Appendix B. Simple Optical Sensor for Amine Vapors Based on Dyed Silica Microspheres

B.1. Abstract

A new optical sensing method for sensitive detection of amine vapors down to ppb levels is described. The sensor is based on the pH indicator Bromocresol green, adsorbed onto a silica sphere matrix. When the amines adsorb onto the matrix, the color changes from orange to blue. The color change is detected with a fiber optic spectrometer. Sensor performance is demonstrated for the aliphatic amines tert-butylamine, diethylamine and triethylamine and also for ammonia, pyridine and aniline. The response for the aliphatic amines is linear with concentration up to 2 ppm with a detection limit of approximately 1.4 ppb for tert-butylamine. The microsphere sensor is more sensitive than other optical amine sensor designs described in the literature. The sensor response varies with temperature, with lower sensitivity and faster response at higher temperatures allowing for adjustment to prioritize sensitivity or speed. At 80 ºC the response time is 2-20 s, with maximum signal after approximately 2 min and a recovery time of 2–10 min depending on concentration of amine vapor. Sensor response is highly reproducible and fully reversible.

B.2. Introduction

Sensing low concentrations of chemical vapors is an area of great interest with many practical applications. Amine vapors are of particular interest since both aliphatic and aromatic amines can induce toxicological responses at low concentrations.[1,2] Aliphatic amines can be found in many wastewater effluents from industry, agriculture, pharmacy, and food processing.[3] Hence sensitive and rapid detection of amines is valuable in environmental and industrial monitoring as well as in food quality control.[4] Simplicity, robustness, low weight and high sensitivity are attractive characteristics for chemical sensors in virtually all applications. In addition, the ideal sensor should be capable of continuously monitoring specific analyte levels free from interference with other common organic vapors.

Several different techniques have been developed for amine sensing. Conventional real-time monitoring of gases has commonly been performed employing electrochemical sensors.[5] These are usually based on the oxidation of amines on various anode materials or on chemically modified electrodes.[6,7,8] Biosensors have been constructed employing immobilized amine oxidases or amine dehydrogenases.[9] Other methods of sensing include piezo crystal detectors with PVP (polyvinylpyrrolidone) coating[10] and measurements of resistance in polypyrrole films[11]. Several of these techniques have inherent disadvantages such as the need for reference electrodes, the development of surface potentials and irreversibility. Many of these problems can be circumvented by employing fiber-based optical sensing.

Numerous amine and ammonia sensors employ optical transduction methods. Charlesworth et al. described a fiber optic fluorescence based sensor for amine vapors utilizing a film of the pH-sensitive molecule 2-napthol and reported a sensitivity of 24 ppm.[12] Qin et al. designed an optical sensor for amine detection based on dimer-monomer equilibrium of indium(III) octaethylporphyrin in a polymeric film and reported a sensitivity of 0.1 ppm (detection limit of 50 ppb) for the most lipophilic amines.[13] McCarrick et al. constructed a visual indicator based on a calix[4]arene, bearing nitrophenylazophenol chromogenic functionalities, complexed with lithium. The modified calixarene underwent a color change from yellow to red for trimethylamine concentrations above 20 ppb. The color change results from deprotonation of an acidic chromophore.[14]

Silica microspheres have been widely employed for the construction of gas-phase chemical sensors.[15,16,17] Their popularity is a result of the ease with which silica sphere matrices are prepared and modified. Silica spheres are easily derivatized and due to the mild reaction conditions it is possible to incorporate various molecules, dyes, organic and organometallic reagents into the silica matrix. Silica sphere matrices are also chemically and mechanically stable and the average pore size, pore size distribution, surface area, refractive index, and polarity of the resultant matrix can be controlled and tailored.[18] These properties enable construction of selective chemical sensors. In a recent paper Onida et al. described a neutral amine-templated mesophorous silica system, impregnated with Reichardt's dye.[19] The resulting material is pink when dehydrated, but turns white when air is readmitted or polar solvents adsorbed. The non-dehydrated system changes color reversibly when exposed to amines and ammonia, but is not affected by other polar or non-polar substances. The system was proposed as a possible ammonia gas sensor.

The amine sensor we describe is based on optical monitoring of micron-sized silica spheres dyed with the pH indicator bromocresol green, spread in a multilayer on a glass slide. This multilayer responds optically to gas-phase sub-ppm (down to 1.4 ppb) concentrations of amines with an increase in absorbance at 620 nm.

