High-Speed Fluorescence Detection of Explosives-like Vapors

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In this paper, we report on the preparation of novel cross-reactive optical microsensors for high-speed detection of low-level explosives and explosives-like vapors. Porous silica microspheres with an incorporated environmentally sensitive fluorescent dye are employed in high-density sensor arrays to monitor fluorescence changes during nitroaromatic compound (NAC) vapor exposure. The porous silica-based sensor materials have good adsorption characteristics, high surface areas, and surface functionality to help maximize analyte–dye interactions. These interactions occur immediately upon vapor exposure, i.e., in less than 200 ms and are monitored with a high-speed charge-coupled device camera to produce characteristic and reproducible vapor response profiles for individual sensors within an array. Employing thousands of identical microsensors permits sensor responses to be combined, which significantly reduces sensor noise and enhances detection limits. Normalized response profiles for 1,3-dinitrobenzene (1,3-DNB) are independent of analyte concentration, analyte exposure time, or sensor age for an array of one sensor type. Explosives-like NACs such as 2,4-dinitrotoluene and DNB are detected at low part-per-billion levels in seconds. Sensor–analyte profiles of some sensor types are more sensitive to low-level NAC vapor even when in a higher organic vapor background. We show that single-element arrays permit the detection of low-level nitroaromatic compound vapors because of sensor-to-sensor reproducibility and signal averaging.

There is a high demand for fast and reliable explosives vapor detectors suitable for security purposes, remediation assessment, forensic analysis, and land mine detection. Difficulties in explosives vapor detection methods include sensitivity, selectivity, durability, reversibility, sampling, speed of detection, dynamic range, and stability. Methods for detecting low-level NACs and explosives compounds and/or their associated degradation products in vapor or solution have been discussed by Yinon and Zitrin. Various chromatographic methods, as well as amperometric gas-phase sensing and optical techniques have been employed. The EPA analysis method 8330 employing HPLC is a widely accepted approach but can prove to be expensive and time-consuming if samples have to be transported to an off-site laboratory for analysis. The new methods and technology for explosives-like vapors...
Figure 1. Excitation and emission spectra for different surface-modified porous silica microspheres stained with the environmentally sensitive dye Nile Red. The excitation spectra are recorded at the emission maximums for each sensor type and vice versa for the emission spectra. Sensors A–D are listed in Table 1. The legend shows the microsphere functionality contained on the surface for each porous silica bead type. Excitation and emission spectra show bathochromic shifts with increasing surface polarity.

Figure 1A shows the excitation spectra and Figure 1B shows the emission spectra for the different sensor types described in Table 1. The excitation spectra are recorded at the emission maximums for each sensor type, and vice versa for the emission spectra. The excitation and emission spectra show bathochromic shifts with increasing surface polarity.

Vapor detection discussed herein are not aimed at replacing reliable chromatographic-based methods; however, they may serve to complement and support such methods in a high-speed and reliable fashion, such as when a simple "yes/no" answer is needed to detect the presence of explosives-like compounds. This method and other approaches are currently being examined as potential systems for detecting buried land mines.

The necessity for extremely high-sensitivity detection is made more difficult by the complex backgrounds in which buried explosives reside. Recent results from George et al. suggest that 2,4-dinitrotoluene (2,4-DNT) is the best signature compound for vapor-phase detection above buried TNT land mines. Although DNT vapor levels may differ depending on the source and environment, a properly calibrated sensor may not be needed for field use, as long as the sensor has a defined limit of recognition (LOR) for its intended target species, as suggested by Zellers et al. For instance, if a sensor has the ability to recognize DNT's vapor signature pattern regardless of concentration levels or background interferences, it might be suitable for land mine detection.

