ACS SENSORS

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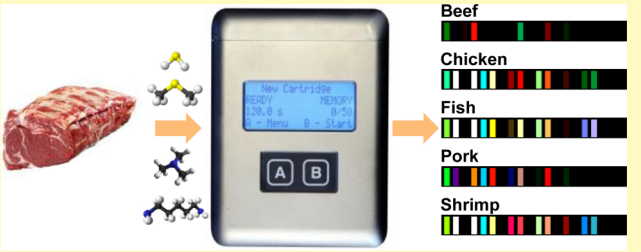
Portable Optoelectronic Nose for Monitoring Meat Freshness

Zheng Li and Kenneth S. Suslick*

†Department of Chemistry, University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: A disposable colorimetric sensor array (CSA) made from printing various chemically responsive dyes was combined with a hand-held device for on-site assessment and monitoring of the freshness of five meat products: beef, chicken, fish, pork, and shrimp. The hand-held device takes advantage of an on-board diaphragm micropump and a commercial 1D CMOS camera (CIS) which enables the real-time collection of colorimetric data. The sensor array shows excellent sensitivity to gaseous analytes, especially amines and sulfides at low ppb levels; excellent discrimination among meat volatiles in terms of meat type and storage time was demonstrated with multiple chemometric approaches including principle component analysis, hierarchical cluster analysis, and support vector machine analysis. This optoelectronic nose proves to be a promising supplement to other available techniques for meat product inspection.



KEYWORDS: *optoelectronic nose, hand-held device, colorimetry, meat freshness, quality control*

The quality control of meat products has attracted considerable attention during the past decade and has strong potential for the application of new chemical sensing techniques.[1−3] The primary factors that determine meat freshness during storage are the concentrations of sulfurous compounds and biogenic amines, which are two major metabolites from the microbial decarboxylation of amino acids.[3,4] The degree of meat deterioration and bacterial contamination can therefore be indirectly determined by measuring the emission of relevant volatile organic chemicals (VOCs).[5,6] Numerous analytical techniques for monitoring meat spoilage have been developed, including FT-IR spectrometry,[7,8] HPLC,[9] GC-MS,[10,11] and chemifluorescence.[12−14] Most of those methods, however, demand sophisticated instrumentation, lack portability, or require time-consuming sample preparation. There remains therefore an urgent need for new methods for simple, rapid, and sensitive sensing of sulfurous and amine volatiles for application to assessment of food and especially meat freshness.

One of the alternative approaches for effective sensing of meat freshness is an electronic nose,[15] i.e., the use of the composite response of an array of, typically, metal oxide or conductive polymer sensors.[16,17] For nearly all electronic nose technologies, the sensors' responses depend primarily upon physical sorption of analyte molecules onto or into the sensor elements that induce changes in the weight or conductivity. Such classes of sensors, however, suffer substantial drawbacks, including poor chemical specificity, sensor drift, and sensitivity to changes in humidity.[15,16,18] Those limitations also make these sensors less reliable for discrimination among mixtures with highly similar composition.

In the past decade, our group has developed colorimetric sensor arrays (CSAs) as a novel type of optoelectronic nose for the detection of various analytes.[18−23] The CSAs are distinct from traditional electronic noses that solely rely on physical or nonspecific intermolecular interactions and instead probe a wide range of chemical reactivity based on the use of chemically responsive dyes in hydrophobic matrices.[24,25] Digital imaging of the color changes of the array enables the identification of a composite pattern of responses as the "fingerprint" for a given odorant compared against other similar ones. Our colorimetric sensor array technique has seen successful applications relevant to the food industry, including identification vapor phase or aqueous solutions of different brands of coffee,[26] beer,[27] soda,[28] and sweeteners[29] and the rapid identification of cultured bacteria and fungi.[30,31]

The design of the colorimetric sensor array in this work utilizes metal ion chromogens (e.g., Pb(II) plus a pH indicator) to target emitted sulfides, and Brønsted/Lewis acidic or basic dyes (e.g., bromocresol green) to detect acidic or basic analytes, especially biogenic amines. We have very recently reported the use of this 20-element sensor array for the quantification of trimethylamine and the simulated diagnosis of trimethylaminuria (TMAU, also known as "fish malodor syndrome").[32] Herein, we described another possible application of the same colorimetric sensor array in the determination of meat freshness. To make it a fully portable and field-deployable technique, the sensor array was integrated with a hand-held gas analyzer[33] as the sensing platform (Figure 1a) to perform all

