



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.

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1. Introduction

Persons who may be exposed to hydrogen sulfide (H₂S) 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 H₂S [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

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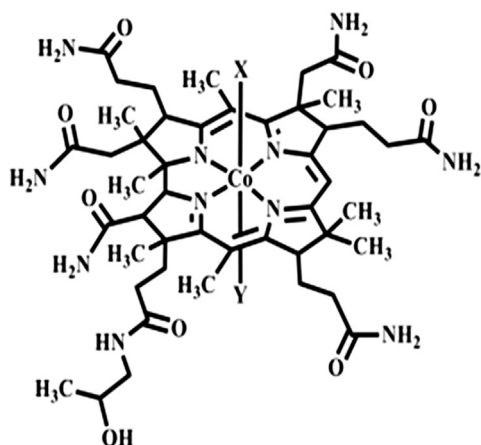


Fig. 1. Structure of cobinamide (Cbi).

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 AESLs exist.

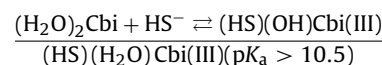
H₂S is a corrosive and flammable gas that can be lethal at concentrations >500 ppm [10]. It is commonly used or produced in oil and gas refining, waste water treatment, mining, tanning and pulp and paper processing industries [11]. Both acute and chronic H₂S exposure can be injurious to humans. Known for its characteristic “rotten egg” smell, many workers believe the distinct odor is a suitable means for detecting H₂S. However, a person can become “desensitized” due to olfactory fatigue within 15 min of exposure to low H₂S concentrations (100–150 ppm) or more rapidly at higher H₂S concentrations [12]. Although early odor detection of H₂S is beneficial, NIOSH and OSHA stress that odor is not a reliable indicator, especially at elevated H₂S concentrations. Thus, appropriate respiratory protection with an ESL 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-h 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 ESL 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.

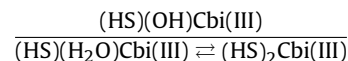
Cobinamide (Cbi), a cobalt-centered Vitamin B₁₂ derivative, is known to have a high affinity for cyanide (CN⁻), but can also bind up to two sulfide (HS⁻) ions [16–18] (Cbi structure is shown in Fig. 1, where the X and Y ligands can be OH⁻, H₂O, HS⁻, or CN⁻). At neutral pH in water, Cbi exists as the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

ing agent, reacts with (H₂O)₂Cbi(III) in three consecutive and rapid steps [16]:

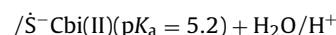
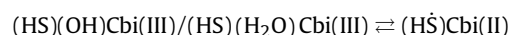
1.1. Complex formation:



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



1.2. Inner-sphere electron transfer and reduction of Cbi



1.3. Addition of second HS⁻ to Cbi(II):



The main product formed is a complex of Cbi(II) with $\dot{S}SH^{2-}$ [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; Fig. 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 H₂S-poisoning antidote [17]. Recently, Cbi [CN(H₂O)Cbi] on paper showed rapid detection of hydrogen cyanide (HCN) with characteristic spectral shifts at 583 nm [19]. Here, OH(H₂O)Cbi on paper will be used to study the effects of reaction with H₂S to determine if a dual-ESL could be developed, or if an interfering effect from H₂S would occur.

2. Experimental

2.1. Chemicals and materials

Aquohydroxocobinamide, [OH(H₂O)Cbi](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 (Na₂S; flakes, technical) and ascorbic acid were purchased from Fisher Scientific and dissolved in 1 mM NaOH (Fisher Scientific, certified) or deionized water, respectively. Stock H₂S gas was purchased at concentrations of 1001 (±2%) ppm, 10.0 (±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 MΩ-cm deionized in-line water system (Thermo Scientific Micropure). Cartridges designed for protection against H₂S 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 $\sim 0.9 \mu\text{g}$

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