In this paper, we report on a new sensor approach for low-level explosives vapor detection that offers many advantages over current methods because of sensor shelf life, rapid response profiles, reproducibility, stability, enhanced detection limits, ease of fabrication, and sensor size. We employ porous silica-based microsensor arrays for high-speed detection of explosives-like nitroaromatic compound vapors. Our sensor array has been demonstrated previously for other sensing tasks and information can be extracted in multiple dimensions (time, wavelength and spectral window, intensity). Each microsensor within the array is a 3- or 5-μm porous silica bead impregnated with the environmentally sensitive dye Nile Red. When Nile Red is sorbed to different porous silica microspheres with varying surface functionalities, the resulting excitation and emission spectra are shown to be dependent on the surface polarity (Figure 1).

The sensor array is positioned on an imaging system with a charge-coupled device (CCD) camera detector, and fluorescence changes are monitored before, during, and after a vapor pulse is presented. Upon vapor exposure, the sensors undergo characteristic and reproducible intensity and wavelength shifts that are used to generate time-dependent fluorescence response patterns. These patterns can be used to train pattern recognition computational networks. Subsequent exposure to the same analyte vapor enables the network to identify the vapor by its characteristic response pattern. This study reports the detection limits, sensor-to-sensor reproducibility, sensor lifetimes, and high-speed and characteristic response patterns of high-density sensor arrays. Pattern recognition analysis is not the focus of this study.

Employing porous silica sensor types in high-density optical sensor arrays has shown promise for detecting low-level explosives...
EXPERIMENTAL SECTION

Materials. Benzene, toluene, p-xylene, ethanol, and 22 mm \( \times \) 30 mm glass cover slips were purchased from Fisher. Nile Red dye, 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), 2,6-DNT, and p-nitrotoluene (4-NT) were purchased from Aldrich and used without purification. South African TNT vapor strips were obtained from the Defense Advanced Research Projects Agency. The carrier gas used in the experiments is ultra-zero-grade air from Northeast Gas, Inc. (Salem, NH). A 1010 Precision Gas Diluter (Tedlar bag gas dilution system) and sample bags were purchased from Custom Sensor Solutions, Inc. (Naperville, IL). All optical filters employed were purchased from either Chroma Technologies Corp. (Brattleboro, VT) or Omega Optical (Brattleboro, VT). The 750 \( \mu m \) outer diameter single-core optical fiber used for the excitation/emission spectra was purchased from Spectran Corp. (Sturbridge, MA), and the optical imaging fiber employed for high-density array sensing, as described previously, was purchased from Galileo Electro-Optics Corp. (Sturbridge, MA). The following porous silica microsphere packing materials were removed from HPLC columns (Phenomenex, Torrance, CA) and employed as substrates to which the fluorescent dye is physisorbed: (A) Spherex, NH2, (B) Phenosphere, CN, (C) Jupiter, C4, and (D) LUNA, OH. See Table 1.

Bead Sensor Fabrication. The porous silica microspheres were rinsed thoroughly with ethanol and allowed to dry in room air overnight. Each of the microsphere types were individually stained with a solution of 0.5 mg/mL Nile Red in toluene by placing ~50 mg of microsphere material on a vacuum filtration system, rinsing with toluene, and then passing excess Nile Red solution over the beads. Nile Red is readily sorbed to the surface of the modified porous silica microspheres, and nonadsorbed dye was removed by subsequent rinsing steps with toluene and deionized water. The stained microsphere sensors were placed in an open 4-mL glass vial, placed in an oven (110 °C) to dry for 1 h, and then stored in the dark at room temperature.

Array Fabrication. All vapor tests employed an array of sensors electrostatically held to the surface of a glass cover slip or positioned in the distal wells on the face of an etched imaging fiber. The etched imaging fiber arrays were prepared as described previously except that the microsensors were not placed into the etched wells with a solution-based deposition process. A dry microsensor “slurry” was deposited and rubbed onto the etched distal tip of the optical imaging fiber and the bead sensors assembled spontaneously into the wells (one sensor per well). The excess beads were wiped with a soft dust-free cotton swab and then a sharp burst of air was delivered with a dry air gun to remove any loose beads (2-s air pulse). The cover slip arrays were prepared by depositing a small amount of microsensors onto a glass cover slip and smearing the sensors with a latex glove.