B.3. Experimental

Reagents. Silica microspheres (5 μm diameter) were obtained from Alfa Aesar. All amines were analytical or reagent grade products and used without further purification. Triethylamine, tert-butylamine and aniline were obtained from Aldrich, diethylamine from Sigma and pyridine from EM Science. The pH indicator dye Bromocresol green was purchased from Sigma.

Silica bead sensors. The amine sensor comprised a thin multilayer of silica spheres with an adsorbed indicator dye. A uniform suspension was obtained by sonicating a mixture of 60 mg silica spheres, 24 mg bromocresol green and 400 μL acetone for 2 min. Glass plates were cleaned in piranha solution (3:1 conc. H_2SO_4:30% H_2O_2) and stored in methanol until used. (Caution! Piranha solution reacts violently with organics. Use with care.) A couple of drops of silica suspension (total volume 10 μL) were manually applied to a clean glass plate kept tilted at an angle of ~11°. This created a thin, locally uniform layer of silica spheres (1 to 3 layers of spheres deep), as the drop spread and dried. The sensor was allowed to dry overnight in a desiccator. The sensing films were a deep orange color, which changes to blue when exposed to amine vapors.

Instrumentation. Figure B.1 shows a schematic of the optical sensor system. Nitrogen was used as the carrier gas for all experiments. Amine vapor samples were prepared in Tedlar bags at concentrations between 500 ppm and 70 ppb. The amine vapor was diluted with a gas diluter (Custom Sensor Solutions, Model 1010 Precision Gas Diluter) before entering the system through a glass tube (c). The flow rate of diluted amine vapor through the glass tube was 1300 mL/min. This is high enough to saturate the space around the sensor with diluted amine vapor at the desired concentration, and so the sensor is not

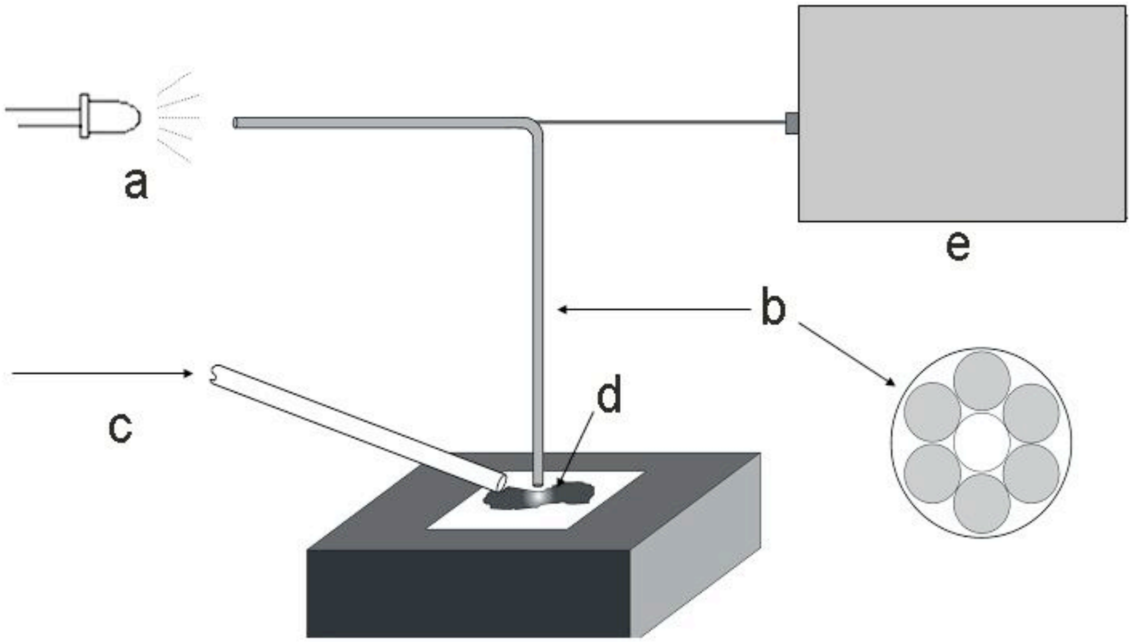

Figure B.1 Schematic diagram of the optical sensor system. An optical fiber (b) carries both incoming light from the LED source (a) and the reflected light from the sensor (d) to the spectrometer (e). The amine vapor is diluted in nitrogen and flows to the sensor through the glass tubing (c).

