

# A Novel Colorimetric H<sub>2</sub>S Measurement for Environmental and Oil and Gas Applications

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## ABSTRACT

This paper provides a novel colorimetric method to measure hydrogen sulfide in water, air, natural gas and oil. A bismuth ion based reagent reacts with sulfide to form bismuth sulfide nanoparticles, causing the solution to change color. The bismuth sulfide nanoparticles formed have limited quantum confinement effects and are kept in colloidal solution using the soluble polymer poly(acrylic acid). A linear relation between optical density and hydrogen sulfide concentration is observed, and it is proven that the reagent is reproducible and independent of the reaction environment. The lower limit of detection is dictated by the resolution of the optical spectrometer, and the upper limit is determined by the bismuth ion concentration in the reagent. This measurement range can be extended by using longer optical pathlengths or by changing the mixing ratio of reagent to sample.

**Keywords:** hydrogen sulfide, colorimetry, nanoparticles, sensor

## 1 INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) is found naturally in surface water and well water but also in many oil and gas fields. It is a flammable, colorless gas that smells like rotten eggs at low concentrations and is typically formed under anaerobic conditions. It is both toxic and a flammable gas; although it smells strongly of rotten eggs at first, it can cause olfactory paralysis at concentrations as low as 100 ppm. At 1000 ppm, H<sub>2</sub>S can be lethal within a few minutes. The presence of H<sub>2</sub>S is highly corrosive to metals, steel, polymers and even concrete. This process is considerably accelerated by low pH and the presence of carbon dioxide. Parts susceptible of damage should be replaced with H<sub>2</sub>S resistant materials at or above the NACE-specified critical concentration of 0.05 psi partial pressure.

There are many methods to measure H<sub>2</sub>S including iodometric titration, gas chromatography with a special sulfur detector and gas detection tubes. These methods are either cumbersome, inaccurate, or limited to use in a laboratory setting. In addition, lab measurements typically underestimate the sulfide concentration due to scavenging, oxidation and other losses during sampling and transport.

Currently, the lead acetate tape analyzer is the most common laboratory technique used to measure low concentrations of H<sub>2</sub>S. The measurement makes use of the principle of metal ions reacting with sulfide to form colored metal sulfides – in this case, H<sub>2</sub>S reacting with lead acetate to form a lead sulfide stain. The intensity of this stain is directly proportional to the concentration of H<sub>2</sub>S. The colorimetric method described in this paper uses the same chemical principle, but the resulting metal sulfides are instead kept in solution for optical interrogation. As a result, the measurement is as easy as mixing two fluids together followed by quantification with a portable spectrometer. This makes an onsite measurement possible, overcoming the problem of scavenging, oxidation, and other losses during transport to the lab. Furthermore, the method is accurate and less prone to operating errors.

## 2 CHEMISTRY

### 2.1 Metal Selection

Metal ions used for hydrogen sulfide sensing have to fulfill several requirements. The metal ions should be selective for sulfide, and the result should be a colored species to allow for optical detection. The size of the particles formed is also important and needs to fall within a specific range. Larger particles will precipitate more easily because of the large difference in density between water and metal sulfide. For example, lead sulfide has a density of 7.61 g/cm<sup>3</sup> compared to 1.00 g/cm<sup>3</sup> of water. Small particles, on the other hand, are semiconductor nanoparticles exhibiting quantum effects. These metal sulfides have size dependent optical properties. Variation in reaction conditions would change resulting particle size, which makes these effects undesirable for making a reproducible measurement.