Received: August 9, 2016
Accepted: October 24, 2016

DOI: 10.1021/acssensors.6b00492
ACS Sens. XXXX, XXX, XXX−XXX

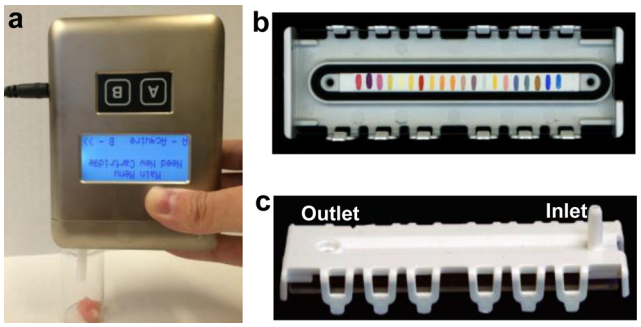


Figure 1. Sensing device assembled from a colorimetric sensor array inside a hand-held analyzer. (a) Gas sampling from a meat sample into the hand-held analyzer (5.0 × 3.7 × 1.6 in.^{3}). (b) Top view of the 20-element colorimetric sensor array mounted in a polycarbonate cartridge (3.1 × 1.1 × 0.4 in.^{3}). (c) Side view of the cartridge.

colorimetric measurements. As a result, we demonstrate the successful quantification of four representative sulfides and amines, along with the precise identification spoilage of five meat products vs time.

EXPERIMENTAL SECTION

Reagents and Materials. Five kinds of raw meat, including beef (sirloin steak), chicken (thigh), fish (cod fillet), pork (loin chops), and shrimp, were purchased from a local supermarket and tested during storage. All reagents were analytical-reagent grade, purchased from Sigma-Aldrich, and used without further purification.

Gas Analyte Generation and Calibration. All individual gas analytes at their selected concentrations were prepared by mixing the gas stream of prediluted analyte with dry and wet N_2 using MKS digital mass-flow controllers (MFCs) to reach the desired concentrations and relative humidity (see Figure S1, Supporting Information, SI). Before each calibration, gas flow was run for 30 min to achieve a stabilized concentration; for calibration, analyte concentrations were measured using in-line FTIR analysis with a MKS Multigas Analyzer (model 2030). Effects of humidity were not investigated in this study, as the insensitivity of these colorimetric sensors to changes in humidity was well-established in our previous work.[34]

Meat Storage and Sampling Protocol. 0.5 g meat samples were placed in a sealed 20 mL scintillation vial to accumulate volatiles prior to freshness measurements. Each meat sample was stored either in a kitchen refrigerator (2 ± 1 °C) or at room temperature (24 ± 1 °C) for length of time varying from 0 to 96 h. The sensor array was exposed to the ambient air to equilibrate for 2 min before sniffing; the array was then exposed to meat volatiles for another 2 min. The headspace gas of the vial was sampled into the sensor array cartridge through a short Teflon tube at a flow rate of ∼580 cm^3/min (sccm), during which the vial was open to the ambient environment. Before- and after-exposure images of the array were collected (Figure 1a) using the hand-held analyzer. Three independent trials were run for each meat sample.

Sensor Array Preparation. The linear colorimetric sensor arrays were printed as per details in recently published papers,[35,36] except that the polypropylene membrane strips were first solvent-welded to cartridges using $CHCl_3$ to eliminate potential contaminants from adhesives. Twenty sensor elements were immobilized in matrices made of organically modified silicates and 2-methoxyethanol, and printed on the polypropylene substrate at 2 mm center−center distance (Figure 1b and c) using an array of floating stainless steel rectangular pins. Once printed, the arrays were dried under vacuum for 2 h at room temperature, and stored in N_2-filled aluminized Mylar bags before any measurement was performed. The chemical dyes and formulations used in each spot are listed in SI Table S1.

Raw Data Process. 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 meat volatiles. For visualization purposes only, all color difference maps herein are displayed by scaling a relevant color range from 3-bit (i.e., 3−10) to the 8-bit color scale (i.e., 0−255). Signals for each channel were defined as the difference between each analyte trial measurement (analyte-n) and the averaged nonexposed controls (i.e., $R_{\text{analyte-n}} - R_{\text{control-avg}}$), and noise was defined as the standard deviation among the controls (i.e., $\sigma_{R2} = \Sigma_n(R_{\text{control-n}} - R_{\text{control-avg}})^2/(N-1)$). The signal-to-noise ratio (S/N) was calculated for each data channel and incorporated in the final database for statistical analyses.

