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Development of a Hydrogen Sulfide End-of-Service-Life Indicator for Respirator Cartridges Using Cobinamide

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Abstract

An inexpensive paper-based sensor was developed for detecting low ppm concentrations of hydrogen sulfide gas. A piece of filter paper containing aquohydroxocobinamide [OH(H₂O)Cbi] was placed on the end of a bifurcated optical fiber, and the reflectance spectrum of the OH(H₂O)Cbi was monitored during exposure to 10.0 ppm hydrogen sulfide gas (NIOSH recommended exposure limit). Reaction of sulfide (HS[−]) yielded an increase in reflectance from 400–450 nm, and decrease from 470–550 nm. Spectral changes were monitored as a function of time at 25, 50, and 85% relative humidity. Spectral shifts at high-er humidity suggested reduction of the Cbi(III) compound. The sensor was used to detect hydrogen sulfide breakthrough from respirator carbon beds and results correlated well with a standard electrochemical detector. The simple paper-based sensor could provide a real-time end-of-service-life alert for hydrogen sulfide gas.

Keywords

Optical Sensor; Diffuse Reflectance; Aquohydroxocobinamide; Hydrogen Sulfide; End-of-Service-Life Indicator

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Supplementary Material

Additional information is available and noted throughout the text.

1. Introduction

Persons who may be exposed to hydrogen sulfide (H_2S) in the workplace are recommended to wear a self-contained breathing apparatus (SCBA) or an air-purifying respirator (APR) fitted with NIOSH-approved cartridges for H_2S [1]. When the carbon in APR cartridges becomes saturated, the cartridge's "end-of-service-life" (ESL) has been reached. Metal oxides, among other chemical impregnants, are added to the carbon for enhanced removal of low molecular weight gases, but saturation still occurs. The carbon within a cartridge becomes saturated from the front to the back of the cartridge, ultimately leading to breakthrough— i.e., penetration of the gas through the cartridge [2]. Currently, no definitive method exists to determine when ESL occurs while a respirator is being worn. Prior to 1976, the smell or irritation of a gas was used to indicate breakthrough, but by the time a user can smell a gas, dangerous concentrations may already be present within the respirator. According to OSHA regulation 1910.134, sensory warning properties cannot be used to determine cartridge change-out [3]. Software models provided by respirator manufacturers are currently used to help users estimate when breakthrough will occur [4]. Unfortunately, the user may not be aware of unpredictable input data for the model such as types and concentrations of toxic chemicals, relative humidity, and breathing rate. In addition, most of the software models were developed from organic vapor data.

In 1984, NIOSH published standards for certifying sensors that indicate imminent breakthrough to encourage sensor development [5]. These standards provide criteria for certifying both passive and active end-of-service-life indicators (ESLIs and AESLIs, respectively [6]) and require that a sensor indicates when 90% of the carbon is saturated, without hindering normal use of the respirator [2, 7]. The sensors are designed to be embedded in the back part of the carbon bed of a cartridge, enclosed in a clean environment. AESLIs are intended to provide a real-time alert (e.g. flashing LED) when the cartridge is near its maximum absorption capacity and vapor breakthrough is imminent. Current challenges in developing APR sensors are the effects of humidity, selectivity, size, weight, and power restrictions. Additionally, manufacturers prefer to limit sensor costs to about \$1 per cartridge, and \$20–\$50 for sensor-related fixtures and electronics [5]. Only a few colorimetric and qualitative ESLIs are commercially available, e.g. for mercury vapor; these rely on subjective visual identification of a color change [8, 9]. For passive colorimetric ESLIs to be effective, the user must routinely monitor the sensor for color change [2]. This is inappropriate in poorly-lit environments, fogging respirators, or for color blind persons. Currently, no NIOSH-certified AESLIs exist.

