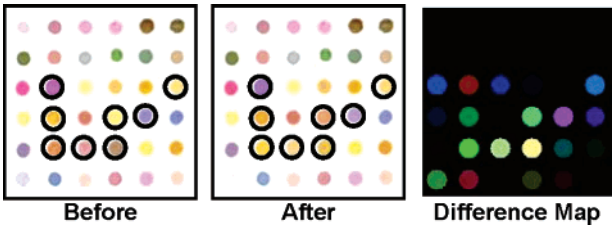


**Figure 1.** Images of the gas-phase colorimetric sensor array before and after exposure to head-gas from Goose Island Pils. Dyes that changed color the most are circled. The colorimetric sensor array for gas-phase analysis (as shown) has 36 dyes, whereas for liquid-phase analysis the array contains 25 dyes. For the purposes of effective visualization, the color range shown in the color change map representation is expanded from RGB values of 4–35 (i.e., 5 bit) to 0–255 (i.e., 8 bit).

Because the sensor dyes and substrates are both hydrophobic, we have even been able to use such arrays directly immersed for aqueous solutions containing organic compounds without interference from the presence of 55 M water (*32*). The color change pattern of the dye array before and after exposure to an analyte provides a color "fingerprint" for each specific analyte (**Figure 1**), and this simple array system makes facile identification of a wide variety of aqueous organic solutions possible over a concentration range from 0.1 to $10^{-5}$ M. Complex

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**Table 1.** Categorization of the 18 Beers Tested

| Name | Alcohol Content (% v/v)[a] | Specific | Subcategory | Category [a] |
|---|---|---|---|---|
| Pilsner Urquell® | 4.40 | Czech Pilsener | Czech Lager | Lager |
| Miller® Lite | 4.17 | Light Lager | American Lager | |
| Miller® Genuine Draft | 4.66 | Macro Lager | | |
| Point Special Lager | 4.6 | | | |
| Miller® High Life™ | 5.00 | | | |
| Icehouse™ | 5.50 | | | |
| Leinenkugel's® Original Lager | 4.6[b] | | | |
| Leinenkugel's® Red Lager | 4.9[b] | Dunkel Lager | | |
| Goose Island Pils | 5.00 | German Pilsener | German Lager | |
| Celebrator Doppelbock | 6.70 | Doppelbock | | |
| Tommyknocker Butt Head | 7.90 | | | |
| Leinenkugel's® Honey Weiss | 4.9[b] | American Pale Wheat Ale | American Ale | Ale |
| Fuller's ESB Ale | 5.90 | Extra Special / Strong Bitter (ESB) | English Ale | |
| Guinness® Draught | 4.20 | Irish Dry Stout | Irish Ale | |
| Domaine DuPage™ | 5.90 | Saison (country style) | French Ale | |
| Bürgerbräu Wolnzacher Roggenbier | 5.50 | Roggenbier (rye beer) | German Ale | |
| Hacker-Pschorr Weisse | 5.50 | Hefe Weizen (wheat beer) | | |
| Leinenkugel's® Berry Weiss | 4.7[b] | Fruit Beer | Specialty | Specialty |

[a] Information obtained from http://beeradvocate.com/beer/style/. [b] Information obtained from Leinenkugel's official website (http://www.leinie.com).

mixtures present no inherent difficulty for the colorimetric sensor array: obviously, the composite response of the sensor array does not give a component-by-component analysis, but for purposes of identification or quality control such an analysis is unneeded. Moreover, owing to its high selectivity and low cost, the colorimetric sensor array may prove to be suitable for industrial applications in the analyses of foods and beverages; for example, 14 different commercial soft drinks have been analyzed and easily differentiated by the dye array (*32*).

As an obviously important beverage, beer has been intensively examined by numerous scientists, and some have even published on the subject (*19*; *22*−*24*). In the work presented here, two colorimetric sensor array systems, optimized for sensing in liquid and gas phases, respectively, were used to analyze 18 commercial beers. The main focus of this paper is to show the ability to identify one beer from another and to show classification of beer type based on the colorimetric response of the sensor arrays. This effort develops a simple method that may prove to be useful for the quality control of beers, as well as a test of the general applicability of our sensor arrays.