Database Analysis. Two unsupervised statistical methods, principal component analysis (PCA) and hierarchical cluster analysis (HCA), were performed for database clustering using MVSP software (Kovach Computing Services, Pentraeth, Isle of Anglesey, UK); in all cases, minimum variance (i.e., "Ward's Method") was used for HCA clustering. For quantitative cross-validation, predictive classification was carried out using support vector machine (SVM) analysis (SI Tables S3 and S4).

RESULTS AND DISCUSSION

While there have been some limited studies of colorimetric sensor arrays for monitoring specific meat quality,[6,37−40] the previous work has been limited by lack of sensitivity (ppm LODs), lack of portability, limitation of analytes (only amines or aldehydes were monitored), and limitation to a single meat (either chicken or pork).

As we demonstrate below, we have developed a portable hand-held, self-contained reader/analyzer that permits us to collect in situ and real-time data of meat spoilage. Our sensor array has considerably greater chemical diversity and is consequently more versatile and broader in its responses than prior work:[6,37−40] our array responds to a variety of analytes (e.g., sulfides, amines, and other analytes as well), rather than to a single class of analytes; consequently, our sensor arrays have much better ability to discriminate among subtle differences among meat samples. In addition, because of better imaging and superior printing methods, we attain higher sensitivity (LOD < 35 ppbv for all individual gas analytes). Finally, we demonstrate the versatility of our device and are able to analyze and differentiate spoilage in five meat products rather than only a single meat.

Sensor Response to Individual Gas Analytes. The capabilities of the sensor array to detect VOCs associated with meat spoilage were investigated first, prior to the measurement of meat samples. Specifically, we measured array response to four relevant gases released by spoiled meats: hydrogen sulfide, dimethyl sulfide, trimethylamine (TMA), and cadaverine (CAD). Figure 2 shows the color difference maps from exposures to a series of concentrations of these gases after 2 min exposure; easily visible color changes were observed for all analytes at sub-ppm concentration, and the patterns allow for easy differentiation even by eye. For the two sulfides (Figure 2a and b), the sensor array response largely arises from metal-containing dyes (spots 14−17 and 19) and reflects metal ion ligation of the sulfides (i.e., Lewis acid−base interactions). In comparison, sensor response to amines (TMA or CAD) mainly comes from vapochromic species (spots 1−2), pH indicators (spots 4−6 and 8−11), as well as metal-containing dyes (spots 14 and 16−18), indicating the significant analyte-induced changes in local polarity and Brønsted basicity.

Overall sensor response (i.e., Euclidean distance (ED) from the changes in all 60 RGB values from 20 sensor elements) for each of these four VOCs as a function of concentrations is monotonic and shown in the SI Figure S2. Limits of detection (LOD) for each of these gases are well below 0.25 ppm, which

DOI: 10.1021/acssensors.6b00492
ACS Sens. XXXX, XXX, XXX−XXX

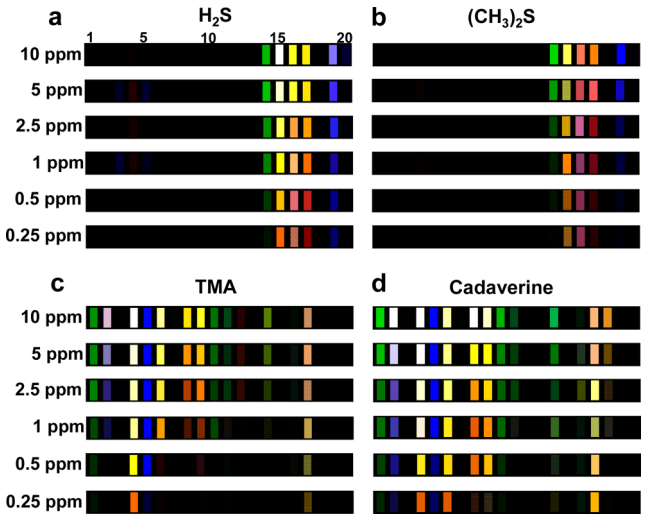


Figure 2. Sensor array response to (a) H_2S, (b) $(CH_3)_2S$, (c) TMA, and (d) CAD at concentrations ranging from 0.25 to 10 ppm; patterns are averages of 3 independent trials. For visualization, the color range is expanded from 3 to 8 bits per color (i.e., the RGB color range of 3−10 was expanded to 0−255).

is roughly the lower limit of concentration that can be reliably delivered by our gas mixing apparatus. Extrapolation of the calibration curves gives LODs of 8 ppb for hydrogen sulfide, 33 ppb for dimethyl sulfide, 4 ppb for TMA, and 7 ppb for CAD, with estimated relative errors in the LODs < 10% (Table S2 and Figure S3, SI).