H_2S is a corrosive and flammable gas that can be lethal at concentrations >500 ppm [10]. It is commonly used or produced in oil and gas refining, waste water treatment, mining, tanning and pulp and paper processing industries [11]. Both acute and chronic H_2S exposure can be injurious to humans. Known for its characteristic "rotten egg" smell, many workers believe the distinct odor is a suitable means for detecting H_2S . However, a person can become "desensitized" due to olfactory fatigue within 15 min of exposure to low H_2S concentrations (100–150 ppm) or more rapidly at higher H_2S concentrations [12]. Although early odor detection of H_2S is beneficial, NIOSH and OSHA stress that odor is not a reliable indicator, especially at elevated H_2S concentrations. Thus, appropriate respiratory protection

with an ESLI is required. Although the number of fatalities associated with H₂S is not known, the recent surge in oil and gas extraction in the United States increases the occupational risk of H₂S exposure. The NIOSH C (“C” = ceiling, 10 min maximum) Recommended Exposure Limit (REL) for H₂S is 10 ppm, with an immediately dangerous to life or health concentration of 100 ppm [1]. Thus, a person should not be exposed to concentrations above 10 ppm H₂S for more than 10 min during a 10-hr workday. Exposure to low H₂S concentrations can cause stress and anxiety, while high H₂S concentrations can cause loss of consciousness, permanent brain damage, or death [13].

Portable electrochemical detectors are commonly used to detect H₂S. Typical detectors have a range of 0.0–500. ppm H₂S, with limits of detection ~0.5 ppm and common resolutions of 1 ppm [14, 15]. Although widely used and offering moderate to high sensitivity, electrochemical detectors and other common H₂S detection systems (e.g., gas chromatography with various detectors) are too large and costly to be useful as an ESLI incorporated into the carbon bed of a respirator. Spectroscopic detection methods offer moderate to high sensitivity, miniaturized designs, low power requirements, and detection limits in ppb–ppm range. Paper is a good substrate for real-time, low-cost sensors; it offers a bright, high-contrast backing for spectrometric applications and is highly porous with a large surface area, advantageous for rapid diffusion of gas-phase analytes. A potential disadvantage of paper is inhomogeneous coating of the indicator, which can cause diffusion and poor reproducibility.

Cobinamide (Cbi), a cobalt-centered Vitamin B₁₂ derivative, is known to have a high affinity for cyanide (CN[−]), but can also bind up to two sulfide (HS[−]) ions [16–18] (Cbi structure is shown in Figure 1, where the X and Y ligands can be OH[−], H₂O, HS[−], or CN[−]). At neutral pH in water, Cbi exists as the mixed aquo-hydroxo complex OH(H₂O)Cbi, termed aquohydroxocobinamide [18]. H₂S, a reducing agent, reacts with (H₂O)₂Cbi(III) in three consecutive and rapid steps[16]:

1. Complex formation:

1b. Addition of second HS[−] at higher concentrations:

2. Inner-sphere electron transfer and reduction of Cbi:

3. Addition of second HS[−] to Cbi(II):

The main product formed is a complex of Cbi(II) with $\dot{S}SH_2^{2-}$ [16]. Reduction of cobinamide yields a color change from red-orange (with a peak absorbance at ~510 nm) to a pale yellow observed (in Supplementary Information; Figure S1). Here, the distinct spectral shifts exhibited by the reaction of Cbi with H₂S was used to generate a simple paper-based diffuse reflectance sensor. Cobinamide [OH(H₂O)Cbi] was chosen as the indicator because it has a

high affinity for HS^- and is currently under study as a H_2S -poisoning antidote [17]. Recently, Cbi $[\text{CN}(\text{H}_2\text{O})\text{Cbi}]$ on paper showed rapid detection of hydrogen cyanide (HCN) with characteristic spectral shifts at 583 nm [19]. Here, $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ on paper will be used to study the effects of reaction with H_2S to determine if a dual-ESLI could be developed, or if an interfering effect from H_2S would occur.

2. Experimental

2.1 Chemicals and Materials

Aquohydroxocobinamide, $[\text{OH}(\text{H}_2\text{O})\text{Cbi}](\text{Co(III)})$ was synthesized from hydroxocobalamin as previously described [20]. A bench-top ultraviolet-visible (UV-VIS) spectrometer (Thermo Scientific Evolution 300) was used to determine the concentration of cobinamide stock solutions using a molar extinction coefficient of $2.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ [21]. Sodium sulfide (Na_2S ; flakes, technical) and ascorbic acid were purchased from Fisher Scientific and dissolved in 1 mM NaOH (Fisher Scientific, certified) or deionized water, respectively. Stock H_2S gas was purchased at concentrations of 1001 ($\pm 2\%$) ppm, 10.0 ($\pm 5\%$) ppm, and at $>99\%$ purity from Matheson. All gases were balanced in nitrogen. Gelman Sciences A/E Borosilicate Glass fiber filter paper (without binder, 330 μm thick, and 1 μm pore size) was used as the support media. Deionized water was from an 18 M Ω -cm deionized in-line water system (Thermo Scientific Micropure). Cartridges designed for protection against H_2S were used for breakthrough experiments.