enclosed in a chamber. The amine sensor (d) (approximately 5 x 10 mm) is mounted on a temperature controlled aluminum block. A white LED (a) was employed as the light source. The output of the LED is passed into the excitation bundle of a six-around-one fiber optic probe (b). The inset of Figure B.1 shows a view of the end of the fiber optic probe facing the sample. Six illumination fibers surround a single read fiber. The diameter of each individual optical fiber was 0.5 mm. The end of the probe is held a few millimeters above the amine sensor. Reflected light is collected by the read fiber of the probe and is analyzed with a fiber optic spectrometer (e) (Ocean Optics S-2000 fiber optic spectrometer). The absorbance of the light by the sensor over time was analyzed as described below using software supplied by Ocean Optics Inc.

Each new amine sensor was activated by flushing with 5-10 ppm tert-butylamine before use. This was necessary to achieve reproducible results and maximum sensitivity. The activation was only necessary prior to the first use of the sensor. The reason for the enhanced sensitivity after activation with amine is unclear.

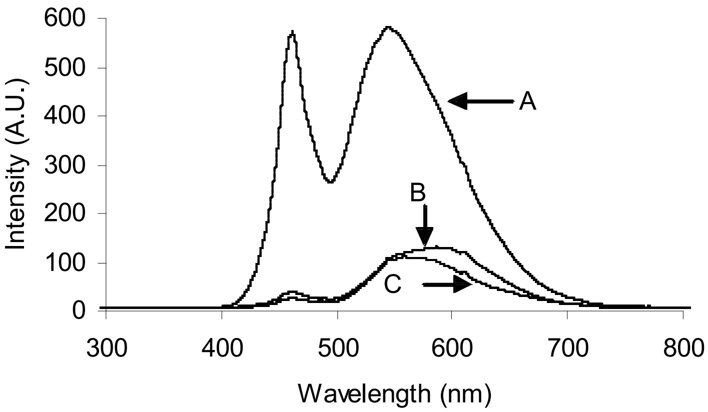

Figure B.2 The diffuse reflectance spectrum of the LED from a white surface (A), the activated sensor (B) and the sensor exposed to 3.5 ppm tert-butylamine adsorbed onto it (C). The absorbance reported in this paper is the change in reflected light intensity between the activated sensor and the sensor with adsorbed amine.

Data acquisition. The reported absorbance in this paper is the change in light absorption between the activated sensor and the sensor with analyte amines adsorbed onto it, where absorbance is defined as $A= -\log (I/I_o)$. Conventionally, light absorbance of a substance is compared to absorbance of a white surface, i.e. I_o is the intensity of the light reflected off a white surface. In this sensor system it is more convenient to employ the clean sensor as the absorbance reference, I_o. The main advantage is that the difference in the intensity of reflected light between the sensor with and without amine is much smaller than the intensity difference between the sensor and the white background. Figure B.2 gives the raw diffuse reflectance spectra. Curve A shows the reflectance spectra of the LED source from a white surface. Curves B and C show the reflectance from the activated sensor and the sensor with absorbed amine, respectively. The figure also shows that the maximum intensity difference with and without amine adsorbed onto the sensor occurs around 620 nm. Hence all absorbance data was acquired at 620 nm, except for spectra covering the whole wavelength region, with curve B used as the absorbance reference, I_o.

To determine the effect of temperature variations, the sensor system was tested with 1.4 ppm of various amines for 2 min at temperatures between 20 ºC and 120 ºC. All other experiments were performed at the optimal temperature of 80 ºC. The sensitivity was examined for tert-butylamine, diethylamine and triethylamine with concentrations ranging between 0.1 and 2 ppm for diethyl and triethylamine and 1.4 ppb to 28 ppm for tert-butylamine. The aromatic amines pyridine and aniline were only briefly examined at much higher concentrations (approximately 40 and 200 ppm).

For each series, the sensor was exposed to amine vapor for 2 min at each concentration. After the amine vapor was turned off, the sensor was flushed with pure nitrogen until at least 95% of the original signal was recovered.

B.4. Results and discussion

Sensor Response Mechanism. The sensor is based on the spectral properties of pH indicator bromocresol green. Like most pH indicators, bromocresol green (tetrabromo-m-cresolsulfonphthalein) is a weak organic acid whose absorbance spectrum is quite different from the absorbance spectrum of its conjugate base. The structure of bromocresol green and its conjugate base are shown in Figure B.3. A bromocresol green solution changes from yellow to blue over the pH range 3.8-5.4, as the equilibrium shifts to the deprotonated, arylmethine form of the dye. [20] Bromocresol green was selected as the pH indicator because of its appropriate endpoint and the high uptake by the silica beads, probably due to its many polar groups. Other indicators proved to be less effective.