## MATERIALS AND METHODS

**Sample Preparation and Instruments.** Eighteen beers were purchased from local stores and were used directly and freshly from their containers. Loss of $CO_2$ is minimized by conducting parallel quadruplicate experiments immediately after opening of the containers. $NaH_2PO_4 \cdot H_2O$ and $Na_2HPO_4$ were dissolved in purified water (obtained using NANOpure Ultrapure Water System, Barnstead International, Dubuque, IA) to make 500 mL of a 0.3 M phosphate buffer solution at pH 7.0 [the same buffer as used in prior aqueous sensing (*32*); as long as the same reference solution is used for all samples, its specific content (e.g., salt solution, pH) will not affect the results]. A ThermoOrion 920A-plus pH-meter was used for pH measurements. Three carbonated solutions of ethanol were prepared at 4, 5, and 6% ethanol concentrations by dissolving pure ethanol (AAPER Alcohol and Chemical Co., Shelbyville, KY) in carbonated water (Vess Seltzer Water); as listed for each beer in **Table 1**, these concentrations were chosen because commercial beers normally have similar alcohol contents. For comparison, a fourth, noncarbonated, solution was prepared with 5% ethanol in phosphate buffer. The carbonated ethanol solutions were tested immediately after preparation.

**Sensor Array.** The composition and preparation of the colorimetric sensor arrays were described previously (*29*−*32*). The arrays used in these studies were produced by transfer from an ink-well array to the hydrophobic membrane using an array of dipped stainless steel pins. Printed arrays are available commercially (liquid-sensing array is a 25-dye array, CSI.083; the gas-sensing array is a 36-dye array, CSI.031) from ChemSensing, Inc. (Champaign, IL; www.chemsensing.com).

**Data Acquisition.** Data acquisition was carried out using ordinary flatbed scanners following previously reported procedures (*29*−*32*). All experiments were done in quadruplicate.

For all aqueous-phase experiments, an Epson Perfection 1250 flatbed scanner was used. The array was first saturated in an aqueous liquid without dissolved organics (i.e., phosphate buffer) and imaged. After exposure to an analyte solution, rapid color changes in the dyes were readily observed and digitally imaged. The colors of the analyte solutions have no significant effects because the liquid layer between the sensor array and flatbed scanner is extremely thin ($<100\ \mu$m). With the use of a well-designed flow cell, the analyte solution required could be made less than 100 $\mu$L.

For all gas-phase experiments, an Epson Perfection 1670 flatbed scanner was used for imaging. The array was first imaged in air immediately before the addition of the beer sample. Five hundred microliters of beer was then applied to a piece of filter paper secured in a custom-made Teflon array holder with a sensor array inside; the holder was then sealed. The color change of the dye array was imaged after full equilibration with the headgas.

**Data Processing.** Simply subtracting the before-exposure image from the after-exposure image (red value minus red value, green minus green, blue minus blue) provides a color change profile for each analyte solution, as shown in **Figure 1**. The center of each dye spot (~300 pixels, 10 pixel radius) is averaged to avoid edge artifacts using Photoshop or customized software, ChemEye (ChemSensing, Inc.). The color change profiles are simply 3*N*-dimensional vectors (where $N =$ number of dyes) that can be easily analyzed by using standard statistical and chemometric techniques. In addition to the quadruplicate data, an average response was also calculated for each analyte. The full set of digital data is available in the Supporting Information.

It is convenient to visually display these vectors as color change maps by representing each spot as the absolute value of its color change in RGB. For purposes of display, the color ranges of the images are expanded; for liquid analysis (**Figure 2**), RGB values of 10−41 (i.e., 5 bits) were expanded to 0−255 (i.e., 8 bits), and for gas analysis (**Figure 3**), from 4−35 to 0−255. This visual representation in no way affects the actual digital data used for chemometric analysis. The color change profiles obtained from liquid-phase and head-gas analyses were compiled into two libraries, both with 94 entries (5 for each of 18 beers plus 4 ethanol control samples), consisting of 75-dimensional vectors for liquid-phase analysis (25 red, green, and blue color changes of the

