A Hand-Held Optoelectronic Nose for the Identification of Liquors

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S Supporting Information

ABSTRACT: Successful discrimination of 14 representative liquors (including scotch, bourbon and rye whiskies, brandy, and vodka) was achieved using a 36-element colorimetric sensor array comprising multiple classes of cross-reactive, chemically responsive inks. In combination with a palm-sized image analyzer, the sensor array permits real-time identification of liquor products based on vapor analysis within 2 min. Changes in sensor spot colors before and after exposure to the vapors of the liquors that are partially oxidized as they are pumped over the sensor array provides a unique color difference pattern for each analyte. Facile identification of each liquor was demonstrated using several different multivariate analyses of the digital data library, including principal component, hierarchical cluster, and support vector machine analysis. The sensor array is also able to detect dilution (i.e., "watering") of liquors even down to 1% addition of water. This colorimetric sensor array is a promising portable adjunct to other available techniques for quality assurance of liquors and other alcoholic beverages.

KEYWORDS: colorimetric sensor array, hand-held device, colorimetry, liquor, quality control
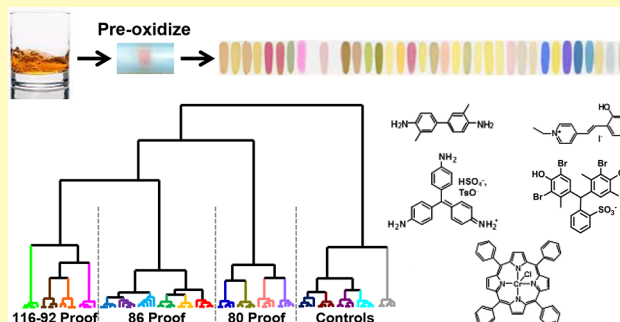
L iquors (i.e., distillates from the fermentation of grains, fruits, or vegetables[1]) have a long history; indeed, one of the earliest mentions of chemists in printed English refers to "Chymistes, the distillers of waters⋯".[2] Early records indicate liquor production dates at least back to the 17th century in Ireland, where local monks were producing a distilled alcohol known as the water of life, in Latin as "aqua vitae" and in Gaelic as "uisge beatha", from which "whiskey" derives.[3] Literally thousands of liquor products of different brands, types, ages, and proof are presently available, and this popularity of liquors provides incentives for potential adulteration or contamination by water, low-end liquors, or other inexpensive additives.[4] The consumption of counterfeit liquors can prove to be a public health problem as well, e.g., from methanol contamination. For these reasons, the quality control of liquors becomes imperative for regulation of the liquor market and for protection of consumers' health. Easy analysis of liquors in the field, outside of laboratory settings, has become an urgent need as part of such quality control monitoring, and this requires the ability to distinguish even subtle differences among liquor samples.

In recent years, a variety of common analytical techniques have been developed for the analysis of liquor components in either gaseous or liquid phase, including gas chromatography (GC),[5−7] high performance liquid chromatography (HPLC),[8,9] mass spectrometry (MS),[10−12] infrared or UV−vis spectrometry,[13−15] and solid-phase microextraction (SPME).[16,17] Chromatographic or spectroscopic methods only gives ppm or sub-ppm level detection for most analytes; below that level, preconcentration of low-concentration components using SPME is necessary.[18] Unfortunately, due to the variation in

partition coefficients among polar vs nonpolar compounds, SPME inherently gives uneven preconcentration so that the analysis gives inaccurate distribution of components in the original mixture. The array-based sensors (e.g., electronic noses), as first proposed in the early 1980s, provide a composite response.[19−23] Examples of electronic or optoelectronic noses employed in liquor assessment include chemiresistive metal oxides,[24] mass-sensitive quartz crystal microbalances,[25] photonic crystals,[26,27] and UV−vis or fluorescence.[28−34] Those devices, however, often have limitations in chemical specificity or diversity, which makes it problematic for capturing the subtle differences among highly similar analytes.[21−23] A notable exception is the very recent work from Bunz and co-workers using fluorescent polymer arrays.[29,35,36]