The array response to amines is essentially reversible, with the response to sulfides. In our opinion, good reversibility of any sensor array is actually a double-edged sword: the advantage of high reversibility is that one can monitor in real time changes in analyte concentrations (up or down) as soon as equilibration occurs. For some toxic gases (including trimethylamine), we have previously shown that our colorimetric sensor arrays are generally reversible and equilibrate typically within 2 min, often in 10 s, as we have previously published.[32,34] The disadvantage of reversibility, however, is that there is no improvement in sensitivity with increased dosage. Past experience has taught us that our sensor arrays are best thought of as a "chemical fuse" in analogy to an electrical fuse: it is reversible up until a threshold of too high a concentration (which would take too long to flush away) or too aggressive an analyte (which reacts essentially irreversibly with the colorants). Since our colorimetric sensor arrays are meant to be disposable, irreversibility presents no difficulty, in contrast with traditional electronic nose technology where sensor drift remains highly problematic.[16]

Statistical Analyses on Four Gas Analytes. To evaluate the ability of our sensor array to discriminate among single analytes, three types of statistical analyses were performed on the collected sensing data: hierarchical cluster analysis (HCA),[41] principal component analysis (PCA),[42] and support vector machine (SVM)[43] analysis. HCA and PCA are both unsupervised exploratory data analyses, i.e., "clustering": HCA is commonly used to evaluate the "dissimilarity" among data points and cluster them in multivariate vector space, while PCA is to estimate the dimensionality of the data and attempts to project data into as few dimensions as possible.

The resulting HCA dendrogram of four VOCs at six concentrations of each plus a N_2 control in triplicate replicates is shown in Figure 3. Each analyte at each concentration is discriminable without confusions or errors. In the cases of

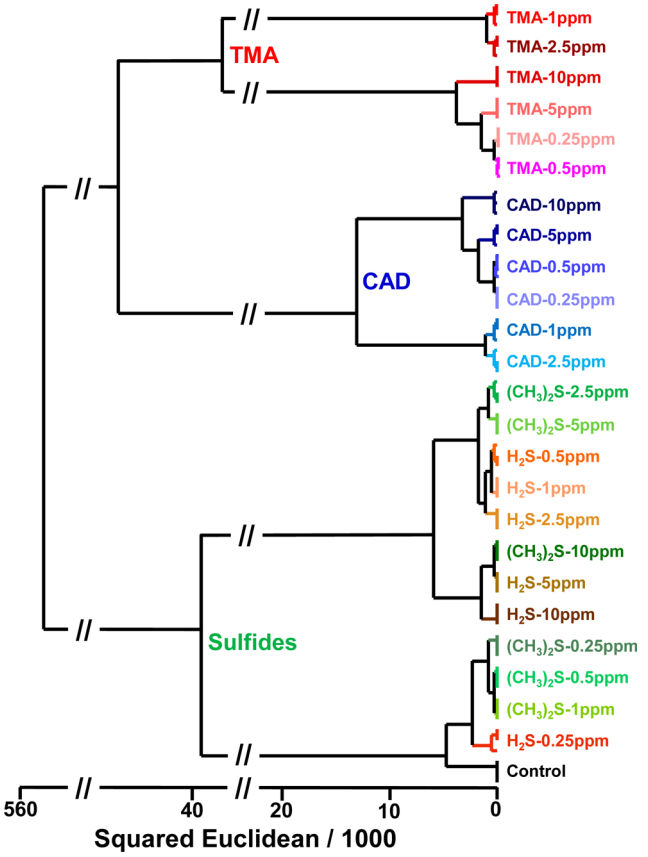


Figure 3. Dendrogram showing hierarchical cluster analysis of 4 relevant gases released by spoiled meat. 75 trials in total are shown over 0.25−10 ppm concentration range plus a N_2 control. No confusions among triplicate trials are observed.