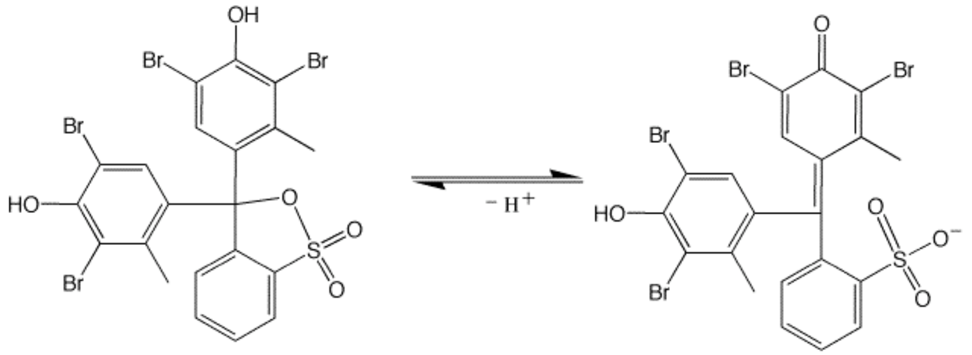

Figure B.3. Bromocresol green and its conjugate base.

Characteristics of the Optical Amine Sensor. Figure B.4 shows the response of the sensor to diethylamine, triethylamine, tert-butylamine and ammonia. By using the sensor itself as a reference, the baseline is set to zero and the absorbance peaks are clearly defined. The maximum absorbance is located at 620 nm for all amines. Thus the absorbance at 620 nm was monitored to evaluate the response of the sensor to temperature and concentration, as well as saturation and recovery times. Figure B.4 also demonstrates a sensitivity difference between diethylamine, triethylamine, tert-butylamine and ammonia. In particular the response is significantly lower for ammonia. In addition, the sensor was also tested with aniline and pyridine, with the resulting relative sensitivity: diethylamine > triethylamine ≥ tert-butylamine > ammonia >> aniline > pyridine.

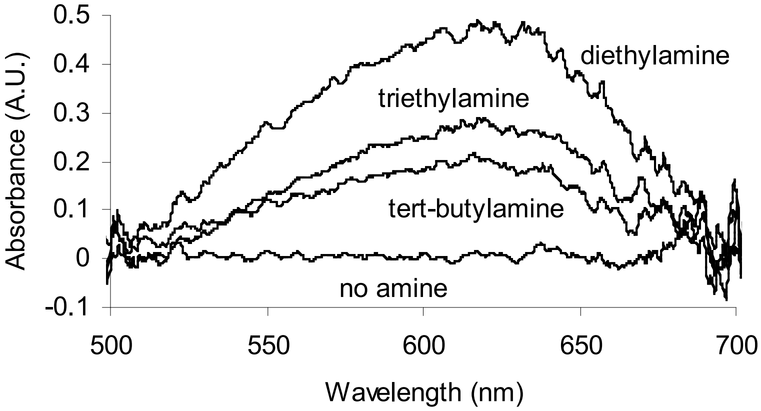

Figure B.4. Absorbance spectra of the sensor with 5 ppm of tert-butylamine, diethylamine and triethylamine, employing the sensor as absorption reference. The response varies significantly between the amines and the difference is correlated to the amines $k_{B,}$ not their acidity in the gas phase.

The response depends ultimately on two factors, the basicity and the hydrogen bonding capability in relation to adsorption of the amine on the silica surface. In solution the dialkyl amines have the highest pK_a while in the gas phase the trialkyl amines are the most basic. The tendency of alkyl groups to stabilize charge through a polarization mechanism accounts for the basicity of triethylamine in the gas phase. The combined effects of polarization and solvent stabilization due to hydrogen bonding result in a leveling of amine basicities in solution compared to the gas phase[21]. For example, solvent stabilization by hydrogen bonding results in dialkylamines being slightly more basic than trialkylamines. The response pattern, from the relative absorbance strength diethylamine > triethylamine > tert-butylamine > ammonia, suggests an environment where hydrogen bonding is important, similar to that of a solution. It is likely that the amines are hydrogen bonded to hydroxyl groups on the silica surface, which corroborates

Table B.1. Table of pK_a and gas basicity constants for the investigated amines. The amines are ordered from highest to lowest response.