Many metal sulfides are semiconductors which have a size-dependent band gap at small dimensions. The model derived by Brus[1] describes this effect for colloidal particles based on an effective mass approximation. The model is widely used although it has some discrepancies at the smallest particle sizes [2]. However, the model is sufficient to get an understanding about the influence of the particle size on the absorption spectrum. Pesika[3] described the energy ( $E'$ ) of the size dependent band gap of nanoparticles by:

$$E' = E_g + \Delta E \quad (1)$$

with

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e m_o} + \frac{1}{m_h m_o} \right] - \frac{1.8e^2}{\epsilon_2 R} + pt \quad (2)$$

where,  $E_g$  is the bulk semiconductor band gap;  $\hbar$  is the reduced Planck constant;  $e$  is the elementary charge;  $\epsilon_2$  the dielectric constant of the semiconductor;  $R$  the radius of the particle;  $m_o$  the mass of a free electron and  $m_e$  and  $m_h$  are the effective masses of the electron and hole respectively. The first term in the second equation is the kinetic energy of both the electron and the hole, and the second term is their Coulombic attraction. The polarization term ( $pt$ ) is given by:

$$pt = -\frac{0.124e^3}{\hbar^2 (4\pi\epsilon\epsilon_o)^2} \left[ \frac{1}{m_e m_o} + \frac{1}{m_h m_o} \right] \quad (3)$$

where  $\epsilon$  is the relative permittivity, and  $\epsilon_o$  is the permittivity of free space.

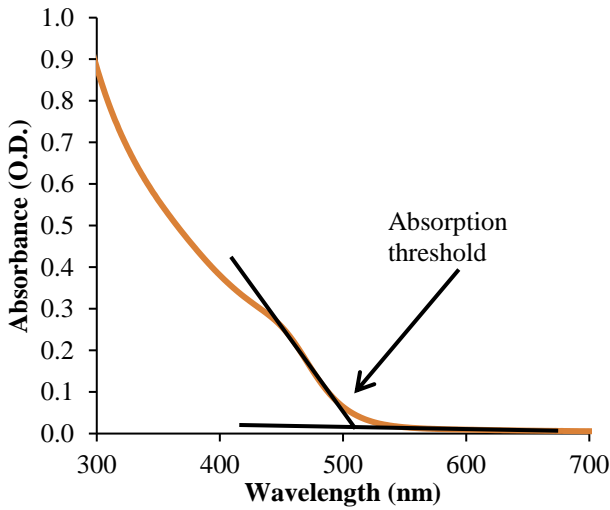


Figure 1: Definition of absorption threshold

The energy ( $E'$ ) is equivalent to the absorption threshold of the nanoparticle which is the wavelength at which absorption begins (Figure 1). The polarization term (Eq. (3)) is independent of particle size. The kinetic energy of the hole and the electron is reduced by increasing particle radius ( $R$ ) and so, bulk behavior is approached at larger diameters.

Chemical sensing with nanoparticles requires good reproducibility; thus, there is a need for reproducible particle size or particles with bulk characteristics. Particle size is dependent on reaction conditions including mixing method and temperature. The metal ion selected should form metal sulfide nanoparticles that grow to a size where no or minimum quantum effects exist but still remain small enough to avoid precipitation and optical scattering.

	$E_g$	$m_e$	$m_h$	$\epsilon_2$	ref
$\text{Bi}_2\text{S}_3$	1.57	0.68	0.8	10.9	[4]
CdS	2.4	0.19	0.8	5.6	[5]
PbS	0.41	0.11	0.9	18.2	[6]
ZnS	3.82	0.25	0.59	3.82	[5]

Table 1: Literature values used in the effective mass approximation model

The absorption threshold of several metal sulfides are shown in Figure 2. This figure shows that bulk like behavior of lead sulfide will require relatively large particles. Zinc sulfide, however, would be an excellent material but only absorbs in the UV range were many organic compounds can interfere with the measurement. Cadmium and bismuth are therefore the most suitable metals to be used for the detection of hydrogen sulfide. Bismuth was selected as the metal of choice for its non-toxicity and larger dynamic range of measurement. Based on the model with the parameters listed in Table 1, a maximum particle size just above 4 nm (see Figure 2) would be preferable whereas particle sizes close to 3 nm would be sufficiently independent of particle size while also preventing precipitation.