TMA and CAD, completely separate clusters of clusters are seen for each analyte in the concentration range measured. For the sulfide a supercluster is formed, separate from the amines, and there are no confusions between H_2S and $(CH_3)_2S$ and any given concentration.

The PCA score plot based on the first two principal components (PCs) displays a similar pattern of clustering results as compared to HCA with no overlap among clusters (SI Figure S4a). The scree plot (SI Figure S4b) shows that 13 dimensions are needed to account for >95% of the total variance of the data, which reflects the broad chemical diversity present among the sensor elements. Given the limited set of analytes (albeit tested over a significant range of concentration), the scree plot does not provide a thorough probe of the dimensionality of the sensor array.

SVM analysis offers a supervised and more quantitative method for data classification, which aims to classify new entries into the known and predetermined groups of data points. The results of SVM analysis using a standard leave-one-out permutation model are shown in SI Table S3. All the groups give 100% classification accuracy, except for one error from trials of 0.25 ppm of CAD, which is mistaken for the group of 0.25 ppm TMA; i.e., the overall cross-validation accuracy is above 98.6%.

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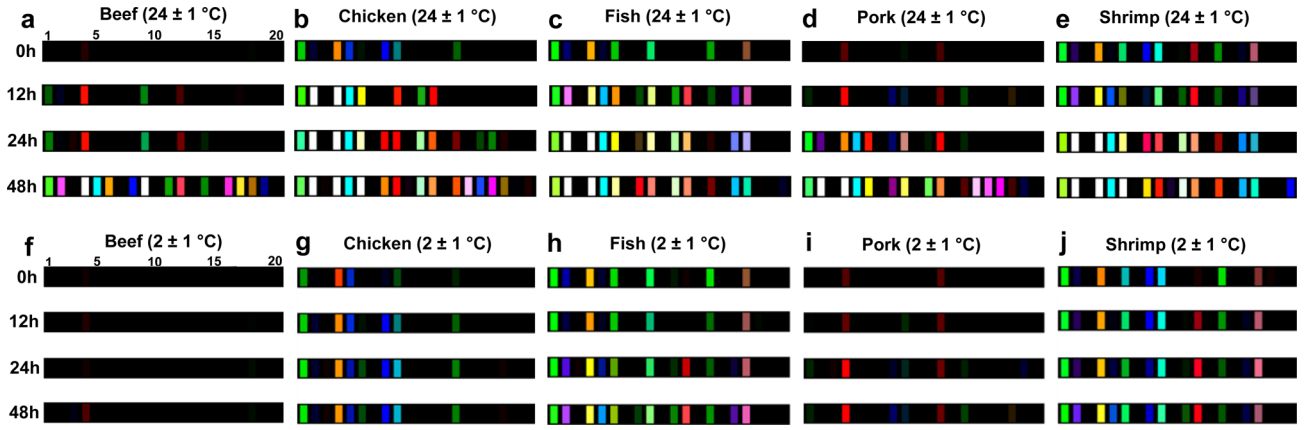

Figure 4. Sensor array response to five meats at 24 and 2 °C during 48 h storage. Upper row: (a) beef, (b) chicken, (c) fish, (d) pork, and (e) shrimp at room temperature (24 ± 1 °C); lower row: (f) beef, (g) chicken, (h) fish, (i) pork, and (j) shrimp under refrigerated conditions (2 ± 1 °C); triplicate trial averages. For visualization, the color range is expanded from 3 to 8 bits per color (i.e., RGB color range of 3−10 expanded to 0−255).

Sensor Response to Meat Samples. Having confirmed our sensor array's low limits of detection and recognition toward individual analytes, we employed the sensing device to monitor the real-time emissions of the complex odor mixtures from meats as they spoil. Five meat products were monitored for 96 h both at room temperature (24 ± 1 °C) and while refrigerated (2 ± 1 °C). Color difference maps of the volatiles released by these five meats are shown in Figures 4 and S5).