Amine	pK_a [22]	Gas Basicity (kJ/mol) [23]
Diethylamine	10.84	919.4
Triethylamine	10.75	951.0
Tert-butylamine	10.68	899.9
Aniline	5.23	850.6
Pyridine	4.58	898.1

studies suggesting that interaction of adsorbates with the hydroxyl sites on the silica surface generally accounts for the major part of adsorption.[24] The response for pyridine and aniline was orders of magnitude smaller than for the aliphatic amines. The detection limit for aniline is approximately 200 ppm while no response was detected for 230 ppm pyridine. This can be explained by the lower basicity of these compounds (Table B.1).

The correlation between basicity and response indicates that response is mainly determined by basicity of the amine. There is also a difference in adsorption of the amines, however. The strength of the hydrogen-bond interaction between a silica surface and an amine can be measured using spectroscopic methods. Van Cauvelaert et al. measured a significantly stronger interaction between silica and triethylamine compared to butylamine.[25] They concluded that the strength of the interaction depended both on the acid-base properties of the molecule and the steric effects between large groups and the silica surface. This suggests that it should be possible to enhance the selectivity of the sensor by employing a derivatized silica surface, which could select for not only the acid-base properties of the amine, but the shape as well.

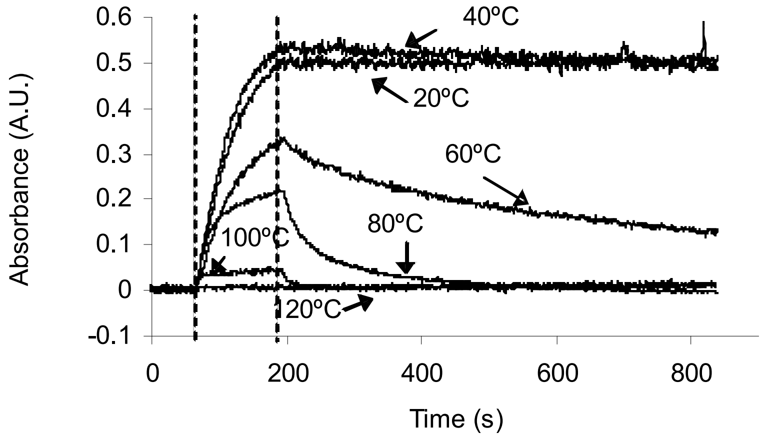

Figure B.5. Absorbance versus time at different temperatures for 1.4 ppm tert-butylamine. Both signal strength and the recovery time depends on temperature. The amine is flowed over the sensor for 2 min (between the dashed lines in the figure) and then turned off. For the lowest two temperatures, 20 ºC and 40 ºC, very little recovery occurred due to evaporation within 10 min of the turn-off of amine vapor. In the range 60–100 ºC evaporation occurs at increasing rates at the cost of decreasing signal. At 120 ºC there is no signal for 1.4 ppm tert-butylamine.

Temperature Dependence. The effect of temperature on the operation of the sensor system was investigated by comparing sensitivity and detection time at 620 nm for 1.4 ppm tert-butylamine vapor at temperatures between 20ºC and 120ºC (Figure B.5). For each temperature, the amine vapor was flowed over the sensor for 2 min followed by 10 min of recovery time. Sensitivity, response time and recovery time are all dependent on temperature. At temperatures below 60ºC the evaporation of amine within 10 min is neglible and the sensor is very sensitive but effectively irreversible. Above 60ºC, the sensitivity and recovery time both decrease with temperature. At 120ºC there is no longer any response for an amine vapor concentration of 1.4 ppm and hence no higher temperature was investigated. For all experiments described in the next section, 80ºC was employed as the operational temperature as a compromise between a reasonable recovery time of ~10 min and loss of sensitivity at higher temperatures.