To overcome these limitations, our group has developed colorimetric sensor arrays as optoelectronic noses, which make use of the chemical diversity available in molecular sensors (specifically, chemically responsive dyes). Our colorimetric sensor arrays probe a broad range of chemical interactions using a set of chemo-responsive dyes immobilized in relatively hydrophobic matrices.[23,37−40] The change in colors (RGB) of the array before and after exposure to a given odorant are digitally imaged and provide a "fingerprint" that identifies the odorant by comparison to a collected library database. Colorimetric sensor arrays have proven extremely effective for

identification and quantification of analytes in both gaseous and aqueous phases and have found successful application in security screening,[38,41−43] environmental monitoring,[44,45] medical diagnosis,[46] and quality inspection of foods and drinks.[47−49]

The chemical composition of liquor products is enormously complex and generally contains 300−1500 identifiable compounds in different liquors.[5,10,12] Aldehydes and ketones, which are produced from fermentation, the aging process, and storage contribute substantially to the distinctive aroma of alcoholic beverages.[1,50,51] As examples, furfural, vanillin, and diacetyl are compounds that are widely present in whiskies, rums, and bourbons. Furfural provides an almond-like, grainy flavor; vanillin is a phenolic compound that gives vanilla odor and is abundant in bourbons which are aged in oak barrels. Diacetyl, which has a buttery aroma, is commonly associated with off-flavors of whiskies. These species add a pungent, sharp note to the taste that can be used as standards for the authentication and quality assessment of liquor products.

To target those aldehydes and ketones, we designed several colorimetric sensor elements based on acid-doped, amine-based nucleophiles that are specifically aldehyde- and ketone-sensitive.[52] We combined these new sensors with other classes of chemical dyes to assemble into a generalized, 36-element sensor array (Figure 1a) that also incorporates pH indicators,
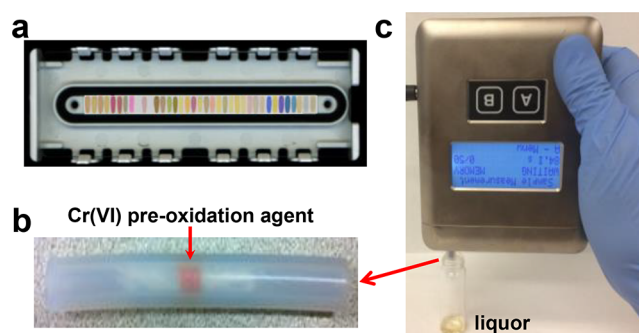

Figure 1. Sensing platform is constructed from a disposable colorimetric sensor array, a hand-held color imaging analyzer, and a disposable preoxidation tube that partially oxidized the incoming liquor vapors. (a) Top view of the 36-element colorimetric sensor array mounted in a polycarbonate cartridge (79 × 28 × 10 mm). (b) Preoxidation tube packed with Cr(VI) on alumina held by glass wool in a Teflon tube (38 mm long, 6 mm O.D.). (c) Sampling of headspace vapor from a liquor sample into the hand-held analyzer (125 × 95 × 40 mm).

Lewis acid/base indicators, redox indicators, and solvatochromic dyes; the array therefore responds not only to aldehydes and ketones but also to a wide range of volatile organic chemicals (VOCs).[38,44]

To improve sensitivity and increase discriminatory power, we have developed a method to partially oxidize the liquor vapor stream before exposure to the array (Figure 1b and c), which produces more chemically reactive species such as aldehydes, quinones, and carboxylic acids.[45] The disposable preoxidation tube is simply attached to the hand-held image analyzer and head-gas vapors drawn through the tube and over the array located inside the analyzer. This provides for the *in situ* collection and real-time analysis of sensor images within 2 min. Our colorimetric sensor array has been tested against a library of 14 commercial liquor products (Table 1).

Table 1. Fourteen Tested Liquor Samples

liquor brand	category	years aged	alcohol content (% v/v)[a]
Willett Kentucky Single Barrel	Bourbon whiskey	10	58
Glenmorangie	Scotch whisky	10	50
Willett Pot Still Reserve	Bourbon whiskey	8−10	47
Deanston	Scotch whisky	12	46
Dalwhinnie	Scotch whisky	15	43
Evan Williams Black Label	Bourbon whiskey	~7	43
Evan Williams Single Barrel	Bourbon whiskey	9	43
Highland Park	Scotch whisky	12	43
Lagavulin	Scotch whisky	16	43
Macallan	Scotch whisky	17	43
Glenfiddich	Scotch whisky	15	40
Grey Goose	Vodka	N/A	40
St-Rémy VSOP	Napoleon Brandy	>4	40
Templeton Small Batch	Rye whiskey	6	40

[a]The U.S. defines proof as twice the ABV (alcohol by volume) concentration.

