Preoxidation for Colorimetric Sensor Array Detection of VOCs

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S *Supporting Information*

ABSTRACT: A disposable preoxidation technique that dramatically improves the detection and identification of volatile organic compounds (VOCs) by a colorimetric sensor array is reported. Passing a vapor stream through a tube packed with chromic acid on silica immediately before the colorimetric sensor array substantially increases the sensitivity to less-reactive VOCs and improves the limits of detection (LODs) ~300-fold, permitting the detection, identification, and discrimination of 20 commonly found indoor VOC pollutants at both their immediately dangerous to life or health (IDLH) and permissible exposure limit (PEL) concentrations. The LODs of these pollutants were on average 1.4% of their respective PELs.

Figure 1. Schematic illustration of the preoxidation technique. A Teflon tube (2 cm × 3 mm i.d.) is packed with chromic acid to pretreat the gas flow containing a VOC before it is passed over the colorimetric sensor array.

Exposure to volatile organic compounds (VOCs) can have serious harmful effects, including a wide range of sensory irritation and acute and chronic diseases (e.g., nervous system impairment, asthma, and cancer[1−3]). The detection and identification of VOCs therefore are particularly important for environmental, chemical workplace, and even personal home monitoring.[4] Currently, the concentration of VOCs is generally determined by standard analytical methods[5] such as GC or GC−MS,[6] which require expensive and nonportable instrumentation. Various other more mobile sensors for VOC detection exist, including the use of surface acoustic wave, semiconducting metal oxide-based, conductive polymer-based, and quartz crystal microbalance sensors,[7,8] and new techniques continue to be reported.[9] The performance of these sensors and the electronic nose devices[10,11] made from them still fall short of the demands of many applications because of low sensitivity, low selectivity, lack of reproducible sensor production, interference from humidity, limited stability, or changing responses due to sensor aging.[11c,f,12] A real need for the development of high-performance portable VOC sensors therefore remains.

In recent years, our group has developed a disposable colorimetric sensor array methodology for use as an "optoelectronic nose"[13] that has been applied successfully for the identification of a wide range both of gases/vapors[14] and of analytes in aqueous liquids.[15] This array utilizes strong interactions between the analyte and a diverse set of chemically responsive colorants whose colors depend on local polarity, Brønsted acidity/basicity, Lewis acid−base interactions, and redox reactions. The array utilizes nanoporous pigments created from the immobilization of dyes in organically modified siloxanes (ormosils).[16,17] Porous sol−ge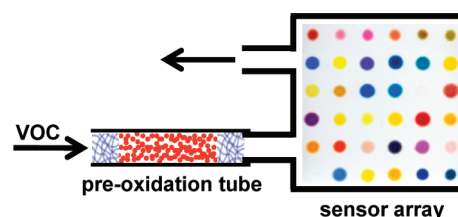l glasses provide excellent matrices for colorants by virtue of their high surface area, relative inertness, good stability, and optical transparency. The use of nanoporous pigments significantly improves the stability and shelf life of the colorimetric sensor arrays and permits direct printing onto nonpermeable polymer surfaces.[14,17]

While these colorimetric sensor arrays work exceedingly well for *reactive* volatiles, they have *not* had especially high sensitivity to less-reactive vapors.[14f] For example, common VOC indoor air pollutants (e.g., aromatic hydrocarbons, chlorocarbons, other organic solvents) are generally not especially reactive and are not detected at low concentrations by our colorimetric sensor array. We report here a dramatic improvement in the sensitivity of colorimetric sensors for the detection and identification of such less-reactive VOCs.

To improve the array response, we developed a disposable preoxidation technique in which a vapor stream is passed through an oxidation tube before reaching the array (Figure 1). Though most indoor pollutant VOCs are relatively inert, their oxidation byproducts (e.g., carboxylic acids, phenols, aldehydes, etc.) are reactive species that are much more easily detected. Since each VOC produces a different mixture of oxidized derivatives, the array response to these more reactive volatile byproducts provides a unique and much more sensitive signature for the initial VOC. We chose 20 VOC pollutants commonly found in indoor air[1,18] (listed in Table 1) as representative analytes; using this preoxidation method, we can discriminate among all of them at both their immediately dangerous to life or health (IDLH) and permissible exposure limit (PEL) concentrations.

