Disposable Colorimetric Paper-Based Probe for the Detection of Amine-Containing Gases in Aquatic Sediments

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ABSTRACT: Amine compounds are considered highly important in environmental pollution, industrial, and medicinal fields. The objective of this work was to develop a disposable, highly accurate, highly selective, and low-cost paper-based probe through the combination of color change of seven pH indicators for the detection of amine compounds in the gaseous state. The probe was designed with seven rings which were printed using the wax-printing technique and colored with different pH indicators. The colors of the probe were analyzed using red, green, and blue (RGB) values extracted from the images obtained with a homemade smartphone application. The chemometric tools, principal component analysis, and hierarchical cluster analysis methods were adapted to further classify amine gases. The colorimetric probe showed an excellent capability for detecting the amines with high accuracy, prompt response, and high selectivity. These dye arrays have been proven to detect ethanolamine (NH₂CH₂CH₂OH), dimethylamine ((CH₃)₂NH), and trimethylamine ((CH₃)₃N) gases at parts per million scale.

1. INTRODUCTION
The broad range of using amine and amine-related compounds in industrial and medicinal applications makes it significantly urgent to understand the associated risks and concerns for leaking these compounds into the aquatic environment. The family of amines containing secondary and tertiary amines and quaternary amine salts can be important for the formation of several toxic compounds. The amines and amine degradation products are carcinogenic compounds and may be found in drinking water supplies and can pose potential risks for whole communities with resulting public health issues. Ethanolamine (EA, a primary amine) is the most commonly used solvent for designing to capture and store CO₂ from combustion flue gases (or postcombustion capture). However, this choice often results in potential health risks and environmental problems related to by-products or degradation products such as nitrosamines and nitramines in the atmosphere and water ecosystem. Moreover, the biogenic amines are formed through the decarboxylation of amino acids or by the amination of ketones and aldehydes in plants or living organisms, and they may cause strong tastes and smells. For example, diethylamine (DET) and trimethylamine (TMA) are typical by-products of the breakdown of amino acids through the decaying process in the protein-rich tissues of fish. The amine compounds are widespread in aquatic environments and directly associated with many natural and industrial sources.

Several analytical approaches for the detection of amines have been developed in recent decades by using modern instrumentalations, such as capillary electrophoresis—mass spectrometry (CE–MS), MS, and high-performance liquid chromatography (HPLC), and well documented in the literature. These methods are among the most important methods for precise quantitative analysis but they are often time-consuming and require tedious sample pretreatment, high cost, and considerable skill. In addition, they use potential toxic organic solvents of HPLC grade quality. The immune-enzymatic methods can also be applied for routine analysis with semiquantitative determination of biogenic amines. However, the chemical analysis of amines in environmental samples poses particular challenges and obstacles: namely high volatility, low limit of detection (LOD), low molecular weight, and chemical instability. Therefore, it is urgent and desirable to develop more sensitive and effective methods for amine detection without complex analyzing procedures in complex environment matrices.

The development of inexpensive analytical methods allowing real time to distinguish between different types of volatile compounds is of great interest. Among them, paper-based analytical devices (PADs) have rapidly developed in recent years because of low-cost and easy-to-use analytical tools. They are widely reported in point-of-care systems, environmental areas, and food contamination. PADs present several advantages, such as an inexpensive device and reliable measurements with speed and efficiency using small volumes of sample solutions, over other analytical methods. Moreover, their simplicity lies in the creation of hydrophilic micro-channels on cellulose and polymers by mean of different hydrophobic patterning materials, such as wax, inks, and polymers. To date, the combination of PADs with traditional analytical instruments such as MS, CE, and electrochemical devices offers an interesting approach to the implementation of cost-effective biochemical analysis.
Based on the colorimetric approach, some groups used a single color spot on a polymer substrate for monitoring food quality.21–23 As mentioned above, single compounds can be monitored with single color spots but it is impossible in case of complex compounds. To overcome this drawback, colorimetric sensors based on color spot matrixes were proposed using chemometric tools for discriminating compounds.24,25 For example, Bueno’s group used a plastic-based device and chemometric for discriminating triethylamine, isobutylamine, and isopentylamine using Alizarin, bromophenol blue, chlorophenol red, methyl red, and thymol blue. Chemometrics is closely related to statistics and mathematics, where the chemical information and correlation quality parameters are extracted to analyze chemical data. The chemometric tools give the relationships between the variables and samples and convert into new dormant variables.26,27 Until now, the chemometric tools have been developed or integrated in commercial software, such as R-software, MATLAB, SPSS, Origin, and Microsoft Excel.