EXPERIMENTAL SECTION

Reagents and Materials. All solid or liquid reagents were analytical-reagent grade, purchased from Sigma-Aldrich, and used without further purification. The Scotch whiskies (Dalwhinnie 15 yrs, Deanston 12 yrs, Glenfiddich 15 yrs, Glenmorangie, Highland Park 12 yrs., Lagavulin 16 yrs, and Macallan 17 yrs), the Kentucky bourbons (Evan Williams Black Label, Evan Williams Single Barrel, Willett Pot Still Reserve, and Willett Single Barrel), and the other liquors (Grey Goose vodka, St-Rémy brandy, and Templeton rye) were used as received.

Sensor Array Fabrication. A generalized colorimetric sensor array for liquor detection was prepared from 36 sensor inks, including 6 aldehyde/ketone responsive dyes,[52] and 30 other classes of sensor elements from prior studies[53] chosen for optimum responsiveness to these analytes. The chemically responsive dyes for each sensor spot are listed in Support Information (SI), Table S1. Approximately 200 nL of each chemically responsive ink was robotically printed onto a polypropylene membrane (Sterlitech PP021605820) as bars sized 4 mm × 1 mm wide with 1.2 mm center−center distance using an array of stainless steel rectangular pins mounted in an Array-It (Sunnyvale, CA) NanoPrint printer. Once printed, the sensor array strips were mounted in customized polycarbonate cartridges that fit into the hand-held device for image collection and analysis (Figure 2). The arrays were then dried under vacuum for 1 h at room temperature, and stored in N_2-filled Mylar bags. Before use, a Viton O-ring was placed in a groove around the array strip and a standard glass microscope slide was snapped into the cartridge to create a leak-free seal that permits a gas stream to be pulled over the sensor array.

Liquor Vapor Sampling. A hand-held device equipped with a color contact imaging scanner and an onboard micropump was used to expose the sensor arrays to the analyte vapors and to collect before- and after-exposure images of the sensor array. 0.1 mL of each whiskey specimen was placed in an open, 20 mL scintillation vial, and the head-gas sampled by the hand-held device at a flow rate of ~550 cm³/min through a short Teflon tube packed with a preoxidation reagent. The sensor array was equilibrated to the ambient air for two min and then exposed to the liquor vapors (partially oxidized) for another 2 min. Five replicates were collected for each liquor sample.

Preoxidation Reagent. The oxidizing reagent (i.e., chromic acid loaded on an inert oxide support) was made as previously reported[42,45] by mixing porous Al_2O_3 nanopowders (~10 nm diameter, surface area ~100 m²/g, 2.5 g), $Na_2Cr_2O_7$ (0.5 g), 98% H_2SO_4 (0.75 mL), and H_2O (10.0 mL). Water was then removed under vacuum at 60 °C for
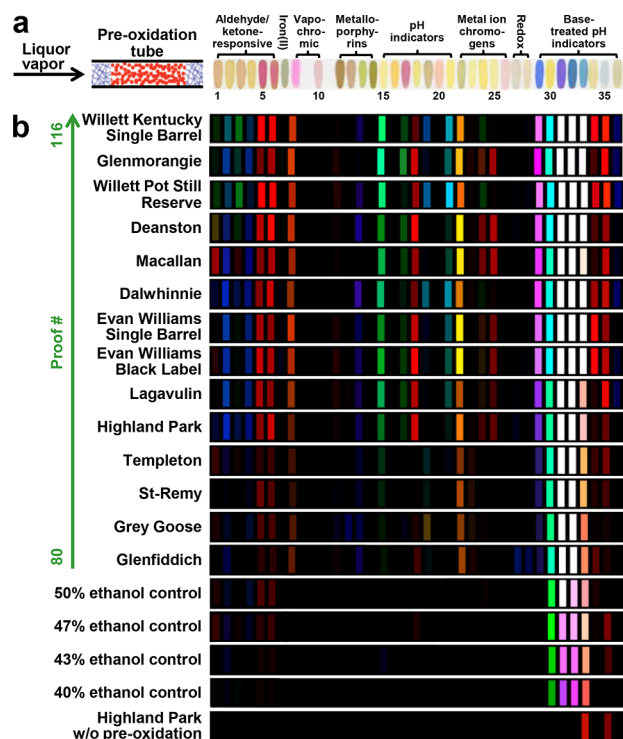
Figure 2. (a) Scheme of the preoxidation of liquor vapors before exposing to the 36-element colorimetric sensor array. (b) Sensor array response to 14 liquor samples, 4 ethanol controls at relevant alcoholic concentrations, and the control without preoxidation; each pattern is the average of 5 independent trials with 2 min exposure. The color range is expanded from 3 to 8 bits per color (i.e., the RGB color range of 3–10 was expanded to 0–255) for display purposes.