Instrumentation. Double Monochromator System. Excitation and emission spectra for Nile Red-stained porous silica microsensors (Figure 1) were acquired using a single-core optical fiber and a double-monochromator fluorescence system as described previously. In brief, a slurry of each sensor type was attached and held to the distal tip of a 750-\( \mu m \) single-core optical fiber by simply dipping the distal tip of the optical fiber into a portion of the sensor stock. The fiber was then placed onto the double-monochromator system for signal measurement by a photomultiplier tube (PMT) detector. The excitation spectra were recorded at the emission maximum and the emission spectra were recorded at the excitation maximum for each sensor type.

Imaging and Vapor Delivery System. The fabricated sensor arrays were positioned onto a custom-built imaging system with a sparging apparatus employed for vapor delivery as described previously. The system employs an inverted Olympus fluorescence microscope incorporating a 75-W Xe excitation source with detection by a 640 \( \times \) 480 pixel SensiCam high-performance CCD camera (Cooke Corp., Auburn Hills, MI). In all testing events, Zeiss microscope objectives were employed and the CCD chip was binned 2 \( \times \) 2. A CCD is used to provide S/N enhancements for the sensor types employed; i.e., the individual CCD pixels are matched to the size of the microsphere sensors and uncorrelated noise is removed by monitoring many individual sensors simultaneously (see below).

Analyte vapors are delivered to the sensor arrays by employing a vacuum-controlled system similar to that reported by Kauer and

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Table 1. Porous Silica Microspheres Employed

<table>
<thead>
<tr>
<th>sensor name</th>
<th>size (( \mu m ))</th>
<th>microsphere material*</th>
<th>surface modification</th>
<th>pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3</td>
<td>Spherex</td>
<td>amino (NH2)</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>Phenosphere</td>
<td>cyano (CN)</td>
<td>80</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>Jupiter</td>
<td>butyl (C4)</td>
<td>300</td>
</tr>
<tr>
<td>D</td>
<td>3</td>
<td>LUNA</td>
<td>hydroxyl (OH)</td>
<td>100</td>
</tr>
</tbody>
</table>

* Materials are named according to the distributor (Phenomenex).
Shepherd and which has also been employed previously for volatile organic compound vapor detection. To deliver low-level VOC vapors, a Tedlar bag gas dilution vapor delivery system was employed (see below). All analytes such as solid 2,4-DNT, solid 1,3-DNB, etc., are individually placed in sealed flasks for vapor delivery by a vacuum-controlled sparging apparatus. For “air” (blank) delivery, an empty sealed flask is employed in order to purge the carrier (“air”) gas onto the sensors. A saturated explosives-like vapor plug can be delivered to the sensor arrays in pulsatile fashion without raising temperatures. It should be noted that vapor delivery is based on dilution of the NAC vapor stream and not by employing calibrated vapor generators as in the system discussed by Pella. Prior to delivery of analyte vapor onto a sensor, a diluent air stream can be used to lower vapor concentrations below saturation. The NAC concentration levels described herein are conservative estimates based on previously published vapor pressure data. It is likely that the concentration levels of explosive vapors being delivered to the sensors are somewhat lower than those calculated because the latter values do not take losses into account such as sticking to the Teflon tubing and/or other surfaces of the vapor delivery system. It is also important to note that analyte vapors are not preconcentrated prior to sensor exposure. Although vapor pressure data vary from source to source, the following values are employed in this study as the saturated vapor pressures at 22–25 °C: DNT; 290 ppb; 2,4,6-TNT vapor strips, 5 ppb; 1,3-DNB, 1 part per million (ppm); and 4-NT, 215 ppm. Figure 2 shows the representative NAC structures.