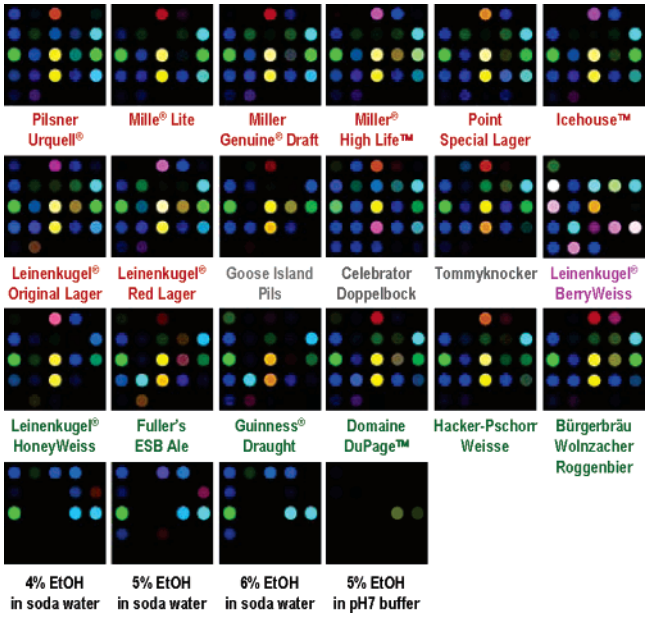


**Figure 2.** Average color change profiles of 18 commercial beers and 4 control ethanol solutions for liquid-phase analysis done in quadruplicate. The names are coded with different colors: red, American and Czech lagers; gray, German lagers; green, ales; magenta, specialty; black, controls. For the purposes of effective visualization, the color range shown in these representations is expanded from RGB values of 10–41 (i.e., 5 bit) to 0–255 (i.e., 8 bit); the complete digital data are provided as Supporting Information.

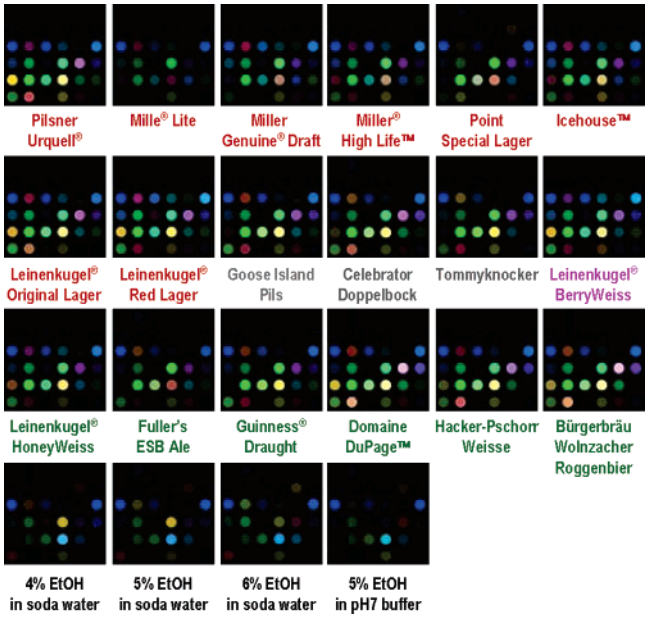


**Figure 3.** Average color change profiles of 18 commercial beers and 4 control ethanol solutions for gas-phase analysis. The names are coded with different colors: red, American and Czech lagers; gray, German lagers; green, ales; magenta, specialty; black, control. For the purposes of effective visualization, the color range shown in these representations is expanded from RGB values of 4–35 (i.e., 5 bit) to 0–255 (i.e., 8 bit); the complete digital data are provided as Supporting Information.

25 dyes in the aqueous-phase sensor array) and a 108-dimensional vector for gas-phase analysis (36 RGB color changes of the 36 dyes in the gas-phase sensor array), respectively. Both of the digital libraries are provided as Supporting Information.

**Chemometric Analyses.** Principal component analysis (PCA) and hierarchical clustering analysis (HCA) (*33*) were performed on the libraries using Multi-Variance Statistical Package (MVSP, Kovach Computing Services, Anglesey, Wales; www.kovcomp.co.uk) software.