0.5 h. The resulting gel was further dried by flowing dry nitrogen for 4 h. 40 mg of this oxidizing reagent was packed into a Teflon tube (3.5 cm long with 3.2 mm I.D.) and held in place with glass wool plugs (Figure 1b).

Hand-Held Scanner Details. The construction and specifications of the portable reader used in this study is shown in the previous published work.[54] Raw data was collected by the color contact imaging scanner. Reflectance data were normalized against a one-time calibration where 100% reflectance was defined from a blank, unprinted polymer film and 0% reflectance by all illumination turned off.

Raw Data Processing. Analyte response was calculated from the differences between the observed red, green, and blue (RGB) values for each sensor element before and after exposure to liquor volatiles. All color difference maps herein are displayed by scaling a relevant color range from 3-bit (i.e., 3–10 RGB values) to 8-bit color (i.e., 0–255) for visualization purposes only. Signals for each channel were defined as the difference between each analyte trial measurement (analyte − n) and an averaged nonexposed controls (i.e., $R_{analyte-n}$ - $R_{control-avg}$), and noise was defined as the standard deviation among the controls (i.e., $\sigma_{R2} = \Sigma_n (R_{control-n} - R_{control-avg})^2/(N - 1)$). For the measurement of signal-to-noise ratio (S/N), signal and noise were calculated for each dimension using all trials in the data set (i.e., red, green, and blue values of 36 sensor elements; 108 dimensions in total).

Data Library Analysis. Color difference patterns were created using Matlab. Two unsupervised statistical methods, principal component analysis (PCA) and hierarchical cluster analysis (HCA), were performed for database clustering using MVSP software (Kovach Computing Services, UK); in all cases, minimum variance (i.e., "Ward's Method") was used for HCA clustering. Support vector machine (SVM) analysis was performed using custom software that makes use of an open source SVM library, LIBSVM, using a linear kernel with default parameters.

■ RESULTS AND DISCUSSION

Overview of Liquors. Five common categories of liquors were examined in this study: scotch, bourbon, rye, vodka, and brandy (Table 1). Scotch whisky is produced at a distillery in Scotland and must be distilled from water and malted barley to an initial ethanol content of <94.8% by volume. Scotch is bottled with the addition of no other substances other than water and plain caramel coloring and must be aged in oak barrels for at least three years. Bourbon is an American whiskey specifically from Kentucky that consists mostly of corn (at least 51%), as well as barley, wheat, and rye, distilled to no more than 80% ethanol by volume, and aged in new charred oak barrels. Rye whiskey, as the name implies, is made mainly of rye grain with the same distilling and aging requirements of bourbon. We also examined, for comparison, brandy (i.e., French distillate from wine grape fermentation) and vodka (i.e., grain or potato distillate) liquors.

Qualitative Colorimetric Sensor Response to Liquors. Liquor analysis by traditional electronic nose technology has often been problematic because the dominant analyte to which prior sensors respond is ethanol. Consequently, subtle differences among liquors with similar alcohol contents have been difficult to detect.[21−23] In contrast, the colorimetric sensors used in this array are not especially sensitive specifically to alcohols. Instead, we convert the complex volatile mixture that makes up the headspace vapor of each liquor to a stream of partially oxidized VOCs by passing it through an alumina bed on which a Cr(VI) oxidant had been deposited. This partial oxidation produces complex degradation products that, as we shall see, are a reproducible mixture of more chemically reactive oxidation products (e.g., aldehydes, quinones, and carboxylic acids). This provides a much more sensitive and distinctive signature than simply detecting the vapor of the pristine liquors (as shown in Figure 2b by comparing array response to Highland Park vapor partially oxidized (pattern 10) vs Highland Park without preoxidation (pattern 19)).