For vapor analysis, digital images of the array were acquired before and after exposure to a diluted vapor mixture using an ordinary flatbed scanner [see Figure S1 in the Supporting Information (SI)], and the changes in the red, green, and blue (RGB) values of each spot were measured after exposure to the

Table 1. Twenty VOC Pollutants Commonly Found in Indoor Air

VOC	IDLH (ppm)	PEL (ppm)	LOD$_{no-preox}$ (ppm)[a]	LOD$_{with-preox}$[b]		LOD$_{no-preox}$/ LOD$_{with-preox}$
				ppm	% of PEL	
acetone	2500	1000	1100	16	1.6	69
benzene	500	1	5000	0.20	20	10000
camphene[c]	225	45	140	1.1	2.4	130
chloroform	500	50	290	0.60	1.2	480
p-dichlorobenzene	150	75	100	1.6	2.1	63
ethanol	3300	1000	130	0.50	0.05	260
ethyl acetate	2000	400	760	7.4	1.9	100
ethylbenzene	800	100	350	1.3	1.3	270
formaldehyde	20	0.75	50	0.10	13	500
D-limonene[c]	130	26	100	0.90	3.5	110
methyl ethyl ketone	3000	200	1400	2.2	1.1	640
phenol	250	5	0.50	0.60	12	0.80
isopropanol	2000	400	260	18	4.5	14
styrene	700	100	100	0.50	0.5	200
toluene	500	200	300	1.3	0.7	230
1,1,1-trichloroethane	700	350	8000	5.0	1.4	1600
1,2,4-trimethylbenzene[c]	135	27	300	0.60	2.2	500
m-xylene	900	100	500	0.50	0.5	1000
o-xylene	900	100	500	0.60	0.6	830
p-xylene	900	100	550	0.60	0.6	920
average	1006	214	1000	3.0	1.4	330

[a] LOD without preoxidation. [b] LOD with preoxidation. [c] The IDLH and PEL of this VOC are unknown and have been estimated as 5% and 1% of its saturated vapor pressure, respectively.

VOC (Tables S1 and S2 in the SI). The vapor of each VOC was typically produced by bubbling nitrogen through the corresponding pure compound and then further diluted with dry and wet nitrogen to achieve the desired concentration in a gas stream at 50% relative humidity (RH) at a flow rate of 500 sccm (see the SI for further details). VOC concentrations were confirmed using in-line FT-IR analysis in real time with a MKS 2030 multigas analyzer.

The influence of preoxidation on the array response was investigated by examining several different strongly oxidizing solid reagents in various amounts. The optimum array response occurred with preoxidation tubes (2 cm × 3 mm i.d. Teflon tubing) loaded with 30 mg of chromic acid ("sulfochromic acid") on silica (250 μL of H_2SO_4 and 400 mg of $Na_2Cr_2O_7$ per gram of silica; see the SI for details), so this formulation was used in all of the subsequent experiments. The color difference maps of the array response with preoxidation for the 20 VOCs at their IDLH concentrations are shown in Figure 2. These maps provided molecular fingerprints for each of the 20 VOCs (i.e., every VOC showed a different and specific color difference pattern). It should be noted that the array response does not arise only (or even primarily) from the VOC itself but also has contributions from the oxidation products of the VOC. Monitoring the gas composition immediately exiting the preoxidation tube using the MKS multigas analyzer confirmed that under our conditions only partial oxidation occurred, with a different fraction of each VOC being oxidized.

For quantitative comparisons of the color changes of the array, we can define a 108-dimensional vector (i.e, 36 changes in RGB values) for each trial, which can be compared and classified by standard chemometric techniques. We prefer the use of hierarchical

cluster analysis (HCA), which is a model-free method based on the grouping of the analyte vectors according to their spatial distances in their full vector space.[19] As shown in Figure 3, in quintuplicate trials, all 20 VOCs and a control were accurately classified with no errors out of 105 trials. We also collected array responses to the 20 VOCs after 5 min exposure at their PELs, as shown in Figure S2. Even at the PELs, HCA (Figure S3) indicates that all 20 VOCs and a control can be accurately identified with no error or misclassification out of 105 cases.