The array response to the volatiles released by the meat samples are mainly dominated by biogenic amines for samples stored up to 4 days, while sulfides appear to be released after 48 h storage, as indicated by the response in metal-containing chromogens (spot 15, $Pb(OAc)_2$, and spots 19−20, $HgCl_2$). Response curves of the five meat products as a function of storage time are shown in Figure 5. As one would expect, the overall sensor response grows significantly faster for meats stored at room temperature compared to refrigerated samples. Even from the refrigerated samples, however, growth in the concentration of volatiles is observed by the sensor array over time (Figure 5b). The array response increases more than 10-fold faster at 25 °C than at 2 °C. The magnitude of overall sensor response to meat vapors with the same storage duration at 25 °C follows the order fish > shrimp > chicken > pork > beef, which is determined by differences in the protein compositions of the five meats and probably more importantly, by differences in the bacteria strains[29,30] that are growing on the meats during spoilage.[1,3]

Statistical Analyses on Meat Samples. To better illustrate the sensor's capabilities to quantitatively assess meat freshness, PCA, HCA, and SVM analyses were conducted on the database collected for spoilage of meat samples. HCA shows the clustering of the data with three distinct classes of responses, as shown in Figure 6. The lowest sensor array response cluster is labeled "fresher" and corresponds to the control, 0 h storage of all five meats, 12 h storage of four meats other than chicken, and 24 h storage of beef and pork. The middle response cluster, labeled "less fresh", contains 24 or 48 h storage of most meats and 12-h-old chicken. The most responsive cluster, "spoiled", is formed from the 72 and 96 h storage of most of the meats. Overall, there is excellent clustering among the triplicate samples of each meat at each time point, except for two subgroups containing 12 and 24 h storage of beef and 72 and 96 h storage of shrimp, respectively. The grouping accuracy achieved by HCA is therefore ~90%

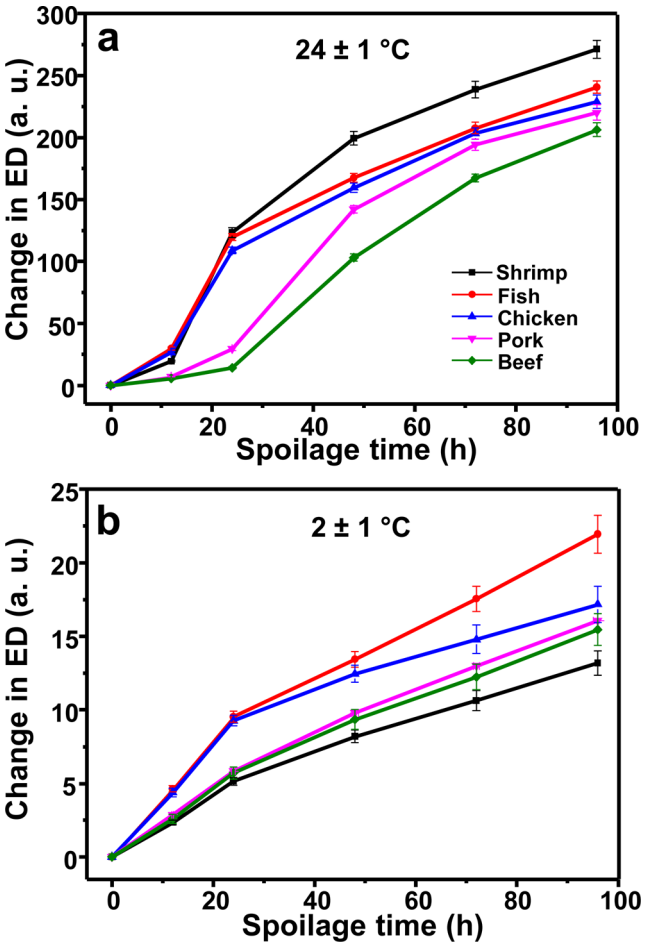

Figure 5. Response curves of sensor arrays to five meat products stored (a) at room temperature (24 ± 1 °C) and (b) in the fridge (2 ± 1 °C). Measurement of each meat sample was replicated in triplicate with 2 min exposures.

among the triplicate trials of five meats with six storage durations plus a control.

PCA demonstrates that the database has a relatively high dimensionality. For the sensor responses to the 5 meat products over 6 different storage times, 9 dimensions are required to capture 90% of the total variance and 14 dimensions for 95% (SI Figure S6). A PCA score plot based