2.2 Preparation of Paper Substrates

Glass fiber paper was cut into uniform 6.0 ± 0.5 mm diameter circles. A volume of $15.00 \pm 0.02 \mu\text{L}$ of $50.0 \pm 0.2 \mu\text{M}$ Cbi was placed onto the center of each piece of paper leading to $\sim 0.9 \mu\text{g}$ $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ per paper. The $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ solution diffused uniformly across the paper circle and the wetted paper was allowed to dry fully for 1 h at room temperature ($\sim 21^\circ\text{C}$). These conditions yielded a reflectance spectrum with acceptable signal-to-noise ratio at 500 nm (1.8×10^4). The spotted papers were stored at 4°C .

2.3 Diffuse Reflectance Instrumentation

When light interacts with a paper's surface, the incidence light can be reflected, interreflected, refracted, absorbed, transmitted, or a combination of these events. Diffuse reflected light (or nondirectional reflectance) is reflected at many different angles due to light scattering. Diffuse reflectance occurs with rough surfaces, including soil [22], paint [23], body tissues [24], crystals [25] and paper [26, 27]. A linear relationship of spectral intensity to sample concentration can be obtained from the Kubelka-Munk equation:

$$F(R) = \frac{(1 - R)^2}{2R} = K/S \quad (1)$$

where R is reflectance, K is the absorption coefficient, and S is the scattering coefficient. The Kubelka-Munk equation is the most common approach to interpret diffuse reflectance and make the data comparable to that of transmittance [287].

An Ocean Optics USB4000 UV-VIS-ES miniature spectrometer (200–850 nm) was used for diffuse reflectance measurements. Cbi-impregnated paper circles were inserted into a custommade, light-tight holder constructed of black, Delrin[®] plastic described previously and shown in Figure S2 [19]. Two holes in each side of the holder allowed H₂S to pass through the holder. The common end of a bifurcated fiber optic (Ocean Optics, core diameter 600 μm, fused silica) was connected to the bottom of the holder directly under the filter paper. The two distal branches of the fiber were connected to a tungsten halogen light source (Ocean Optics LLS, 215–2500 nm) and the USB spectrometer, respectively.

2.4 System Optimization

Integration time for individual scans was set at 300 ms to yield a signal that was 85% of the spectrometer's saturation value (limited by the A/D converter to 65k counts), while the number of scans-to-average was chosen to optimize signal-to-noise. The spectrometer software measures the intensity of reflected light returning to the detector from the paper and converts the data to an apparent absorbance; the term “apparent absorbance” is used here because the configuration is not in a traditional transmittance configuration, rather a reflectance configuration to reduce the overall footprint of the sensor. Apparent absorbance was converted to reflectance (Equation 2) and then to the Kubelka-Munk Function (Equation 1) by:

$$R=10^{-A} \quad (2)$$

where A is absorbance. Thus, the diffuse reflectance spectra—plotted as F(R)—will be used to study the spectral shifts upon H₂S exposure to Cbi.

2.5 H₂S Flow Experimental Setup

All H₂S exposure experiments were performed at the NIOSH/NPPTL facility in Pittsburgh, PA; full explanation of testing can be found online [29]. Two Interscan[®] electrochemical instruments (Model RM-17-0 and RM-17-2) specific to H₂S were used with detection ranges of 0.00–19.99 ppm (resolution 0.01 ppm) and 0–1000 ppm (resolution 1 ppm), respectively. The 0.00–19.99 Interscan[®] was used for the initial H₂S exposure experiments and to monitor effluent breakthrough concentrations from NIOSH-approved canisters. This detector was calibrated with the 10.00 ppm H₂S gas. The 0–1000 ppm Interscan[®] was used to verify the H₂S challenge concentration throughout breakthrough experiments and was calibrated with the 1001 ppm H₂S. Gas flow was controlled from a PC using a LabVIEW virtual instrument program (National Instruments). Percent relative humidity (%RH), temperature, test time, challenge and breakthrough H₂S concentration were stored by the software. Each instrument was calibrated before the start of each experiment.