## RESULTS AND DISCUSSION

Molecular recognition of an analyte is, of course, a function of the intermolecular interactions of that analyte. Our colorimetric approach (*29*−*31*, *34*) to molecular recognition uses a cross-responsive array of chemically diverse dyes; the choice of the dyes in our colorimetric sensor array makes use of a wide range of intermolecular interactions, rather than simply physical adsorption [which is the dominant interaction in most prior electronic nose technology (*5*), e.g., adsorption into polymers (*35*) or onto metal oxide (*36*) surfaces]. The chemically responsive dyes fall into three classes: (1) metal ion containing dyes that change color in response to Lewis basicity (i.e., electron pair donation and metal ion ligation), (2) pH indicators (*37*) that change color in response to Brønsted acidity/basicity (i.e., proton acidity and hydrogen bonding), and (3) dyes with large permanent dipoles [e.g., zwitterionic solvatochromic dyes (*38*)] that change color in response to local polarity. To some extent, of course, all dyes have some attributes of each of these three classes. To analyze aqueous solutions or head-gases with high humidity, it is important that the dyes chosen must be hydrophobic and must be printed on a hydrophobic membrane.

Beer can be generally classified as either lager or ale. The classification depends on the type of yeast used in the brew and the temperature at which fermentation takes place. Ales use yeast that ferment at the "top" of the fermentation vessel, which allows a higher temperature (15−25 °C) with a quicker fermentation period (~8 days or less). Lagers are brewed with bottom-fermenting yeast that ferment more slowly and at colder temperatures (12−18 °C), and they are often further matured at cool temperatures. Ale yeasts produce more byproducts (e.g., esters) than lager yeasts; thus, ales are generally more complex than lagers. Ales are also generally higher in alcohol content. There are also specialty beers, which often employ techniques, ingredients, and traditions from both lagers and ales but focus more on vegetable or fruit flavorings. In addition to the general division of lagers from ales, there are, of course, many more subtle subclasses of beers based on ingredients, style of handling, country of origin, etc. In these studies, 18 commercial beers were examined with the colorimetric sensor arrays for both liquid-phase and head-gas analyses: 11 lagers, 6 ales, and 1 specialty; detailed categorization of the beers used in this study is shown in **Table 1**. Four ethanol solutions were also analyzed as control samples for comparison.

**Colorimetric Sensor Array Responses.** Color change profiles were obtained from liquid-phase experiments for the 18 commercial beers, as shown in **Figure 2**. Distinct and highly reproducible patterns were obtained for each beer. Four ethanol solutions at different ethanol concentrations with and without added $CO_2$ gas were examined as controls: 4, 5, and 6% v/v ethanol solution in soda water and 5% v/v ethanol solution in pH 7 phosphate buffer. Upon examinatinon of **Figure 2**, it is obvious that the strong array responses to the beers do *not* come primarily from ethanol, water, or dissolved $CO_2$, because the ethanol control solutions gave much weaker responses than almost all of the beer samples. Moreover, changing the ethanol concentration from 4 to 5 to 6% v/v induces only a slight change in color change patterns, whereas far more dramatic color changes were observed among the beers due to the changes in concentrations of other chemicals to which the arrays are more sensitive. This is in part due to the hydrophobic nature of the

array, which makes the array nonresponsive to water and less responsive to other highly polar solutes (e.g., methanol and ethanol).

Similar to the liquid-phase analyses, average color change profiles were obtained from head-gas analysis experiments for the same 18 commercial beers, as shown in **Figure 3**. Distinct and highly reproducible patterns were again obtained for each analyte, although the color changes were weaker than those in liquid-phase analysis. Compared with the four ethanol control solutions, it is also obvious that the strong responses from the complex mixtures present in other beers did *not* primarily come from ethanol, humidity, or $CO_2$, because the ethanol control solutions gave much weaker responses than almost all of the beers.

**Principal Component Analysis.** PCA is a mathematical transformation used to extract variance between entries in a data matrix by reducing the redundancy in the dimensionality of the data. It takes the data points (changes in RGB values for each of the dyes in the array) for all analytes and generates a set of orthogonal eigenvectors (principal components, PCs) for maximum variance. The maximum total number of PCs is equal to $3N - 1$, where $N$ is the number of dyes in the array (i.e., 75 dimensions for the aqueous-phase sensor array and 108 for the gas-phase sensor array). PCA essentially concentrates the data's variation among analytes into the minimum number of dimensions. Generally speaking, the larger the number of PCs necessary for a certain level of discrimination (e.g., 95% of the total data variability), the better the sensor will be able to discriminate among similar analytes.

As shown in Supporting Information Figure 1 for the liquid-phase data, PCA shows that 22 dimensions are required to capture 95% of all the discriminatory information and that 37 dimensions are required for 99% discrimination. For the head-gas data PCA (Supporting Information Figure 1), 32 dimensions are required to capture 95% of all the discriminatory information and 51 dimensions are required for 99% discrimination. The number of PCs is even larger than that for liquid-phase analysis, in part because the gas-phase sensor array contains 36 dyes rather than 25. In general, other electronic nose and electronic tongue techniques typically have *95−99% of discrimination in their first two dimensions*.