Tedlar Bag Vapor Dilution System. Thirty liters of 4000 ppm analyte (e.g., toluene, benzene, p-xylene) were prepared with ultra-zero-grade carrier air in a 40-L Tedlar bag, according to eq 1, sample concentration (ppm V) = \[ \frac{V_A (\mu L) D (g/mL) \times 22.4 (L/mol) \times 10^6(\mu L/L)}{[1000 (\mu L) \times M W \times V_S (L)]} \] (1)

where \( V_A \) is analyte volume (\( \mu L \)) added to the 40-L Tedlar bag, \( D \) is analyte density (g/mL), \( M W \) is analyte molecular weight, and \( V_S \) is total sample volume (L), e.g., the amount of diluent air added. Four Tedlar bag samples (air, toluene, benzene, p-xylene) were prepared by adding the proper amount of solvent analyte (none added for “air” sample bag) with a syringe needle into a flowing diluent air stream. Precise control of flow rates was accomplished by rotometers (Fisher), and proper filling time was calculated according to the required sample concentration. The molecular weight, density, and volume of solvent (\( \mu L \)) added for 30 L of carrier air to produce 4000 ppm analyte vapor in the bags are respectively as follows: (a) toluene 92.14 g/mol, 0.8669 g/mL, and 569.33 \( \mu L \); (b) benzene 78.11 g/mol, 0.8765 g/mL, and 477.4 \( \mu L \); and (c) p-xylene 106.17 g/mol, 0.8611 g/mL, and 660.7 \( \mu L \).

Once prepared, the 4000 ppm Tedlar bag analyte samples sat undisturbed for 12 h at ~20% humidity and ~22.2 °C.

Data Collection and Processing. The CCD camera captures fluorescence changes before, during, and after vapor presentation to the sensor array. Sequences of fluorescent images (frames) were recorded and the mean fluorescence changes for selected microsensors were subsequently converted to text using IP Lab software (Scanalytics, Fairfax, VA). All text data were further processed using Microsoft Excel. The duration of each sequence was approximately 5–14 s and depended on the CCD exposure time and the number of frames designated. A typical sequence could contain 45 images with 5 images (e.g., a baseline) captured before analyte delivery, 15 images during delivery, and 25 postanalyte delivery. It is important to note that the user can modify any part of this sequence in order to deliver vapor in a consecutive (multiple) fashion or to create shorter/longer vapor exposures. Responses from many identical sensors, i.e., tens to thousands, are simultaneously acquired and the resulting fluorescence signals are combined and averaged to improve detection limits by decreasing (or eliminating) the noise in the response. The number of sensors employed in the vapor tests was dependent directly on sensor packing density (on the cover slips) and the magnification employed. The number of sensors analyzed differs from experiment to experiment, but the minimum number of sensors employed for an experiment was 25 in order to show substantial signal-to-noise (S/N) enhancement. All experiments were performed at room temperature (22–25 °C).

Specific parameters for each vapor experiment are listed below and/or in the proper figure caption.

Reproducibility in Sensor Responses. A total of 102 microsensors were monitored before and after a 4.6-s saturated NAC vapor exposure (Figure 4). The y-axis scale indicates all data were standardized to the first time point and the air (background) response was not subtracted from subsequent vapor analytes. Each analyte was delivered only once to this cover slip array consisting of sensor D/Nile Red sensors.

Signal Averaging and Enhanced Signal-to-Noise Ratio. A cover slip array with sensor D/Nile Red sensors was used to monitor vapor signatures for DNT, DNB, and TNT vapor strips as 8% saturated vapor levels (20 mL/min vapor stream and 230 mL/min air diluent) were delivered with the sparging apparatus (Figure 5). Each vapor exposure was done in triplicate, and analyte responses were averaged over three exposures for each sensor. From each sensor’s response average, the air carrier response was subtracted from the analyte vapor responses. Sensor responses were then averaged for 4, 25, 100, 250, and 1000 sensors and the S/N ratios were compared (Table 2). Calculation of each S/N ratio was performed using a similar formula set forth by Skoog and Leary: the average intensity change during the vapor exposure period was divided by the standard deviation of the baseline, i.e., the frames captured prior to vapor exposure. The standard deviation of the baseline was calculated to be in the 99% confidence level by dividing the difference between the maximum and minimum value by five, i.e., two times 2.5σ. The purpose of employing 4, 25, 100, 250, and 1000 sensors was to use simple...
population numbers in order to convey the S/N enhancements as shown in Table 2.