Collected in quintuplicate trials for each liquor sample, the color difference maps show distinctive sensor response patterns, reflecting the chemical complexity of liquors (Figure 2). Judging from the color difference profiles, the response of the array to the partially oxidized liquor vapors is mainly ascribed to two classes of compounds: (i) carbonyls that trigger the aldehyde/ketone sensors (spots 1–6) and (ii) acids (spots 15–21 and especially the base-treated indicators, spots 29–35). In contrast, aqueous ethanol controls at equivalent alcoholic concentrations show much simpler response patterns; the main oxidation reactions of ethanol with chromic acid produce acetic acid, which reacts only with a few sensor elements in the array, specifically those sensitive to volatile acids.

This ready differentiation between aqueous ethanol controls and the real liquors demonstrates that the response seen for the liquors is induced from the partial oxidation of various congeners in the liquors and not merely from ethanol and its oxidation products. Such congeners include a variety of species such as ketones, sulfides, aldehydes, fatty acids, esters, terpenes, and polyphenols; they originate from the initial partial distillation and from the extraction of components during aging (e.g., from burnt oak barrels). The presence of those congeners in liquors distinguish liquors from each other and from dilutions of pure ethanol. As we will see below, the differences in congeners permit discrimination both of large differences in the composition of liquors (e.g., vodka vs brandy

vs whiskies) and of very subtle differences (e.g., different brands of Bourbons or Scotches).

There is a general trend that correlates well the overall sensor array response to the ethanol concentration. As shown in SI Figure S1, the higher the alcohol concentration, the greater the sensor array response, as calculated from the Euclidean distance of the red, green, and blue channels of the color changes (i.e., the square root of the sums of the squares of the difference of after-exposure to before-exposure colors). This correlation is true not only for the total sensor array response, but also for each group of sensor classes (SI Figure S1). This correlation, however, is *not* due to the ethanol concentration itself, however. As noted, the response of aqueous alcohol controls is well below that of the liquors (SI Figure S2). Rather, the correlation between alcohol concentration and array response reflects the greater concentration of congeners in higher proof liquors.

Multivariate Analysis of Liquor Data. A more quantitative analysis of the color difference profiles demands a clustering or classification algorithm that makes use of the high dimensionality of the data. To that end, three types of multivariate analyses were performed on the collected liquor data: hierarchical cluster analysis (HCA), principal component analysis (PCA), and support vector machine (SVM) analysis.[55−57]

As an unsupervised and model-free chemometric analysis, HCA clusters data by determining the "dissimilarity" among all analyte vectors according to their distances apart in their full vector space (i.e., the total 108 dimensions of 36-element sensor array). As shown in the HCA dendrogram of Figure 3, all quintuplicate trials of 14 liquors, 4 aqueous ethanol controls, plus a scotch control without preoxidation show accurate groupings with no errors in clustering (i.e., the error rate is <1%). In addition, we can discern subtle distinctions even between liquors from the same distillery. There is also clustering of liquors by their alcohol concentration (i.e., proof), which fall into three categories: >90-proof (high), 86-proof (medium), and 80-proof (low). This clustering is *not* due to the alcohol concentration per se: the aqueous alcohol controls do not cluster with liquors of the same alcohol concentration. As discussed earlier, this clustering reflects the relative concentrations of congeners compared to the alcohol controls.

Due to the broad range of chemical interactions probed by these colorimetric sensor arrays, the data has a much higher dimensionality than that gathered by other electronic nose techniques, which generally rely only on van der Waals and hydrophobic, weak, interactions. Another model-free chemometric method, principal component analysis (PCA), was used to measure the dimensionality of our sensor array data. PCA creates linear combinations of the initial data (i.e., 108 dimensions from 36 changes in red, green, and blue values) so as to maximize the total variance in as few dimensions as possible. The PCA scree plot of all liquors and controls shows that 13 dimensions are required to define 90% of the total variance and 19 dimensions to define 95% based on the standardized color difference vectors (SI Figure S3); for comparison, traditional electronic nose technologies generally require only two or three dimensions to capture 95% to 99% of the total variance.