The ability of this array to discriminate among many analytes is due in part to the high dimensionality of the data. To probe the dimensionality of the data, we did a principal component analysis (PCA), which generates optimized linear combinations of the original 108 dimensions in order to maximize the amount of variance in as few dimensions as possible; for 105 trials involving 20 VOCs and a control, the PCA results show that the array requires 13 dimensions to capture 90% of the total variance and 23 dimensions to capture 95% (see Figure S4). This extremely high dispersion reflects the wide range of chemical-property space being probed by our choice of chemically responsive pigments.

To quantify the improvement in sensitivity provided by our preoxidation technique, we determined limits of detection (LODs) for these 20 VOCs both with and without preoxidation using our previously described sensor array (see the SI for experimental details).[14a] We define a conservative LOD for our array response as the VOC concentration needed to give 3 times the signal-to-noise (S/N) versus background for the sum of the three largest responses among the 108 color changes. The array response to the 20 VOCs in the absence of preoxidation was not very strong (with the exception of phenol, which is acidic); the color difference maps at their IDLH concentrations with a 5 min
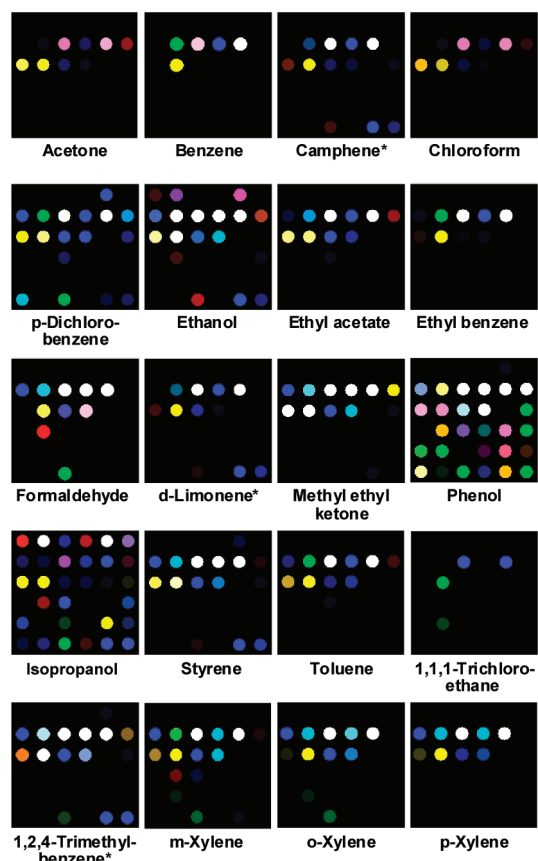
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Figure 2. Color difference maps for 20 representative indoor pollutant VOCs at their IDLH concentrations (Table 1) and a control after full equilibration (i.e., 5 min exposure) at 50% RH and 298 K using a preoxidation tube. For purposes of visualization, the color range of these difference maps has been expanded from 3 to 8 bits per color (RGB range of 3–10 expanded to 0–255); the full digital database is provided in Tables S1 and S2. All of the experiments were run in quintuplicate with 30 mg of chromic acid on silica as the preoxidation reagent. *Camphene, D-limonene, and 1,2,4-trimethylbenzene do not have defined IDLH concentrations, so each was used at a pressure equal to 5% of its saturated vapor pressure.

Figure 3. Hierarchical cluster analysis for 20 commonly found VOCs at their IDLH concentrations and a control. All of the experiments were run in quintuplicate with 30 mg of chromic acid on silica as the preoxidation reagent; no confusions or errors in classification were observed in 105 trials.

exposure without preoxidation are compared to those with preoxidation in Figure S5. For array data collected with the use of preoxidation, the LODs were extrapolated from the 5 min responses at the PELs. The extrapolated LODs in the absence and presence of preoxidation are provided in Table 1. The ratios of LODs without and with preoxidation, also listed in Table 1, indicate an average sensitivity enhancement of >300-fold using preoxidation. Indeed, the LOD was just 1.4% of the PEL on average. In comparison, limits of recognition (LOR) are higher, but it is important to realize that LORs are library dependent, unlike LODs, which are absolute.