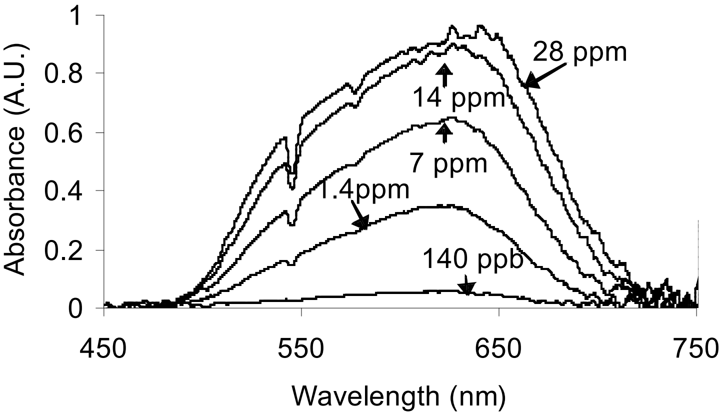

Figure B.6. The absorbance curves concentrations between 0.14 and 28 ppm of tert-butyl amine. The number of adsorption sites seem close to saturation at 28 ppm. The absorbance curves are similar for all concentrations.

Concentration Dependence. Tert-butylamine was detected with a range of concentrations from 140 ppb to 28 ppm (Figure B.6). At 28 ppm the system appears close to saturation and no higher concentrations were tested for the aliphatic amines. The signal strength is clearly dependent on the amine concentration. The maximum absorbance is essentially constant at 620 nm, however, and hence for all other measurements only the peak intensity at 620 nm as a function of time was recorded. Additional data were acquired for tert-butylamine, triethylamine and diethylamine in the low concentration region of 0.11 to 0.54 ppm. Figure B.7 shows the sensor response at 620 nm for triethylamine at 2 min amine exposures between 0.11 and 0.54 ppm.

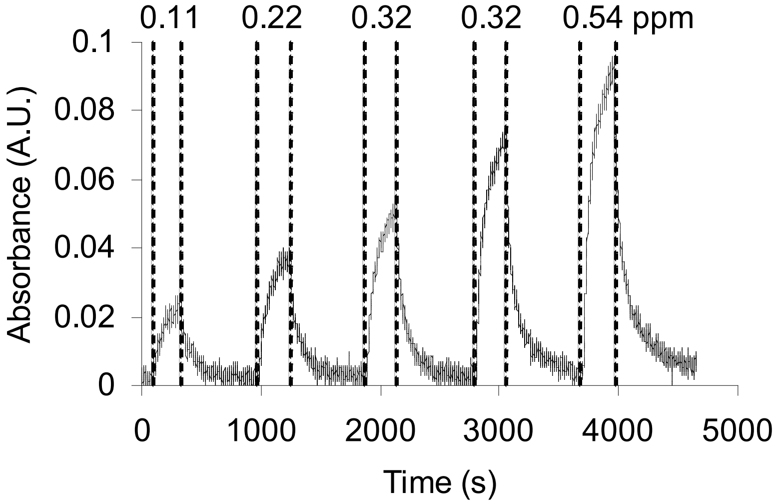

Figure B.7. Successive sensor response at 620 nm for triethylamine at the concentrations 0.11, 0.22, 0.32, 0.43 and 0.54 ppm respectively. This demonstrates sensor reversibility as well as ability to acquire repeated measurements.

A least square regression was employed to model the detector response as a function of concentration for each amine at concentrations between approximately 0.1 and 1 ppm. Figure B.8 shows the response of the sensor after two minutes of amine exposure to different concentrations of tert-butylamine, diethylamine and triethylamine. Linear regression fits the sensor response at low concentrations very well, with a regression constant larger than 0.99 for all three amines. The sensitivity of the sensor, measured by the slope of the regression, differs between the amines. An unexpected feature is the intercept for the tert-butylamine data. The trend lines for triethylamine and diethyl amine pass through the origin, but the tert-butylamine trend line exhibits a non-zero intercept.