PCA inherently is ill-suited for use with high dimensional data. Nonetheless, using a 3D PCA score plot (Figure 4), which only captures 70.5% of the total variance, we see tight clustering of all the analytes into similar clusters observed in the HCA.
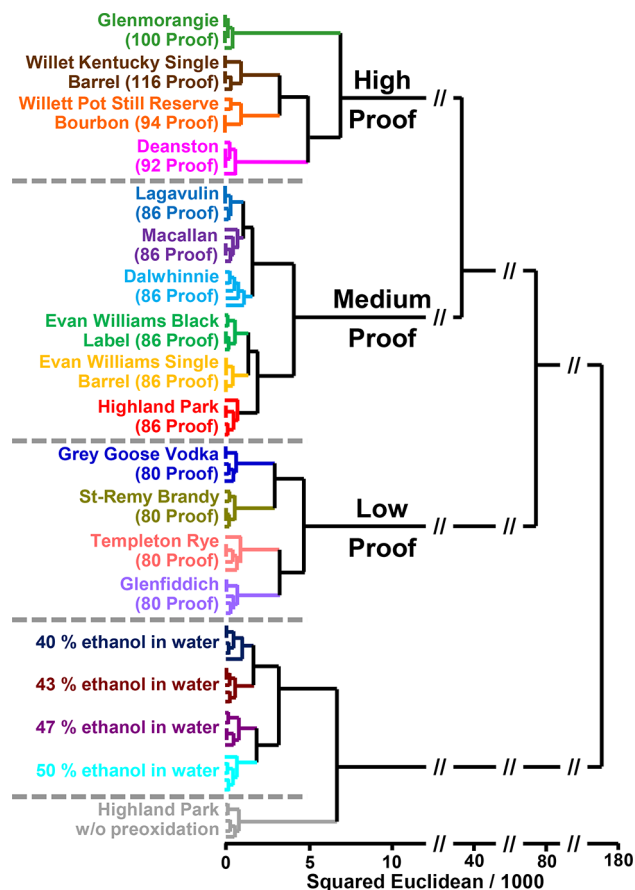

Figure 3. HCA dendrogram of 14 liquor samples (with partial oxidation of the vapors), 4 aqueous ethanol controls (with partial oxidation), and a control from one scotch (Highland Park) without preoxidation.
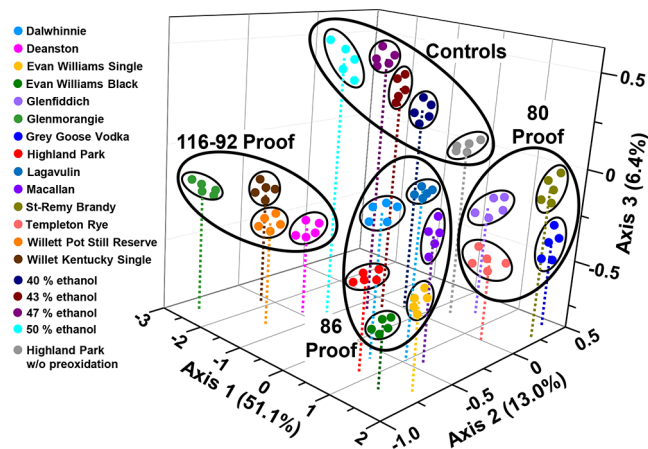

Figure 4. Three dimensional PCA score plot of 14 liquor samples, 4 ethanol controls, and the Highland Park (HP) Scotch without preoxidation; note that the three dimensions plotted account for only 70.5% of the total variance.

There are no significant overlaps among quintuplicate trials of the individual liquors. Similar to the HCA clustering, the PCA shows well-defined boundaries to form four superclusters of high, medium, and low alcohol concentrations with a separate supercluster of the aqueous alcohol controls.

SVM analysis, as a supervised and predictive method for data classification, generates an algorithm to compare an unknown

analyte to an established library of known analytes; SVM is standard for analysis of complex multidimensional data, e.g., face and voice recognition.[25,53] SVM relies on pairwise class prediction and focuses on the data most likely to be misclassified (i.e., data vectors near the decision boundary of any given pairwise class, known as "support vectors") to create optimized decision boundaries that best separate the data for each given pair of classes in multidimensional space. Each pairwise comparison gives a vote, which is tallied to decide the final classification results. Linear discriminant analysis (LDA) has been commonly used in chemical sensor studies; SVM, however, is much more appropriate for the analysis of colorimetric array data set than LDA or other discriminant analyses for two reasons: (i) The homoscedasticity assumption of LDA (i.e., the assumption that the covariance between dimensions is identical between different sample classes) is grossly violated by the cross-reactive nature of the colorimetric sensor array; and (ii) the number of replicates needed for the accurate prediction of classification has to be roughly 10× the number of dimensions (i.e., >100 replicates), which goes far beyond practical experimental procedures.