DOI: 10.1021/acssensors.6b00492
ACS Sens. XXXX, XXX, XXX−XXX

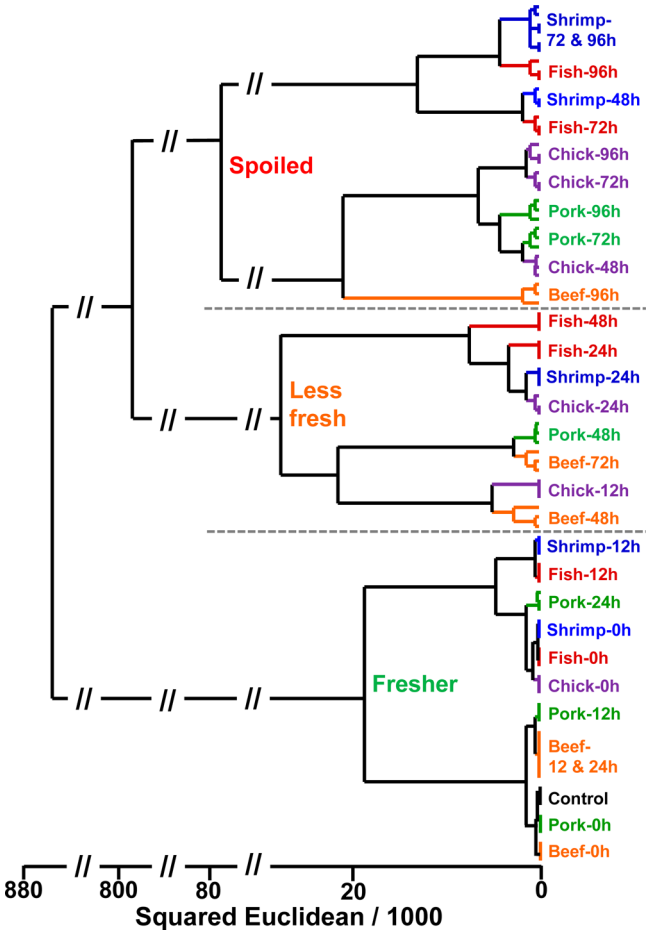

Figure 6. Dendrogram showing hierarchical cluster analysis of the spoilage of 5 meat products stored at 25 °C plus an ambient air control; 93 trials in triplicate replicates.

on the first 3 PCs (which only captures >77.5% of the total variance) shows excellent clustering with again 3 distinct superclusters (labeled fresher, less fresh, spoiled in SI Figure S6).

As with the previously discussed SVM analysis of the individual gas analytes, a leave-one-out permutation cross-validation of the database was carried out. The cross-validation gave perfect identification of all 31 classes (i.e., 5 meats at 6 times plus the air control) with no errors in this more quantitative and predictive classification, i.e., an error rate of <1% (SI Table S4).

Reproducibility of Meat Sample Measurements. To evaluate the consistency of our colorimetric sensing method, reproducibility studies were performed on three separately prepared print batches of the sensor arrays by comparing the responses both to beef and to shrimp. In addition, comparisons were made among three separate purchases (made over a one-month period) of beef and of shrimp, each tested with sensor from the same print batch. For all the reproducibility studies, 0.5 g of each meat product was stored at room temperature for 48 h, and measurements were done in triplicate.

Reproducibility in the array printing were evaluated from the average Euclidean distances from triplicate trials (cf. SI Figure S7 and Table S5): these were found to be 166.4 ± 5.8 and 258.1 ± 10.4 as measured by three print batches of arrays on single purchases of pork and shrimp, respectively. For comparison, the reproducibility of the source meats were evaluated from three separate purchases but measured with arrays from a single print batch: 169.5 ± 11.9 and 254.6 ± 19.0, for pork and shrimp, respectively. That is, the differences in the printing of the arrays are smaller than the differences among the meats from separate purchases.

CONCLUSIONS

We have developed a portable optoelectronic nose that combines a disposable colorimetric sensor array and a hand-held gas analyzer and used it for rapid sensing of the freshness of common meat products. The introduction of metal ion chromogens into the sensor array greatly improved sensitivity toward representative sulfides and biogenic amines, with the detection limits at low ppb levels. The hand-held analyzer permits accurate discrimination among the headspace of samples of five different meats as a function of storage periods from freshly purchased to 4 days with very high accuracy. We have demonstrated excellent repeatability from both separate batches of sensor array printings and from multiple purchases over a period of a month of the same meat product. Our device may find applications in the determination of meat freshness and serve as a useful supplement to other methods of food safety inspection.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssensors.6b00492.

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

AUTHOR INFORMATION

Corresponding Author

*E-mail: ksuslick@illinois.edu.

Notes

The authors declare no competing financial interest.

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DOI: 10.1021/acssensors.6b00492
ACS Sens. XXXX, XXX, XXX−XXX