The system was initially flushed with clean air (oil-free compressed air) at the desired %RH (no H₂S) for 1 h before each experiment and was evaluated by the electrochemical detector to ensure an initial reading of 0.00 ppm H₂S. A blank paper circle was placed in the sensor holder and the reflectance signal was defined as 100% reflectance at each wavelength. A piece of OH(H₂O)Cbi-impregnated paper was then placed in the holder and the appropriate reflectance spectrum recorded. In some experiments, the reflectance spectrum of the

OH(H₂O)Cbi-impregnated paper was designated as the “blank” when the goal was to monitor changes in the OH(H₂O)Cbi spectrum, termed “difference spectra”. For the purpose of this proof-of-concept, 10.0 ppm H₂S was the concentration of interest to expose to the Cbi paper sensor. This is because it is the NIOSH REL. Additional studies will be undertaken for further H₂S concentrations. Relative humidity levels of 25, 50, and 85 %RH at 25.0°C ± 2.5 °C were tested, which are standard %RH in NIOSH/NPPTL certification protocol [30]. These humidity values were evaluated because respirators are used in a wide range of climates with various temperatures and humidity. Air was pulled to the sensor at 1.0 (± 5%) liters per minute (LPM) to avoid back pressure build-up in the sensor holder. This flow rate does not simulate air flow through a canister, but was chosen for convenience to focus on studying the binding between H₂S and OH(H₂O)Cbi.

Three pairs of cartridges used for breakthrough studies were tested at 25°C ± 2.5°C at each of the three values of RH. The cartridges used were NIOSH-approved for protection against H₂S exposure, and were used per manufacturer-defined configurations. Each test was run at a continuous airflow of 64 LPM, with a challenge gas concentration of 1000 ppm H₂S. Each pair of cartridges was mounted into a test apparatus within an airtight testing chamber. A diverter valve allowed the challenge gas to flow into the testing chamber or to waste. The paper sensor (and associated spectrometer and light source) was placed on the effluent side of the cartridge. Air was pulled over the sensor at 1.0 LPM (± 5%) by a Gilian Air Sampling Pump (GilAir-3) from the downstream flow of the cartridges. The test ran until breakthrough of 15.0 ppm H₂S was detected by the Interscan[®]. Data will be presented for 10.0 ppm H₂S, the C REL. Apparent absorbance spectra were obtained at 0, 10, 30, 45 min (for higher %RH), and at 10.0 ppm H₂S breakthrough (time varied for each pair of cartridges). One pair of pre-exhausted cartridges (at 25 %RH) were stored in an airtight bag for 24 h and re-exposed to H₂S to determine if the Cbi paper sensor could rapidly detect imminent breakthrough.

3. Results and Discussion

3.1 Paper Substrate

Glass fiber filter paper was used as the sensor medium; in previous studies, this specific type of paper demonstrated larger reflectance signals, presumably because it is thicker than traditional cellulose filter paper and allowed more light to reach the detector in the presented reflectance configuration [19]. Additionally, glass fiber filter paper is less affected by water vapors. The concentration of Cbi concentration (50.0 ± 0.2 µM) was chosen to directly compare results with previously performed experiments of similar nature using HCN gas [19]. This Cbi concentration on paper was sufficient in detecting small changes in the Cbi reflectance spectrum; higher concentrations of Cbi on paper decreased the sensitivity to slight changes in H₂S concentration upon exposure, where lower Cbi concentrations had undesirable signal-to-noise ratios.

3.2 UV-VIS Spectra of Cbi and Na₂S

Figure 2 shows the absorbance spectra of a 50 µM OH(H₂O)Cbi solution on adding increasing amounts of Na₂S in 1 mM NaOH. The increase in absorbance from 400–450 nm,

decrease from 470–550 nm, and isosbestic points near 470 and 550 nm are similar to those reported for H₂S in solution under anaerobic conditions [16]. The absorption spectrum of the 50 μ M OH(H₂O)Cbi solution is similar to the diffuse reflectance spectra (plotted using the Kubelka-Munk function) of OH(H₂O)Cbi on glass fiber paper (Figure S3).