The results of SVM analysis using a standard cross-validation, the leave-one-out permutation model, are shown in SI Tables S2 and S3. All the analytes give classification accuracy of 5/5 or 100% (i.e., each of quintuplicate trials, when considered as an incoming data, can be successfully classified without error into the training data set as determined by the other four parallel trials), demonstrating the accuracy of the SVM method in the predictive classification of new colorimetric data against an existing library.

Potential Applications in Certification and Quality Assurance of Liquors. Counterfeiting and adulteration of foods and beverages generally, and liquors specifically, is a substantial problem worldwide.[3,58] Due to the extremely high discriminatory power of the colorimetric sensor array, one may speculate that the array could be used in quality assurance for the beverage industry. To demonstrate the potential importance of our sensor system in the beverage industry, a simple set of experiments investigated the effect of the dilution of liquors on the sensor array response. As shown in Figure 5, the color difference profiles collected on a Bourbon whiskey (i.e., Willett Pot Still Reserve) do change with increasing degree of dilution. A monotonic decrease of array response (as measured by the total Euclidean distance of the difference pattern) was observed (Figure 5a). We were able to distinguish among different dilutions of the liquor, even between 1% dilution and the pristine liquor, as shown in the HCA (Figure 5b): no confusions or errors in clustering were observed among the 27 trials. This proof-of-concept experiment shows the ability of the sensor array to distinguish adulterated liquor samples from real ones as a useful tool for quality control in beverage industry.

CONCLUSIONS

In conclusion, a colorimetric sensor array has been developed for the rapid and facile identification of liquors, including scotch, bourbon, rye, vodka, and brandy. The generalized array employs multiple classes of chemo-responsive sensor inks including pH indicators, Lewis acid/base indicators, redox indicators, solvatochromic dyes, and specific aldehyde/ketone sensitive indicators. The head-gas vapor of liquors was partially oxidized by flowing through a disposable tube of chromic acid on alumina to enhance sensor array response. The array was
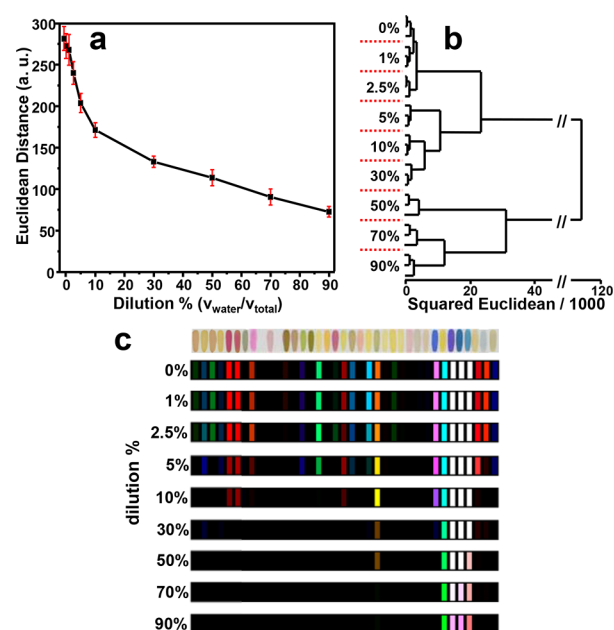

Figure 5. Experiments of the dilution effect on Willett Pot Still Reserve Bourbon. (a) Overall response curves, (b) HCA dendrogram, and (c) averaged color difference profiles of the bourbon at different dilutions. HCA demonstrates accurate and distinct grouping of each dilution, even between pristine and 1% diluted liquor samples. For the purpose of visualization, the color range is expanded from 3 to 8 bits per color (i.e., the RGB color range of 3−10 was expanded to 0−255).

read with a hand-held device for real-time imaging and data analysis. The sensor enables the correct categorization of 14 liquors by their alcoholic content and brand name, with an accuracy rate >99% based on hierarchical cluster, principal component, and support vector machine analyses. The sensor also permits the discrimination of pristine liquors from the aqueous ethanol samples or adulterated liquors, revealing its promising applications in the food and beverage industry for quality control and assurance. Continued investigation on the discrimination of a more complete list of alcoholic beverages (including not just distilled liquors but also wines, ciders, and beers) according to their type and method of preparation, country of origin, and degree of spoilage, adulteration, or contamination is a promising area of research.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssensors.7b00709.

Tables of dye formulations, experimental details, sensor response graphs and statistical analysis (PDF)

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Notes

The authors declare no competing financial interest.

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