High-Speed, Multipulse Delivery. Analyte vapors (50% saturated) were delivered in 0.38-s pulses to an imaging-fiber sensor array during a 42-frame sequence: (3, 3, 10, 3, 10, 3, 10) using the sparging vapor delivery system for a total experiment of 5.4 s. Italicized numbers indicate successive vapor exposures (Figure 6).

1,3-DNB Delivery with Varying Concentration Levels. A cover slip array with sensor D/Nile Red sensors was used to monitor vapor signatures as 1,3-DNB vapor concentrations were lowered (Figure 7). The sparging vapor delivery system was employed to deliver the analyte vapor stream. The vapor concentrations were calculated by diluting the saturated vapor concentration (1 ppm) with air carrier gas. DNB levels were delivered as follows: 200 ppb, 80%-air dilution; 400 ppb, 60%-air dilution; 600 ppb, 40%-air dilution; 800 ppb, 20%-air dilution; and 900 ppb, 10%-air dilution.

1,3-DNB Delivery with Varying Exposure Times. A cover slip array with sensor D/Nile Red sensors was used to monitor vapor signatures as 1,3-DNB exposure times were varied (Figure 8). The sparging vapor delivery system was employed to deliver the saturated DNB vapor.

NAC Vapors in VOC Background. An imaging fiber sensor array employing sensor B/Nile Red sensors was used to monitor NAC vapor (50% saturation) in a relatively high VOC (2000 ppm) background. The Tedlar bag delivery system was used in conjunction with the sparging system for a total flow rate of 150 mL/min (75 mL/min from the Tedlar bag system and 75 mL/min from the flask-purging system). The NACs were delivered using the sparging system and the low-level VOCs were delivered with the Tedlar bag system. Blank air samples, e.g., an empty sealed flask or Tedlar bag filled with carrier air, were used when necessary to deliver 50% analyte when no background vapor was employed. Each vapor trial was done in triplicate, in the following order: air, 2,4-DNT, 1,3-DNB, toluene, benzene, and p-xylene. The binary vapor mixtures were exposed to the sensor array in triplicate: DNT/toluene, DNB/toluene, DNT/benzene, etc.

Sensor Stability over Time. Signature profiles for 10-month-old and 2-day-old sensor stocks were compared for sensor D/Nile Red sensors in their response to saturated 1,3-DNB vapor (Figure 10).

RESULTS AND DISCUSSION

Porous silica microspheres with physisorbed Nile Red dye have proven to be effective sensors for low-level nitroaromatic compound vapors. As the surface polarity increases, e.g., C4 to OH, the sensor's spectra exhibit a bathochromic shift (Figure 1). The surface modifications alter the sensor's excitation and emission spectra, but they are also likely to have an effect on the sensor's ability to attract and adsorb vapor molecules much like thin polymer coatings on surface acoustic wave sensors.49 The bonded phases on the silica surfaces do not fully cover the surface and residual silanol groups are still available for analyte adsorption. The porous silica sensor materials have pore sizes varying between 80 and 300 Å and possess surface chemistries that favor interaction with incoming vapor molecules (see Table 1). This interaction is in agreement with the TNT sensing materials employed by Swager and co-workers17-19 consisting of structurally rigid, porous fluorescent polymers with electron-donating groups that favor interaction with electron-accepting NACs. The electron-accepting and “sticky” NAC compounds (Figure 2) are attracted to the highly adsorptive surface of the porous silica beads to help maximize analyte–dye interactions.

The microsensors are incorporated into two different high-density array platforms: glass cover slips and imaging fiber arrays. Bead sensors are deposited into etched microwells at the distal tip of an optical imaging fiber25,26,35,38 or they are electrostatically held to the surface of a glass cover slip (sensor D/Nile Red beads). This image was acquired with 100-ms CCD exposure and excitation/emission filters 560 (bp 40) nm/640 (bp 35) nm. The image contains over 1000 sensors that are individually addressable. Sensor-to-sensor cross-talk is immaterial because all sensors within the array are identical.