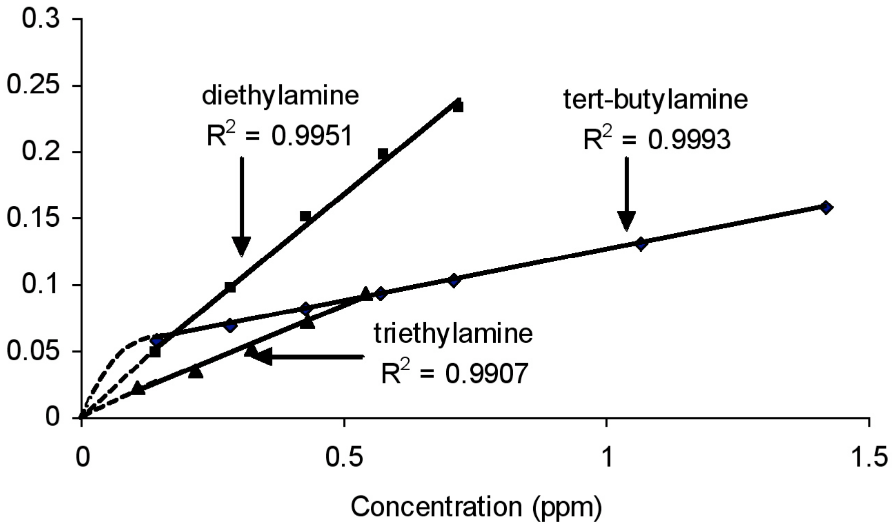

Figure B.8. The relationship between absorbance and concentration of tert-butyl amine, diethylamine and triethylamine. The relationship is linear within the limited domain 0.14 to 1.4 ppm. All correlation coefficients are larger than 0.99. Extrapolated curves are represented by dashed lines.

Activating the sensor with triethylamine yielded the same curve for tert-butylamine as activating with tert-butylamine. To examine if the non-zero intercept was a general feature for primary amines the behavior of ethylenediamine was investigated. The result was a very similar curve to tert-butylamine with a non-zero y-axis intercept. We naturally expect the response of the sensor to be zero at zero concentration. One possible explanation for the result is that at the concentrations used here for tert-butylamine, we have begun to saturate the sensor, and enter a second region of linear response, leading to a flatter curve with a non-zero intercept. This conjecture necessarily leads to a steep slope for the tert-butylamine curve at concentrations below 0.14 ppm (the lowest concentration shown on the graph). Extrapolated curves that intersect the origin and illustrate this possibility are shown in Figure B.8 as dashed lines. Unfortunately, concentrations lower than about 0.14 ppm are unreliable in our setup, due to the difficulties associated with serial dilution and surface adsorption in the gas diluter tubing. The slopes at these low concentrations would be ordered tert-butylamine > diethylamine > triethylamine.

The complexity of the system makes it difficult to ascertain the origin of the two prominent features of the concentration dependence, the faster saturation of binding sites for primary amines than for secondary and tertiary amines, and the relative steepness of the slopes. The bromocresol green very likely interacts with the silica surface by hydrogen bonding involving the OH and SO_3 functional groups on the molecule. The color change is associated with the deprotonation of the dye by the adsorbed amines and presumably the conjugate acid of the amine interacts both with the surface hydroxyls and the dye molecules by strong hydrogen bonding. The nature of the surface hydroxyls is a key factor to consider. Hertl[22] defined two types of hydroxyls possible on the surface. A-type hydroxyls do not participate in hydrogen bonding interactions, and are “free.” B-type hydroxyls are those that are participating in a hydrogen bond. It has been suggested that primary amines have an extended interaction with B-type hydroxyls (hydrogen bonded hydroxyls) on the silica surface compared to secondary and tertiary amines, which interact more with A-type hydroxyls (free hydroxyls)[23]. If there are fewer B-type hydroxyls available, primary amines would saturate faster. This would lead to the non-zero intercept described above. The ordering of the slopes implies that primary amines adsorb and react with the dye at a faster rate than secondary amines, which are faster than tertiary amines.

A concentration series was also produced for ammonia, with concentrations ranging from 1 to 20 ppm (data not shown). The response of the sensor was linear in this region with $R^2 = 0.98$. The sensor was less sensitive to ammonia than to the alkylamines studied. As previously mentioned, this is due to two factors: the lower basicity of ammonia (Table B.1), and the much higher vapor pressure of ammonia, which results in less adsorption onto the silica surface.

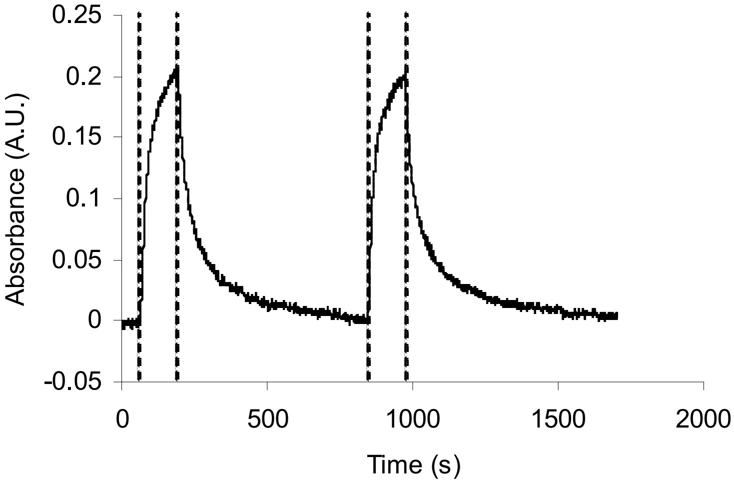

Figure B.9. Absorbance at 620 nm verses time for a pair of 1.4 ppm tert-butyl measurements at 620 nm. The difference in absorbance between the first and second flow of amine is within the error of the gas-diluter.