The ability to discriminate between similar beers with the colorimetric sensor arrays comes from the chemical diversity of the 25 or 36 sensor dyes (and the resulting diversity of chemical interactions with those dyes). The high dimensionality (i.e., high dispersion) of the colorimetric sensor array gives us an unusually high level of chemical discrimination, and hence colorimetric sensor arrays have an exceptional ability to differentiate among very similar analytes.

The choice of dyes and the analytes being probed are not the same in the head-gas data compared to the liquid-phase data. This makes it potentially advantageous to combine the two digital databases. The liquid-phase and head-gas analyses data were therefore combined to form a library of 183-dimensional (i.e., 75 + 108) vectors, and statistical analyses were performed on the combined digital database. The quadruplicate data for liquid and gas phases for each analyte were joined randomly, and the averages of each analyte in the liquid and gas phases were merged.

PCA of the combined data (Supporting Information Figure 1) shows that 38 dimensions are required to capture 95% of all the discriminatory information and 59 dimensions are required for 99% discrimination, which is a higher dimensionality than for either liquid-phase or head-gas analyses alone. As shown in **Table 2**, it is also interesting to compare the number of PCs needed to include 95% of the total discrimination to the total dimensionality of the databases. The fraction of all dimensions needed for 95% discrimination is 0.29 for the liquid-phase database, 0.30 for the head-gas database, but only 0.21 for the combined database. One may conclude, therefore, that combining the liquid-phase and head-gas databases does improve the dimensionality of the data, but not to the extent it would if the two databases were fully independent of each other (i.e., if the PCs of the two databases were orthogonal to one another).

**Table 2.** Principal Component Analysis of the Colorimetric Sensor Array Databases

| database | maximum dimensionality of database[a] | PCs for 95% of discrimination | PCs for 99% of discrimination |
|---|---|---|---|
| liquid phase | 75 | 22 (0.29)[b] | 37 (0.49)[b] |
| head-gas | 108 | 32 (0.30) | 51 (0.47) |
| combined | 183 | 38 (0.21) | 59 (0.32) |

[a] Maximum dimensionality of the database is the total number of measured variables (i.e., changes in red, green, and blue values of each dye in the array or combination of arrays). [b] Fraction of total.

In most chemometric analyses, it is routine to plot the data in the two (or occasionally three) most important PCA dimensions, a so-called "PCA score plot". The score plot is then used to show differentiation between different analytes. Such a score plot will work, however, *if and only if* a very large percentage of the total discrimination can be concentrated to only two (or three) dimensions: a traditional PCA score plot *does not and should not represent the data well* if the sensors have good chemical discrimination (i.e., high dimensionality). In our case, the two most important PCs contain only ~34% of the total discrimination. The extremely high dimensionality of all of these databases is *without precedent* in prior electronic nose technology: prior techniques nearly always are able to incorporate 95% of discrimination in two or three dimensions. For any sensor array with high dimensionality, a two-dimensional (or even three-dimensional) PCA score plot is no longer appropriate for complete and accurate representation of the data. This makes any visual representation of PCA of a high dimensionality database extremely difficult.

**Hierarchical Clustering Analysis.** A very standard statistical procedure, HCA provides a better alternative for visual representation of high-dimensional data, in that an HCA dendrogram incorporates the full dimensionality of the database. HCA groups the analyte vectors according to their intervector spatial distances in their full dimensional vector space (e.g., 75-dimensional for the aqueous-phase 25-dye sensor array and 108 for the gas-phase 36-dye sensor array). There exist various related methods for defining clusters from the set of analyte vectors. The most common of these is the minimum variance method (Ward's method) (*27*), which we use here. The sum of the squared Euclidean distances (SEDs) from the group centroid to each of the vectors in that group is used to evaluate the variance within the group, and the groups with the minimum variance are clustered preferentially. Those clusters are then grouped together to form new larger scale clusters. The operation is performed repeatedly until only one supercluster remains. A dendrogram is generated in this fashion that shows quantitatively the similarities among the various analytes. An HCA dendrogram shows quantitatively the degree of similarity of the array responses among the various analytes using the data's full dimensionality. It also shows any misidentifications or overlap between individual measurements of analytes. In addition, once