Figure 2. The explosives-like nitroaromatic compounds employed for vapor testing: 2,4,6-trinitrotoluene (TNT), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-DNT, and p-nitrotoluene (4-NT).

Figure 3. CCD image of a single-element, high-density sensor array electrostatically attached to the surface of a glass cover slip (sensor D/Nile Red beads). This image was acquired with 100-ms CCD exposure and excitation/emission filters 560 (bp 40) nm/640 (bp 35) nm. The image contains over 1000 sensors that are individually addressable. Sensor-to-sensor cross-talk is immaterial because all sensors within the array are identical.

of one sensor element type on the surface of a glass cover slip is shown in Figure 3. A CCD camera is employed to simultaneously capture the fluorescence vs time response profile for each sensor as vapor is presented in pulsatile fashion. Each of the many hundreds or thousands of sensors is independently addressed and monitored before, during, and after vapor presentation. The size of the array, or the number of individual sensors one can monitor, is limited more by the system’s optics than by the size of individual sensors.

The porous silica microsensors are cross-reactive in nature, i.e., they are broadly selective and are not analyte specific. The sensors are highly sensitive for low-level NAC vapor detection, however, because of their high-surface areas, the bead adsorption characteristics and the “sticky” nature of the NAC molecules. Vapor exposures to a single-element sensor array show that the response profiles are highly reproducible from sensor to sensor for 102 sensors over the family of nitroaromatic compound vapors examined (Figure 4). The same sensor array differentially responds to the following: (a) air carrier gas; (b) 1,3-DNB; (c) 4-NT; (d) 2,4-DNT; (e) 2,6-DNT; (f) TNT vapor strips. It should be noted that although the NAC compounds are quite similar in structure, the resulting response profiles are different for each analyte when exposed at their respective saturated vapor concentrations, i.e., ~5 ppb to ~215 ppm. Diversity in sensor–analyte response profiles and sensor-to-sensor reproducibility are important features for a detection system that is ultimately based on pattern recognition. Air produces a vapor signature resulting from a change in the humidity level between the dry carrier air and the room environment in which the sensors reside.

An important feature and advantage with employing high-density sensor arrays is the ability to combine reproducible sensor responses into an averaged response profile. This signal enhancement essentially removes noise from individual sensors to improve detection limits. S/N enhancement schemes have also been employed by Slaterbeck et al. in which repetitive sensor exposures were averaged instead of averaging over multiple sensors. If each sensor within the array responds with a small signal to a low-level vapor, then their identical response profiles can be combined. The time vs fluorescence responses to low-level vapors for each bead type within the array can be summed and then averaged over the number of sensors employed. Detection limits are enhanced by combining response profiles from many sensors.

As more sensors are incorporated, the S/N ratio theoretically increases by \( n^{1/2} \), where \( n \) is the number of sensors analyzed. The high-density array format allows us to combine the signals from each bead sensor and generate an average signal for a delivered vapor. Figure 5 shows responses for 250 individual sensors (sensor D) for 8% saturated vapor exposures of 2,4-DNT, 1,3-DNB, and TNT vapor strips. In comparison, the average response profile of 1000 sensors is shown. The noise for 1000 individual sensors is essentially removed when the sensor response profiles are averaged. By summing large numbers of sensors, we are able to improve the precision of the measurement and thereby measure decreasing concentrations of analyte. For the three replicate vapor exposures, the S/N ratios for DNT, DNB, and TNT vapor strips improve according to the averaged responses of a designated number of sensors \( n \) (Table 2). The higher than theoretical S/N experimental values may be an artifact of the formula employed for calculation (see Experimental Sec-