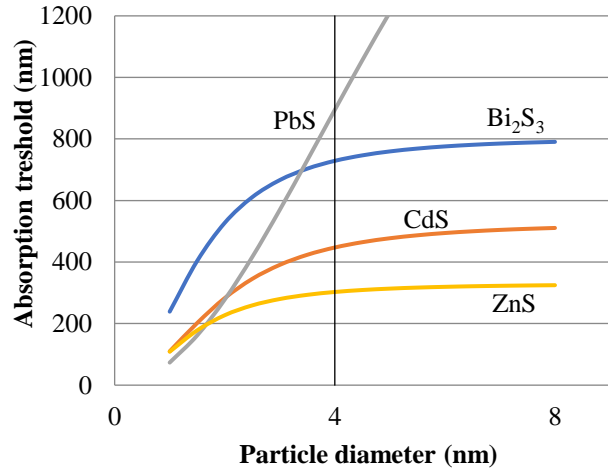


Figure 2: Wavelength of absorption threshold as function of the particle size for several metal sulfides

## 2.2 Stabilization of the $\text{Bi}_2\text{S}_3$ Nanoparticles

Most metal sulfides have limited solubility in water ( $\text{PbS} = 8\text{e-}28$ ,  $\text{CdS} = 8\text{e-}27$ ,  $\text{CuS} = 6.3\text{e-}36$ ,  $\text{Ag}_2\text{S} = 6.3\text{e-}50$ ,  $\text{Bi}_2\text{S}_3 = 1\text{e-}97$ ) [7]. They will form nanoparticles that will aggregate and precipitate. The  $\text{H}_2\text{S}$  sensor requires optical measurement of the color of the metal sulfides in solution, and it is therefore necessary to stabilize the nanoparticles and prevent precipitation for the measurement to be successful.

Many colloid suspensions contain polymers for steric stabilization. These polymers may be absorbed to the particles, chemically attached to their surfaces, or they may be free in solution. Metal sulfide suspended in a polymer containing solution will have a total potential energy ( $V_T$ ):

$$V_T = V_A + V_R + V_{Ster} \quad (4)$$

where  $V_A$ ,  $V_R$ , and  $V_{ster}$  are the potential energy of van der Waals attraction, electrostatic repulsion, and steric interactions respectively. The first two energies will have a minimal effect if the polymer layer is thick enough. Thin polymer layers will have a minimum in the total potential energy that will cause attraction of the nanoparticles. Therefore long polymers will have better changes of stabilization. A suitable polymer solution would have:

- High surface coverage
- Strong absorbance
- Good solvent for the polymer chain
- Low free polymer concentration.

High surface coverage and strong absorbance of the polymer are strongly correlated. Therefore, the first three requirements follow directly from the steric potential energy. The low free polymer requirement is described in the literature [8] as necessary to prevent depletion interaction.

Poly(acrylic acid) (PAA) was chosen from a wide series of soluble polymers for reasons beyond the scope of this paper. The polymer solution will be used under acidic conditions. The acid groups of PAA will have a strong interaction with the metal ions in solution preventing the precipitation of bismuth oxide. Furthermore, it will have a strong interaction with the metal sulfide nanoparticles and very good solubility in water, thus forming a stable suspension.

### 3 EXPERIMENTAL

Sodium sulfide was used as an analog for  $H_2S$  in testing and optimizing the chemistry of the  $H_2S$  measurement. Sodium sulfide is both safer and easier to handle than  $H_2S$  gas. Since the sodium sulfide was used in solution with water, it allowed for thorough liquid-liquid mixing of sulfide and measurement fluid to ensure accurate results. All chemicals were supplied by Sigma Aldrich and used without further purification.

**Bismuth reagent.** A 100 mM bismuth chloride was prepared in 5.3% hydrochloric acid. A solution of 1.75% by weight polyacrylic acid (PAA) and water was prepared by diluting PAA. A portion of the 100 mM bismuth stock solution was diluted in the 1.75% polyacrylic acid-water solution to make a 2 mM bismuth chloride-PAA-water solution. The pH of the solution was adjusted to pH 3 using 6N sodium hydroxide solution.

**Sodium sulfide solution.** A “100 mM” sodium sulfide solution was prepared in water. Precise standards cannot be prepared gravimetrically because the number of water

molecules of hydration varies greatly in the sodium sulfide hydrate. The actual concentration of this solution was determined by iodometric titration.