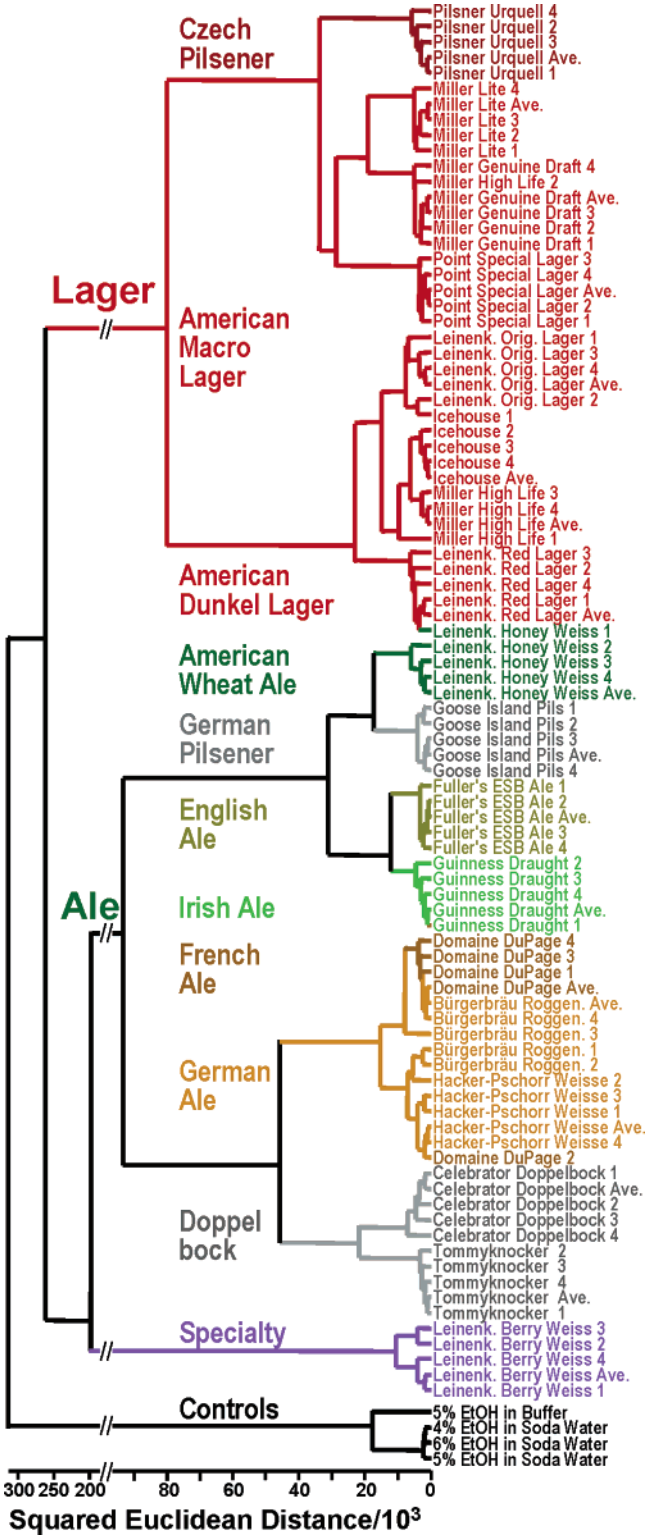


**Figure 4.** HCA dendrogram of 18 different beers and 4 ethanol control solutions obtained from the color change profile database for the combined liquid- and gas-phase analyses, using Ward's method. All experiments were run in quadruplicates, and an average was generated thereof. After the beverage name, the trial number or for average (ave) is given.

a database is established, any new unknown sample can be easily classified using the HCA dendrogram to identify the unknown or at least identify its closest database relation.

The HCA dendrogram for 94 color change patterns (quadruplicate trials plus averages of 18 beers plus four ethanol solutions) is shown in **Figure 4** for the combined database and in Supporting Information Figure 2 for a comparison of all three databases. As shown in the HCA dendrogram (**Figure 4**), excellent classification is seen for the combined data: of 94 cases, there are only 3 misclassifications (2.7% error rate). Furthermore, the classes of beers are generally distinct and coincide well with the commonly accepted classification of beers that are shown in **Table 1**: for example, (1) there is an excellent division between pale lagers and ales; (2) all six American macro lagers cluster closely, but are fully distinct from each other; and (3) specialty beers and ethanol controls are very well separated from the rest. These results suggest that the HCA analysis (i.e., dendrogram) may be used to estimate the classification of unknown beers.