Reproducibility and recovery time. Figure B.9 demonstrates the reproducibility of the sensor, exposed to 2 min of 1.4 ppm tert-butylamine twice with 12 min between each exposure. The difference in absorbance for detection 1 and 2 is well within the error of the gas diluter, which is 15% at these concentrations (from the model specifications). The variation between the two measurements is here 1% of the maximum absorbance.

The recovery time is defined as the time from turn-off of amine vapor to the time when the signal has decreased 95%. The recovery time is a function of concentration, with a value of 8 min for 1.4 ppm tert-butylamine (Figure B.9). This is typical for ppm concentrations. Measurements on sub-ppm concentrations typically had a recovery time of less than 5 min and approached 3 min for ppb concentrations.

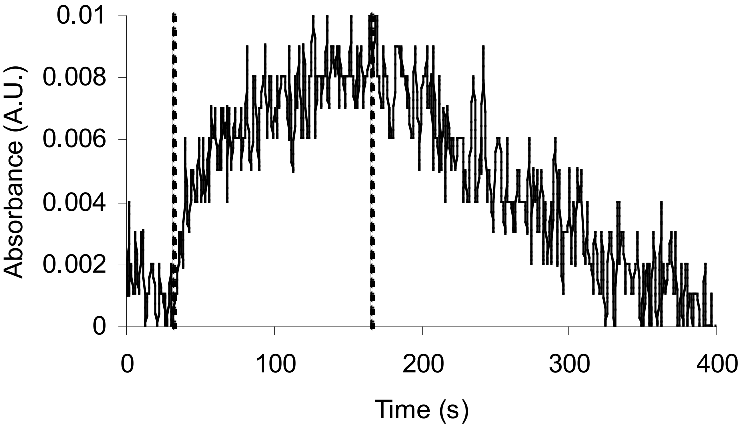

Figure B.10. Detector response for 1.4 ppb tert-butylamine, which approaches the detection limit for this sensor configuration, shown in Figure B.1. The lines marks the time of the flow of amine.

Detection Limit. At 1.4 ppb tert-butylamine vapor the absorbance was approximately 5 times the noise level (Figure B.10) and 1 ppb is hence the detection limit for the experimental arrangement employed in these studies. For these small concentrations it is important to not let the sensor dry out between measurements since the dry sensor is less sensitive than the sensor recently flushed with amine vapor.

Interferences. Analytes other than amines and ammonia could theoretically interfere with the sensor. Water, due its presence in most settings, is one of the most likely molecules that could present interference. Flushing the sensor with water vapor in ppm concentrations had little effect on the sensor response, however. In addition comparable gas concentrations of methanol, acetone, ether and dichloromethane showed no detectable response from the sensor.

Onida et al[19]. investigated a similar silica system and also did not see any interference from common polar molecules and concluded that the basicity of the amine was responsible for the color change. The only compounds that would interfere with the amine measurements would then be substances more basic than the adsorbed dye. Very few molecules have comparable basicities and interference is hence not expected to be a problem in common settings.

B.5. Conclusions

A new optical sensing method for detecting low-concentration amine vapors down to ppb levels has been described. The sensor is based on the spectral properties of the pH indicator Bromocresol green, adsorbed onto a silica sphere matrix. The sensor’s inherent simplicity and ease of manufacturing should make it attractive for further development.

The sensor easily detects sub ppm concentrations of common aliphatic amines and has a linear response up to 2 ppm. The detection limit is below 1.4 ppb, which makes this sensor more sensitive than comparable optical amine sensors in the literature. The response varies with temperature, allowing for adjustment to prioritize sensitivity or speed. The responses for each sensor were reproducible and fully reversible.

The sensor displays different levels of sensitivity for each amine tested. This is due to the basicity of the amine and its ability to hydrogen bond to the silica surface. Derivatization of the silica would enable the creation of sensors that are more selective. An array of chemical sensors, each with a different derivatization, could then determine both the concentration and identity of amines.

B.6. Acknowledgements

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