3.3 Cbi Detection of H₂S

The average apparent absorbance of OH(H₂O)Cbi on glass fiber paper (measured at 500 nm) was 0.15 ± 0.02 (F(R) value equal to 0.08 ± 0.02) with uncertainty in terms of 95% confidence interval. A 13 % relative standard deviation (RSD) was reported for n=7. The spectral changes that occurred on adding 100.0 μ M Na₂S to a OH(H₂O)Cbi solution and exposing Cbi-impregnated paper to 10.0 ppm H₂S for 1 min at 25 %RH under aerobic conditions (diffuse reflectance) were directly compared and are similar (Figure 3). Figure 4 shows the response of OH(H₂O)Cbi on paper (plotted as the Kubelka-Munk function) when exposed to 10.0 ppm H₂S for 1, 5, and 10 min at 25 %RH, where the initial spectrum of OH(H₂O)Cbi on paper was considered the blank (considered difference spectra). The increased signal at 400–450 nm, decreased signal at 470–550 nm, and isosbestic points near 470 and 550 nm are apparent and similar to those previously reported [16]. F(R) versus time of 10.0 ppm H₂S exposure can be seen in Figure S4. The average F(R) values from 400–450 nm increases, while those from 470–550 nm decrease upon H₂S exposure.

The responses of Cbi exposed to 10.0 ppm H₂S (using OH(H₂O)Cbi) and 5.0 ppm HCN (using CN(H₂O)Cbi) for 10 min exposure at 25 %RH were compared and shown in Figure 5 (experiments performed separately) [19]. 5.0 ppm is the NIOSH REL for HCN. Cbi has a high affinity for CN⁻ (10^{14}) and has been used to detect cyanide gas [18]. Different spectral shifts of the Cbi complex were observed for exposure to these two gases. A dual-ESLI sensor could potentially be developed for detection of both HCN and H₂S with identification of HCN by the characteristic signal at 583 nm (i.e. formation of dicyanocobinamide), and H₂S by the increase between 400–450 nm, isosbestic point near 470 nm, and absence of an isosbestic point at 531 nm (observed upon formation of dicyanocobinamide). The average blank signal of Cbi on glass fiber paper measured at 531 nm in terms of the Kubelka–Munk function is $3 (\pm 7) \times 10^{-7}$. Statistically, the limit of detection (LOD) in terms of the Kubelka-Munk function is 2.4×10^{-6} or 0.002 in terms of absorbance, using $\text{LOD} = 3\sigma \pm x$.

3.4 Effect of %RH on H₂S Detection

Increasing the %RH to 50% increased the signal from 400–450 nm and decreased F(R) signal from 470–550 nm. The spectral shifts for 10.0 ppm H₂S at 50 %RH are similar to those at 25 %RH, but at higher F(R) values, suggesting binding of one or two HS⁻ groups to Cbi forming (HS)(H₂O)Cbi, or (HS)₂Cbi, respectively (Figure S5). This observation may be attributed to water vapor adsorption by the paper, which may create a more solution-like medium for the reaction between H₂S and Cbi [31]. F(R) versus time exposure are shown in in Figure S6. The higher response could also be due to a smaller scattering cross-section for glass fiber paper as water fills the air-filled pores of the paper [31]. A small increase in signal from 550–700 nm was observed, which would cause a false positive error in detecting HCN using the characteristic 583 nm peak; data processing would be required upon sensor development. A comparison of Cbi detection for 10.0 ppm H₂S and 5.0 ppm HCN at 50

%RH is shown in Figure S7. The small increase from 550–700 nm observed for higher HS[−] concentrations [16], and here in ascorbic acid under both aerobic and anaerobic conditions. The formation of Cbi(II) using another reducing agent, glucose, also shows a small increase in signal at ~600 nm, with further formation of Cbi(I) showing an increase from 600–800 nm [32].