In comparing the HCA analyses of the combined, the liquid-phase, and the head-gas databases (**Figure 4** and Supporting Information Figures 2 and 3), we observe that the combined database provides the best classification and the lowest error rate (3 of 110 cases; 2.7% error rate). Liquid-phase analysis does a somewhat better job of classification (e.g., 9 of 110; 8.2% error rate) than the head-gas (14 of 110; 13% error rate), but neither the liquid nor the gas analyses alone are as good as the combined database.

Supporting Information Figure 2 shows a comparison of the dendrogram groupings found for all three databases. Again, the dendrogram classifications are most discrete for the combined database and the head-gas analysis, the least accurate. This is certainly consistent with the general impression that taste rather than aroma is the dominant characteristic of beers. It is also worth noting that the clusters formed from the liquid-phase database are not exactly the same as those from the head-gas analysis, which shows that there are differences between the weightings of the chemical classes to which the liquid-sensing arrays are responding versus the weightings of the gas-sensing arrays.

One of the major remaining sources of errors with the colorimetric sensor arrays is in the reproducibility of the printing of the arrays, which (in these studies) were produced by transfer from an ink-well array to the hydrophobic membrane using an array of dipped stainless steel pins (*23*−*26*). The level of reproducibility in array printing in general, however, is improving rapidly using noncontact printing (e.g., cf. Perkin-Elmer PiezoArray).

**Validation.** Testing the reproducibility and reliability of a multidimensional sensor array is much more complicated than for single sensors. Although statistical methods, notably HCA, provide an optimized model of the entire database, it would be reassuring to have a simpler model to test the consistency of the data. The most intuitive and straightforward method is simply to query each trial against the whole data library and to find the closest match, as defined by a Euclidean distance.

To that end, we can define a simple goodness of fit (GOF) to evaluate the similarity between any two vectors, by calculating the Euclidean distance between the two vectors. As seen in eq 1, the GOF is a normalized Euclidean distance, where $a$ is

$$\mathrm{GOF} = 1 - \sqrt{\sum_{i=1}^{i=3N} (x_{ai} - x_{bi})2/(3N \times 510)^2} \qquad (1)$$

the measurement, $b$ is any library entry, $x_i$ is the $\Delta R$, $\Delta G$, or $\Delta B$ value of the $i$th dye, $N$ is the number of dyes, and $3N$ is the total dimensionality of the vector space (e.g., 108 dimensions for a 36-dye array). The normalization factor, $(3N \times 510)^2$, comes from the maximum difference possible between any two RGB values in the before-exposure versus after-exposure

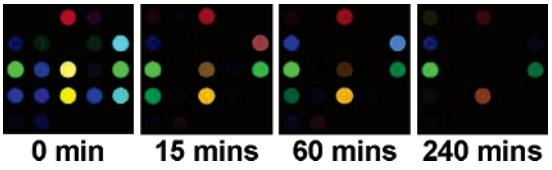


**Figure 5.** Average color change profiles of Miller Lite before and after bubbling with argon gas for 15, 60, and 240 min at ~200 mL/min. For the purposes of effective visualization, the color range shown in these representations is expanded from RGB values of 10–41 (i.e., 5 bit) to 0–255 (i.e., 8 bit).

images: that is, 255 − (−255). Therefore, the GOF value is a number between 0 and 1; a GOF of 1 indicates an exact match.

By calculating a GOF for every quadruplicate trial and average trial (90 entries for the beers only; the controls were not included because they were single entries only; results presented as Table 2 in the Supporting Information) against every entry in the digital data library, we find that the best match for each entry (other than itself) is one of the other entries for that analyte, with five mismatches (i.e., 5.5% error rate). This compares well with the HCA dendrogram misclassification rate of 2.7%: HCA optimizes classifications for the whole database, and so, as expected, its error rate is somewhat less than the more limited pairwise GOF comparison.