Here, we develop a simple, disposable, and low-cost disposable colorimetric paper-based probe (DCP) based on seven popular commercial pH indicators, where the change range of pH of array is in the range of 3−8.8, on the paper for detecting EA (NH2CH2CH2OH), dimethylamine ((CH3)2NH), and TMA ((CH3)3N) by coupling chemometric tools and colorimetric sensing with smartphones. The use of smartphones as a tool in chemical analysis based on a colorimetric approach has been attracted an increased attention because of its portability and big portion of users and has opened up the opportunities for creating new, highly reliable, fast, and online analytical tools.28−30 The built-in camera in smartphones captures color changes for the analytical process. Subsequently, color changes are processed using the algorithms based on hue and saturation coordinates of the HSV (hue, saturation, and value) color space or using the algorithms based on hue and saturation coordinates in RGB (red, green, and blue) colors for getting results. In the best of our knowledge, the studies on gas sensors have been almost performed with the electrochemical sensing approach. We designed the DCP with seven rings on the paper, which were printed by the wax-printing technique and colored with the pH indicators. Images of the spots in DCP were taken with the built-in camera of a smartphone, and then the red, green, and blue (RGB) values were recorded with the home-made Android application. Chemometric tools in Microsoft Excel software were used to analyze the color change of spots on the DCP using principal component analysis (PCA) and hierarchical cluster analysis (HCA). These DCPs are able to distinguish between the different amine-containing gases and show no observable responses to the change in humidity at room temperature.

2. RESULTS AND DISCUSSION

It is known that the colors of pH indicators depend on their protonated and deprotonated forms originating from the modification of the structural indicator through a protonate/deprotonate process. Figure 1 displays the color change profiles of the DCP under amine gas exposure, namely EA, dimethylamine, and TMA. The color change of each spot on the array was observed clearly to discriminate each other depending on the amine species. This difference can be explained by different proton-donating properties of the amines. The pKₐ values of EA, dimethylamine, and TMA are 9.40, 10.73, and 9.81, respectively. However, the color changes of the pH indicators were sometimes so more delicate that it does not reach the extreme color for the full acidic or basic form.31

To overcome this limitation, the RGB values of the color spot were recorded using a smartphone application. Each image of an array was presented by 21 values (each array consists of seven dyes and three color values for each dye). These values can be used as an input of the nonsupervised pattern recognition methods (PCA and HCA).32 PCA is used to evaluate the pattern recognition or the qualitative discrimination through orthogonal directions in the variable space. PCA decreases the number of variables by creating orthogonal eigenvectors (PC1 and PC2). HCA shows a genealogical tree of the samples where the algorithm aims to partition n samples into clusters in which each sample belongs to the cluster based on the linkage distance. The linkage distance determines the distance between pairs of observations or samples. The results from the chemometric analysis PCA and HCA methods are shown in Figure 2.

The color change patterns in the spots on DCP were different according to the species and concentration of amine gases with an optimum exposure time of 10 min. The PCA score plot did not change for elongating the exposure time in excess of 10 min (data not shown). As shown in Figure 2a, first two principal components (PC1 and PC2) exhibited that each amine can be classified into a single group with 71.5% of the total information collected by the extracted RGB values and made possible to discriminate among EA, DET, and TMA. Moreover, the HCA plot was performed through the RGB values extracted from the seven colorimetric spots on the DCP in contact with each of three different amines to also confirm no misclassifications among all amines too (Figure 2b). Besides that, the color change of the DCP with changing amine gas concentration can also be observed with a HCA graph (Figure 3).

To confirm the change of RGB values versus EA concentration, we chose one spot, where it is difficult to observe the change of color by naked-eyes. Figure 4 shows the relationship between RGB values and EA concentration in spot 6. It is clear that there are good linearity between R, G values and EA concentration. This result also suggests that RGB values can be used for the determination of amine concentrations. To demonstrate the versatility of the DCP, calibration curves were constructed using Euclidean distance (ED) values,32,33 which can be expressed by eq 1

\[
ED = \sqrt{\sum (\Delta R_i)^2 + \sum (\Delta G_i)^2 + \sum (\Delta B_i)^2}
\]

(1)
where \((\Delta R)^2\) is variation of \(R\) value of dyes and \((\Delta G)^2\) and \((\Delta B)^2\) have the same meaning for \(G\) and \(B\) values, respectively.

The ED values using Microsoft Excel in analysis process of PCA and HCA are a function of amine concentrations of all spots on DCP. The ED values linearly enhanced with increasing of amine concentrations in range of 1–250 ppm, as shown in Figure 5. The LODs of the DCPs were calculated to be 0.4, 0.2, and 0.5 ppm for EA, DET, and TMA, respectively. The LOD values are comparable as those of other reports such as arrays of chemoresponsive dyes,\(^{34}\) chemiresistive detectors using single-wall carbon nanotube–porphyrin complex,\(^{35}\) colorimetric array,\(^{36}\) CE–MS,\(^{7}\) and HPLC using a dispersive liquid–liquid microextraction process.\(^{37}\) Compared with the LOD of proton-transfer reaction quadrupole mass spectrometer,\(^{8}\) the LOD of this DCP is not better than those but the proposed DCP does not require any synthetic process of chemicals and any expensive equipment except smartphone and computer and skilled personnel.

Figure 2. (a) PCA score plot obtained through the RGB values extracted from seven colored spots in contact with three different amines [(I) EA, (II) dimethylamine, (III) TMA], (b) HCA plot of 21 values with seven different dyes on DCP.

Figure 3. HCA plots were obtained from the RGB values extracted from the seven color spots after exposing with the different concentrations of (a) EA, (b) dimethylamine, and (c) triethylamine.