The spectral shifts observed for 85 %RH varied from those at 25 or 50 %RH. For comparison, ascorbic acid reduction of OH(H₂O)Cbi under aerobic (i.e. occupationally-relevant situations, Figure 6) and anaerobic (Figure S8) conditions showed similar spectral shifts. Bubbling H₂S through a cobinamide solution decreases absorbance at 349 and 520 nm, increases absorbance at 314 and 468 nm and generates isosbestic points at 470 and 550 nm (anaerobic conditions) [16]. Comparing the spectral shifts of reducing reagents (in solution) and H₂S (gas phase) indicates the spectral shifts were due to reduction of Cbi, presumably to the 2+ oxidation state. Additionally, spectral shifts of Cbi reaction with both glucose and nitric oxide (NO) as reducing agents reported an absorbance peak at 469 nm indicating formation of Cbi(II), similarly observed here at 85 %RH [32, 33]. Other reducing agents reported to reduce vitamin B₁₂ and cause similar spectral shifts include fructose [32], sodium borohydride [34], dithiothreitol [33], and sodium formate [34, 35]. Gas phase reducing agents will generally not be present in occupationally-relevant environments, with the possible exception of carbon monoxide, which reacts extremely slowly with vitamin B₁₂ (Co(II)) [36]. Therefore, carbon monoxide is not likely to cause an interference when using Cbi as the indicating reagent. Solution experiments were performed only for comparison of spectral shifts for Cbi + H₂S in the gas phase. Control experiments performed with OH(H₂O)Cbi on glass fiber paper at 85 %RH and 0.0 ppm H₂S did not show changes to the Cbi spectrum. Thus, the spectral shifts at higher %RH suggest reduction of Cbi(III) to Cbi(II) possibly forming [(H)S]Cbi(II), signifying a more effective reaction between H₂S and Cbi. A comparison of Cbi detection for 10.0 ppm H₂S and 5.0 ppm HCN at 85 %RH are shown in Figure S9.

3.5 H₂S Breakthrough of Cartridges

Breakthrough experiments were conducted to determine if the Cbi-based paper sensor could accurately detect H₂S breakthrough from cartridges. The sensor was placed downstream of the effluent gas and simultaneously compared with the Interscan[®] electrochemical detector. The average (n=3) F(R) responses at 10 and 30 min, and at 10.0 ppm breakthrough at 25 %RH are shown in Figure 7a. Figure 7b shows an example of the OH(H₂O)Cbi response at 400–450, 470–550, and 800 nm (used as reference for the entirety of the breakthrough experiment), plotted as 5 point moving average. The F(R) trends were simultaneously compared to the response from the H₂S-specific electrochemical detector. This detector's response is plotted as the second derivative of the concentration vs. time to easily visualize the start of breakthrough (Figure 7b). The complete breakthrough curve for the electrochemical detector can be seen in Figure 8. The Cbi-based sensor efficiently detected low H₂S concentrations breaking through respirator carbon beds, with increased slopes upon imminent breakthrough. The F(R) spectra at various time intervals were similar to those observed for direct exposure of H₂S to the Cbi paper sensor (no carbon bed). Slight variations (e.g. shift in isosbestic points) may be attributed to possible formation of

byproducts from the reaction with chemical impregnants. Without quantitative instrumentation (e.g. mass spectrometer), the final products could not be identified. A small increase in baseline (correlating to ~200 ppb H₂S) was observed on the electrochemical detector readout throughout the majority of the tests (Figure S11). This could be from a small amount of H₂S permeating through the carbon bed; this is common in cartridge testing varying significantly between brands and lots. The permeation could be attributed to vapor moving through the channels within the bed, or formation of chemical byproducts. The cumulative response—which would occur during a user's breathing—observed in the Cbi F(R) breakthrough curves was most likely attributed to the small amount of H₂S breakthrough, though a quantitative change in slope was found upon imminent breakthrough. Cbi also successfully detected breakthrough of HCN from respirator canisters where the F(R) response at 583 nm is plotted against the electrochemical detector response (Figure S11a). The diffuse reflectance response at various times throughout the experiment can be seen in Figure S11b where the spectral shifts are distinctively different than that of H₂S breakthrough—there is no increase from 400–450 nm and no change at 531 nm. HCN breakthrough experiments will be published elsewhere.