The color changes of the array are dependent upon the concentration of the VOC, which provides an easy method for semiquantitative analysis of VOC concentration. For example, by combining the data sets for the 20 VOCs at the IDLH concentrations and the PELs, we can clearly differentiate the array responses to the same analytes at different concentrations (with the exception of ethanol, where the extremely high concentrations required to reach the IDLH concentration and PEL of ethanol saturate the array response). Cluster analysis for the full
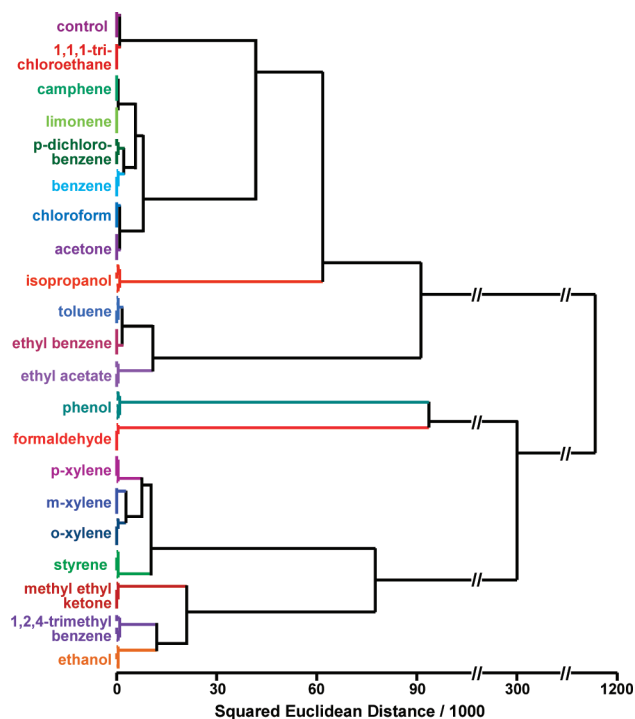
set of IDLH and PEL databases can be seen in Figure S6. For any given VOC, semiquantitative interpolation of its concentration can easily be accomplished using the total Euclidean distance (i.e., the square root of the sum of the squares of the color differences) of the VOC relative to a set of known concentrations in the library.

In real-world situations, changes in humidity are highly problematic for prior electronic nose technologies. The sol–gel formulations used in our optoelectronic nose are essentially impervious to changes in RH. With 50% RH as a control, arrays were exposed to various RH levels without any additional analyte; no significant response to humidity was observed from 10 to 90% RH, either with or without the preoxidation tube (Figure S7). The effect of humidity on the array response to VOCs with preoxidation was also evaluated. As one example, results for o-xylene at different RH are shown in Figure S8 and compared to those for other closely related aromatic hydrocarbons (i.e., BTEX components), all at their IDLH concentrations. As shown, changes in RH do not lead to confusion between o-xylene and even m- or p-xylene. Thus, changes in humidity do not generally affect the response of our optoelectronic nose to analytes, even at low analyte concentrations.

Finally, we investigated the reproducibility and shelf life of the preoxidation reagent (i.e., chromic acid on silica) for VOC detection. Because we detect the partial oxidation products of the primary VOC, one might have legitimate concerns as to the reproducibility of the resulting oxidized mixture. Fortunately, we found excellent reproducibility from batch to batch of the preoxidation reagent, as shown in Figure S9: three separately prepared batches of chromic acid on silica gave nearly identical results in separate tests on toluene and p-xylene (done in

triplicate), which were also easily differentiated from benzene, ethylbenzene, *o*-xylene, and *m*-xylene (all at their IDLH concentrations). In addition, we observed very little change in the array response as the preoxidation reagent aged over a 2 month period (Figure S10).

In conclusion, we have developed a preoxidation technique that substantially improves the colorimetric sensor array detection of VOCs. Twenty VOCs commonly found in indoor air can be identified at both their IDLH and PEL concentrations. Classification analysis revealed that this array with the preoxidation tube has an extremely high dimensionality with the consequent ability to discriminate among a large number of VOCs over a wide range of concentrations. Comparison of the limits of detection of the array for VOCs with and without preoxidation indicated an average sensitivity enhancement of ∼300-fold, with LODs that are only 1.4% of the PELs on average. Such high sensitivity is particularly relevant to future epidemiological studies of the health effects of long-term low-level exposures. While the laboratory studies reported here made use of inexpensive flatbed scanners for imaging, we have a prototype hand-held array reader under development[14] and are working on a wearable device to provide rapid, inexpensive, and highly sensitive personal monitoring of VOC vapors.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental details, Figures S1–S10, and Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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