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Figure 4. Fluorescence vs time response profiles for 102 sensors (sensor D). The profiles show that each of the structurally similar NAC vapors produces a different vapor profile when exposed at its saturated concentration level. These data show substantial sensor-to-sensor reproducibility for the very-low level NAC vapors. The black bar indicates the start and finish of the 4.6 s vapor exposure. The “air” response results from a difference in the humidity levels between the dry carrier air gas and laboratory air (note: the responses shown are not background subtracted). Note the difference in the y-axis scale for 4-NT and 1,3-DNB. Additional experimental settings: 150 mL/min flow rate; 40× objective (NA 0.75); 200-ms CCD exposure time; and excitation/emission filters 530 (bp 30) nm/640 (bp 35) nm.
tion). Thus, incorporating many identical sensor responses allows the detection of 23 ppb 2,4-DNT and 80 ppb 1,3-DNB in clean, dry air. These limits may need to be improved by 1 or 2 orders of magnitude for land mine detection or for other high-sensitivity detection tasks, but further detection limit enhancements may be limited more by sample delivery than by sensor sensitivity or number of sensors employed. For the remainder of this paper, it should be noted that signal averaging of many sensors was employed to improve S/N ratios and enhance detection limits. Any fluorescence intensity changes or transient responses prior to vapor delivery, as in Figure 5, might be the result of lamp fluctuations, CCD noise, slight air currents, humidity changes, electronic noise, etc. It is a difficult task to determine the exact concentrations of the NAC vapors, so we use the theoretical dilution of the saturated vapor pressure as a conservative (upper limit) estimate for the values found in the literature and do not account for losses to surfaces.

As stated, porous silica materials are suited for nitroaromatic vapor detection because of sensor reproducibility and high-speed
Figure 6 shows that three consecutive 0.38-s vapor exposures of 50% saturated vapor result in reproducible response profiles for the cross-reactive sensor array positioned on the distal tip of an optical imaging fiber. The responses are identical, and these data show that the cross-reactive porous silica sensors produce unique response profiles for different analyte vapors in a high-speed and reproducible fashion. Again, diversity in the sensor–analyte response profiles is an important feature for a cross-reactive array.

The average response for 76 sensor B/Nile Red sensors is used to show that the vapor profiles for toluene (~18 700 ppm), 1,3-DNB (0.5 ppm), and air carrier gas are substantially different, even for a single-element sensor array.

Sensor–analyte response profiles are linearly dependent on concentration for DNB and sensor D. Figure 7 shows that as 1,3-DNB concentration levels are varied from 200 to 900 ppb the response profile is nearly linear. By plotting the last data point of the vapor exposure vs DNB concentration, a line with R\(^2\) = 0.9753 is produced (see Figure 7 inset). Not only do the individual sensors respond in a reproducible fashion but the analyte signature profiles are nearly identical regardless of analyte concentration; e.g., if the all data points were normalized to the minimum intensity value, the signature profiles would essentially overlap (not shown). The response patterns are independent of concentration for this specific sensor type (compare the averaged DNB response in Figure 5 to that in Figure 7). Although these sensor types are cross-reactive in nature, linearity was for one analyte in dry air. We speculate that incorporation of this sensor into a multisensor array platform might be an advantage for performing quantitative DNB detection. The sensor–analyte response pattern for sensor D and DNB also seems to be invariant with varying vapor exposure times. Figure 8 shows that sensor response profiles are virtually identical as vapor exposure times are varied from 0.7 to 7.1 s.

To show that NAC vapor can be detected in the presence of a complex background, Nile Red-stained porous silica beads were employed to monitor vapor signatures for binary vapor mixtures. Figure 9 shows that an imaging fiber array of sensor B/Nile Red sensors is more sensitive to the low-level NAC vapor (150 ppb DNT or 500 ppb DNB) in a much higher VOC (2000 ppm) background. The average fluorescence response profiles for 50 sensors over three vapor exposures were used to plot vapor responses for all analytes in the test set (A) and for the binary vapor mixtures (B). These data show that the vapor signatures for sensor B are more dependent on the presence of low-level NAC vapor than on the higher level VOC vapor. The black bar indicates the start and finish of the 2.54-s vapor pulse. XYL, p-xylene; BENZ, benzene; TOL, toluene. Note: the responses shown are not background subtracted. Additional experimental settings include the following: 150-ms CCD exposure time; 10× objective (NA 0.30); and excitation/emission filters 560 (bp 40) nm /630 (bp 20) nm.