Longer breakthrough times were observed as a function of increased %RH. This is due to the solubility between H₂S and water vapor that is adsorbed to the active sites of the activated carbon. Both sensors detected low concentrations of H₂S, suggesting the paper sensor could detect imminent breakthrough in the desired amount of time. Larger F(R) values and closer correlation between the Cbi-based paper sensor and electrochemical sensor were observed for cartridges exposed to 10.0 ppm H₂S at 85 %RH breakthrough (Figure 9 and Figure S12). Although only one concentration of H₂S was studied for direct exposure to Cbi on paper (i.e. 10.0 ppm H₂S), the Cbi paper sensor clearly shows detection at lower concentrations upon imminent breakthrough of a carbon bed (less than 1.0 ppm according to the H₂S-specific electrochemical detector). Unlike traditional chemical sensors, a respirator ESLI must show response at a pre-determined concentration/location within the carbon bed. For an H₂S-specific ESLI, this would be at 10.0 ppm H₂S.

A cartridge that had prior breakthrough was also tested to determine if the paper sensor could rapidly detect H₂S on re-breakthrough, a hazardous situation when intermittent cartridge use occurs. Breakthrough did not occur immediately for this cartridge, suggesting H₂S had redistributed on the carbon and allowed a small increase in service-life. However, breakthrough occurred within 8.5 min compared to 45 min for a fresh cartridge pair (at 25 %RH). The average response of Cbi on paper from 400–450 nm and 470–550 nm corresponded well with the electrochemical detector (Figure 10).

The data suggest that Cbi on paper can rapidly detect imminent H₂S breakthrough which would indicate to the user that the cartridge must be immediately replaced, as per ESLI standards and user instructions [7, 37]. The sensor could eventually be incorporated into the carbon bed of a cartridge to detect, at minimum, 10% service-life remaining. The requirements for ESLIs in respirators are unlike those for conventional chemical sensors. Although the reaction of Cbi with H₂S is reversible, the event and indication of a gas/vapor reaching 90% within the cartridge needs to occur only once, thus an ESLI does not have to show reversibility [2].

4. Conclusions

An inexpensive paper-based optochemical sensor was developed for detecting low concentrations (10.0 ppm) of H₂S gas. Due to the low cost, small size, and ability to detect the NIOSH-recommended C REL concentration for H₂S gas, the sensor has potential to be used as an ESLI in respirators. Distinct spectral shifts were observed for the reaction of one or two HS⁻ groups binding to aquohydroxocobinamide, and the possible reduction of the Cbi(III) complex under conditions of higher humidity.

The Cbi sensor detected H₂S breakthrough from cartridges and breakthrough curves correlated well with a commercially available, H₂S-specific electrochemical detector. Therefore, incorporating the sensor into a cartridge and combining it with a warning signal (e.g. LED) could indicate to the user that the cartridge service-life has almost ended and that the cartridge must be replaced immediately.

The availability of small photodetectors, inexpensive optical fibers, and battery-powered LED light sources suggest that the simple diffuse reflectance configuration could be miniaturized to satisfy the size, cost, and power requirements of ESLIs. The paper medium and diffuse reflectance configuration is versatile and could be used for other gas colorimetric indicators. Soon to be reported elsewhere, the Cbi paper sensor also accurately detects breakthrough of HCN (and cyanogen) through CBRN respirator canisters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Biographies

Lee A. Greenawald is a Ph.D. candidate in the C. Eugene Bennett Department of Chemistry at West Virginia University and a physical scientist student trainee at the National Institute for Occupational Safety and Health in Morgantown, WV. She received her B.S. degree in Forensic Chemistry from Ohio University in 2011. Her research interests include the development of inexpensive and portable sensors that have potential to be used with a respirator to protect users against breathing toxic gases. She has presented at various analytical and forensic-related conferences.

Aaron J. Reeder received a M.S. in Chemistry from Carnegie Mellon University. He has been with the National Institute for Occupational Safety and Health for the past five years and is the lead technician in the air purifying respirator certification laboratory

Gerry R. Boss is a Professor of Medicine at the University of California, San Diego. A major area of his research interest is in developing countermeasures to toxic chemicals. He found that cobinamide is not only an effective cyanide countermeasure, but also that it could be used to quantitatively measure low amounts of cyanide.

Suzanne Bell is an associate professor in the C. Eugene Bennett Department of Chemistry and in the Forensic and Investigative Sciences Department at West Virginia University. Her research interests are in applied and forensic analytical chemistry, chemometrics, and forensic toxicology.