**Potential Applications to Quality Control/Quality Assurance.** Due to the extremely high discriminatory ability of the colorimetric sensor array, one may speculate the array might prove to be useful in applications of quality control and quality assurance for the food and beverage industry. We have conducted two simple experiments along these lines as a proof of concept: we have examined the effects of degassing (i.e., flatness due to loss of carbonation) and of dilution (i.e., watering) on the colorimetric sensor array response. For the first experiment, the array response (done in triplicate) was determined for a single beer after intentional degassing of beer with an argon gas flow. As shown in **Figure 5**, the color change profiles of the array do respond to such degassing, and the changes in the array response are clearly distinguishable even by eye. For the second experiment, the effect of watering of a beer on its array response was determined. As shown in **Figure 6**, the color change profiles do change with increased dilution, and the changes are again clearly distinguishable by eye. **Figure 6** also shows the dendrogram from the triplicate trials plus the average: the data are quantitative, and no confusion was observed among the 16 entries. These two simple examples give us some hope that our approach using colorimetric sensor arrays may prove to be useful for quality assurance/quality control applications of beers and perhaps other beverages.

In summary, a new and very simple analytic method using colorimetric sensor arrays has been successfully applied in the comparison and identification of 18 commercial beers in both liquid and gas phases. The color changes of the sensor arrays produce distinct identifiable patterns for each beer using an ordinary flatbed scanner. The data can be analyzed using the standard chemometric method of hierarchical cluster analysis, and excellent discrimination can be obtained. By combining the numerical data from both the liquid-phase and head-gas experiments, great improvements in discrimination and selectivity can be achieved; identification error rates are below 3%. In the future, new colorimetric sensory dyes (e.g., dyes selective for detection of ions or carbohydrates) can be added to expand the capability of the current array.

We have established in these studies that we can tell the difference even between very subtly different beers with

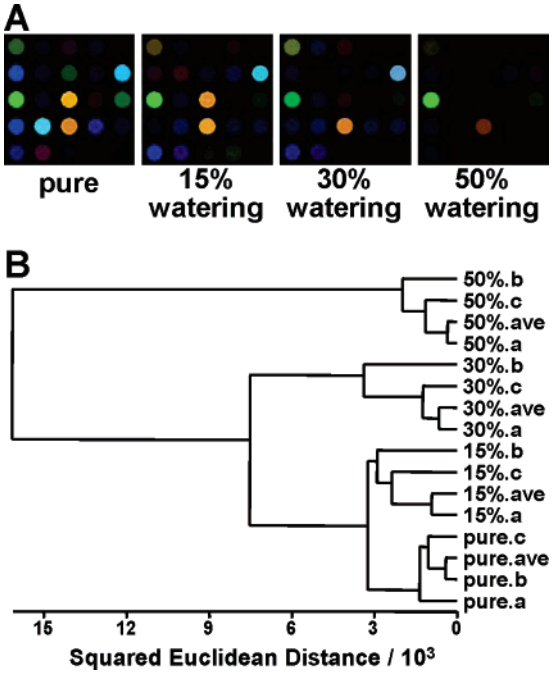


**Figure 6.** Average color change profiles (**A**) and a HCA (**B**) of the effects of watering of Guinness Draught with various amounts of purified water added (triplicate runs plus average at dilutions of 15, 30, and 50% v/v). For the purpose of effective visualization, the color range shown in (**A**) is expanded from RGB values of 10–41 (i.e., 5 bits) to 0–255 (i.e., 8 bits).

reasonable accuracy. We speculate that the colorimetric sensor array will also be able to distinguish readily between a beer in its pristine state and one that has undergone spoilage, has been foxed by overheating or photo-oxidation, has been watered or contaminated, or has loss carbonation. Our preliminary exploration of the last two examples suggests application of the colorimetric sensor array to quality control and quality assurance in the food and beverage industry. In addition, the extremely high dimensionality of the data from our colorimetric arrays suggests that statistical correlations with the evaluations by organoleptic panels (i.e., drinkers) may be accomplished and may prove to have quantitative predictive value. It is important to realize, however, that the colorimetric sensor array is based on the differences in the concentrations of various organic and inorganic components (including pH) of the analytes, and the array responses cannot be translated (at this time, at least) into an actual human perception of taste and smell.

**Supporting Information Available:** Scree plots of the PCAs, HCA of liquid-phase, head-gas, and combined databases, pairwise goodness-of-fit comparisons, and the full digital database for liquid-phase, head-gas, and combined analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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