Figure 8. A cover slip array with sensor D/Nile Red sensors used to monitor 1,3-DNB vapor responses as exposure times were varied. The background air carrier gas was subtracted and the average response for 25 sensors is plotted for each exposure time. Exposure times are varied from 0.7 to 7.1 s, as indicated by the black bars. Additional settings for this experiment are as follows: 20× objective (NA 0.50); 150 mL/min flow rate; and excitation/emission filters 560 (bp 40) nm /630 (bp 20) nm.

Figure 9. An imaging fiber sensor array employing sensor B/Nile Red sensors used to monitor NAC vapor (150 ppb DNT, 500 ppb DNB) in a much higher VOC (2000 ppm) background. The average fluorescence response profiles for 50 sensors over three vapor exposures were used to plot vapor responses for all analytes in the test set (A) and for the binary vapor mixtures (B). These data show that the vapor signatures for sensor B are more dependent on the presence of low-level NAC vapor than on the higher level VOC vapor. The black bar indicates the start and finish of the 2.54-s vapor pulse. XYL, p-xylene; BENZ, benzene; TOL, toluene. Note: the responses shown are not background subtracted. Additional experimental settings include the following: 150-ms CCD exposure time; 10× objective (NA 0.30); and excitation/emission filters 560 (bp 40) nm /630 (bp 20) nm.

individual sensors are not selective or linearly dependent on a specific analyte but are responsive to many analytes. When one target analyte needs to be detected, it may be advantageous to incorporate sensors with some linear dependence and/or selectivity toward that analyte with other sensors in the array retaining cross-reactivity to respond to complex backgrounds. Such partial selectivity has been employed with electrochemical cross-reactive sensor arrays by incorporating semiselective electrodes for the detection of specific ions in solution. Such an approach may benefit a NAC vapor detection system for buried land mines. The processed data presented here are not representative of the processing that would be required to identify or discriminate analytes in the field. An ideal detection system would contain additional processing features, computational networks, and training data and would require an additional processing time (1–2 s) to discriminate between analytes.

Sensor shelf life is also an important feature of any detection system. A 10-month-old stock of sensor D/Nile Red sensors was compared to a stock of the same sensor type that was only 2 days old. Both sensor stocks were tested on the same day with identical testing parameters (see Experimental Section). The nearly identical normalized response patterns for saturated levels of DNB (1 ppm) are shown in Figure 10. The older sensors are still responsive to low-level vapor and respond in the same high-speed fashion as the newly fabricated sensors. This experiment shows that sensor stocks are fabricated identically from one batch to another. For further comparison, the 2-day-old sensor array was tested 9 months later, and the response profile is nearly identical to both sensor response profiles noted above (Figure 10). These signature profiles can also be qualitatively compared to the DNB response in Figure 5 and response profiles in Figure 7. These data suggest that sensor D could be employed to qualitatively identify DNB in pure form regardless of concentration or sensor age.

**CONCLUSION**

The porous silica-based sensors reported in this paper show promise for explosives vapor detection because of their reproducible, inherent sensitivity to NAC vapor, high-speed response profiles, and sensitivity to NAC vapor within a mixture. Sensor stocks can also be reproducibly fabricated from one batch to the next, and sensor shelf life is at least 10 months. The high-density microsensor arrays have signal enhancement built into their design because one can monitor many sensors simultaneously and combine their responses to increase S/N ratios. With high sensor–analyte reproducibility and enhanced detection limits, these sensors have the potential to be used in multisensor cross-reactive arrays employing pattern recognition analysis as has been demonstrated for other vapors at higher vapor concentrations. These sensors may be suited for any situation where there is a need for explosives vapor detection in areas such as forensics, mapping remediation sites, and airport security. A system that also has the ability to correctly identify certain target species by the response profiles regardless of analyte concentration may ultimately lead to better explosives vapor systems for land mine detection.

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