HIGHLIGHTS

- Aquohydroxocobinamide fixed on a paper substrate rapidly binds gaseous H₂S.
- Paper substrate is positioned at end of a bifurcated fiber optic in a diffuse reflectance configuration.
- Spectral shifts of aquohydroxocobinamide is monitored as a function of 10.0 ppm H₂S exposure time, relative humidity, and breakthrough from respirator cartridges.
- Increased relative humidity suggests reduction of the aquohydroxocobinamide compound to 2+ oxidation state.
- Detection of low concentrations of H₂S upon cartridge breakthrough correlated with an electrochemical detector, suggesting proof-of-concept as an inexpensive end-of-service-life indicator.

Figure 1.
Structure of cobinamide (Cbi).

Figure 2. Absorbance spectra of OH(H₂O)Cbi (solid line) upon addition of 0.0–300.0 μM Na₂S.

Figure 3.

Comparison of $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ solution spectra with Na_2S and diffuse reflectance spectra on glass fiber filter paper upon H_2S exposure. The Kubelka-Munk function is plotted for the diffuse reflectance spectra. (A). Aquohydroxocobinamide solution spectra for 50 μM $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ in solution before 100.0 μM Na_2S (solid line) and after Na_2S is added (dashed line). (B). Diffuse reflectance spectra for $\text{OH}(\text{H}_2\text{O})\text{Cbi}$ on glass fiber paper before 10 min exposure to 10.0 ppm H_2S gas (solid line) and after H_2S exposure (dashed line).

Figure 4.

Diffuse reflectance spectra where the reflectance spectrum of OH(H₂O)Cbi on glass fiber filter paper was designated as the “blank” (long dashed line) and response to 10.0 ppm H₂S exposure on glass fiber filter paper as a function of time of exposure: 1 min of exposure (dotted line), 5 min of exposure (short dashed line), and 10 min exposure (solid line).

Figure 5.

Comparison of the diffuse reflectance spectrum of OH(H₂O)Cbi on glass fiber paper exposed to 10.0 ppm H₂S at 25 %RH (dashed line) after 15 min and reflectance spectrum of CN(H₂O)Cbi on glass fiber paper exposed to 5.0 pm HCN at 25 %RH (dotted line) after 15 min. OH(H₂O)Cbi on glass fiber paper was subtracted out and referred to as the blank (solid line).

Figure 6.

(A). Diffuse reflectance spectrum of OH(H₂O)Cbi on glass fiber paper (solid line) and response to 10.0 ppm H₂S after 1 min (dotted line) and 15 min (dashed line). (B): UV-Vis spectra of OH(H₂O)Cbi before (solid line) and after mixing with 5:1 ascorbic acid under aerobic conditions (dashed line).

Figure 7.

(A). Average response of OH(H₂O)Cbi on glass fiber filter paper as a function of time of triplicate breakthrough experiments at 25 %RH. Diffuse reflectance spectra were recorded at 10 and 30 min into experiment, and at 10.0 ppm H₂S breakthrough. (B). Direct comparison of breakthrough curves of the electrochemical detector (dotted line, plotted as the second derivative), and Cbi paper sensor at 400–450 nm response (short dashed line), 470–550 nm response (dot-dashed line) and 800 nm response (solid line, as the reference) plotted as 5-point moving averages. T=0 represents time experiment started.

Figure 8. Electrochemical detector breakthrough curve from the respirator cartridges used in Figure 7b. Inset figure: Expansion of breakthrough curve at low concentrations of H₂S observed through entirety of experiment. Inset text box: H₂S concentration (ppm) at specific time points within experiment.

Figure 9.

(A). Average response of OH(H₂O)Cbi on glass fiber filter paper as a function of time into triplicate breakthrough experiments at 85 %RH. (B). Direct comparison of breakthrough curves of the electrochemical detector (dotted line, plotted as the second derivative), and Cbi paper sensor at 400–450 nm response (short dashed line), 470–550 nm response (long dashed line), and 800 nm response (solid line, as the reference) plotted as 5-point moving averages. T=0 represents time experiment started.

Figure 10.

Breakthrough curve of the pre-exhausted pair of cartridges at 25 %RH. Direct comparison of breakthrough of the electrochemical detector (solid line) and Cbi paper sensor at 400–450 nm response (short dashed line), 470–550 nm response (long dashed line), and 800 nm response (dotted line, as the reference) plotted as 2-point moving averages.