Figure 4. Relationship between EA concentration and (a) \(R\), (b) \(G\), and (c) \(B\) values for the spot number 6 (number of trials = 5).
The experiments for selectivity were carried out for EA, DET, TMA, and some common volatile organic solvents (VOCs). The results showed that DCP did not respond (the colors of DCP did not change) with common VOCs, namely acetone, methanol, ethanol, benzene, chloroform, toluene, and dimethylformamide, at 1000 ppm vapor concentrations of these VOCs. However, the proposed DCP cannot apply for strong basic (e.g., ammonia) or acidic (e.g., H₂S) solutions. Figure 6a exhibits color perceptivity of DCP for each amine and mixed three amines (at 100 ppm vapor concentration of each amine). The corresponding data of PCA score plot also exhibited the difference (Figure 6b), where the mixed three amines were classified into other group. Although PCA score plot and the color of DCP are different between un-mixed amines and mixed amines but it is not easy for calculating specific concentration of each amines. These results imply that our probe can be used for the selective detection of EA, DET, and TMA without any interference of common VOCs.

2.1. Analysis of Real Samples. To evaluate the feasibility of the proposed probe for real samples, recovery tests of each individual amine were conducted using aquatic sediments. By using a spiked method, excellent recoveries of 94.8–108.7% were obtained, as shown in Table 1. These data suggest that the proposed sensor will be applicable to the analysis of amine gases in water samples. This method also showed acceptable repeatability (relative standard deviation) in the range of 0.91–3.70%.

3. CONCLUSIONS
In this work, a simple, disposable, and low-cost colorimetric probe is presented based on paper substrate for detecting gaseous state of EA, dimethylamine, and TMA compounds with high accuracy and selectivity. The dyes’ color changes by the individual amine compounds were analyzed using RGB values extracted from images obtained with a homemade smartphone application. To classify amine gases, the chemometric tools including PCA and HCA methods were used. The proposed DCP has been proven to detect EA, dimethylamine, and TMA gases at parts per million scale. The proposed DCP was applied for real samples with high recoveries. Our developed array system has a potential to be able to provide an early warning of natural gas pollution.

4. EXPERIMENT SECTION
4.1. Chemicals, Materials, and Instrumentation. Bromophenol blue, methyl red, bromocresol green, disperse orange 3, bromocresol purple, fluorescein, and cresol red were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). EA, DET, and TMA were purchased from Alfa Aesar Co. (Great Britain). All other reagents were of analytical grade and used as received. For the fabrication of the DCP, Whatman chromatography paper grade 1 (200 x 200 mm,
pure cellulose paper) was obtained from GE Healthcare (China). The designed DCPs were printed on a sheet of Whatman grade #1 using a wax printer (ColoQube 8570DN, Xerox, USA) followed by heating at 120 °C for 2 min on a drying machine. Wax ink was used for the paper hydrophobization and an insulation agent in this work.

The DCP consisted of circles with an inside diameter of 5 mm and a border of 2 mm (after melting wax ink). To prepare phobization and an insulation agent in this work.

The end of the tube was immersed in the amine solution inside the filtering flask. The generated amine gas from the flask was collected in a gas-sampling bag (FEP gas sampling bag with capacity of 0.5 L, Sigma-Aldrich), as shown in Scheme 1. The volumes of liquid amines and nitrogen gas were calculated to prepare standard amine gas samples with various concentrations by following our previous report.

For sensing amine gases, the DCP was placed in the sensing chamber connected to the gas-sampling bag. The temperature around the chamber was kept at room temperature. The smartphone was used to get images of the DCP before and after amine exposure. All measurements were performed five times.

4.3. Real Sample Application. Amine-polluted waters may be caused by by-products from industry or degradation products from microorganisms and aquatic organisms in the water ecosystem. To evaluate the prepared DCP for practical application, aquatic sediments from a water source of the Changwon River, Changwon City, Korea were obtained. The collected water samples were filtered by filter paper before they were spiked. Specific volumes of amine gases with known concentrations were mixed with water samples, which were contained in closed bottles. The gases from the samples were released by heating the bottle and then transferred to the DCP. The RGB values were collected after the prepared probes were exposed to the gas.

4.4. Data Processing and Analysis on Paper Base. To achieve effective data processing for colorimetric sensor arrays, it was necessary to convert these different obtained-color maps for each analysis to RGB values using a home-made Android smartphone application. These RGB values were extracted at the center of every single spots (15 × 15 pixels) before and after the exposure to the samples. The software used a 256-bit color scale with white corresponding to a color intensity of 255, 255, and 255 and black corresponding to a color intensity of 0, 0, and 0.

To evaluate the ability for the colorimetric DCP to discriminate different analytes, two chemometric tools were used to process input data of RGB values: (i) PCA evaluates the variance in the array response among the range of analytes; (ii) HCA divides the analytes into discrete groups based on the characteristics of their respective responses. HCA forms dendrograms based on the clustering of array response data in the dimensional ΔRGB color space.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2017R1D1A3B03035530 and NRF-2017R1A2B4006388).

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