**Reaction series.** A series of reactions were carried out to construct a calibration curve at room temperature. Five 20 mL vials equipped with stir bars were filled with 4 mL of the prepared reagent. Sodium sulfide solution was added to each vial while stirring at 400 rpm. The spectrum of each reaction mixture was taken in a 2 mm pathlength cuvette using a Cary5000 spectrometer immediately after reaction completion.

### 4 RESULTS AND DISCUSSION

Figure 3 shows the optical absorption at 400 nm of the reagent after reaction with different amounts of  $Na_2S$ . The sensitivity at 400 nm is shown to be 0.838 OD/mM with an  $R^2$  greater than 0.99 (Figure 4). Repeat experiments showed a variance in sensitivity of less than 3%. The spread in sensitivity is remarkably small despite the fact that sodium sulfide is easily oxidized, absorbs water, and the iodometric titration, used to standardize the sodium sulfide solution, has a reported accuracy of 10%.

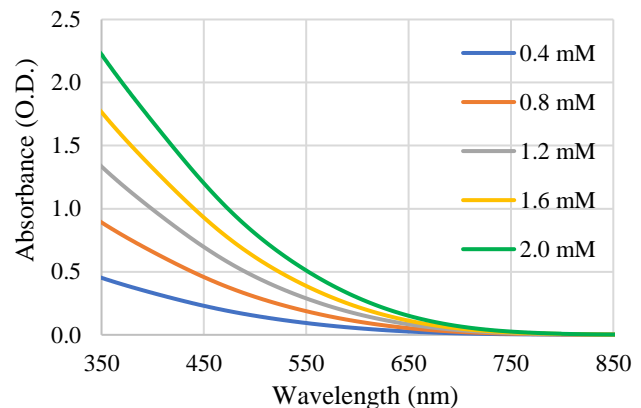


Figure 3: Absorbance curves at various amounts of sulfide

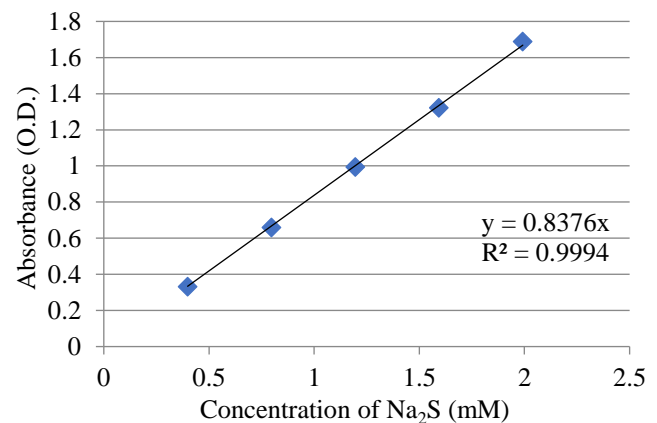


Figure 4: Response of reagent at 400 nm

The lower detection limit is determined by the resolution of the optical spectrometer. Conservatively estimating this limit to 0.01 O.D., the minimum concentration of sulfide that can be detected is less than 0.02 mM in the reacted solution. Assuming a mixing ratio of 1:1, this would mean a sample concentration of 0.04 mM. If necessary, the mixing ratio can be adjusted by adding more sample to detect even smaller concentrations, or the optical path length can be increased. The maximum concentration is set by the bismuth ion concentration in the reagent. The reagent works well up to just below stoichiometry or 3 mM sulfide in the sample. At excess sulfide concentrations precipitation starts to occur, most likely because the excess sulfide causes the nanoparticles to have a negative charge repelling the polymer and thus reducing its efficiency. However, the mixing ratio can be easily 20:1 (reagent:sample), extending the upper range to at least 60 mM. A total measurement range of 0.04 mM to 60 mM is achievable and further extension is feasible.

Figure 5 shows the optical absorption as function of energy. The optical absorption threshold is about 1.94 eV or 637 nm which is slightly shorter than the optimal wavelength. According to the effective mass approximation model with the parameters of Table 1 this would correspond to a maximum particle size of about 2.7 nm or just before the particle size where the bismuth sulfide curve in figure 2 plateaus. However, the small variation in absorption threshold with concentration between 635 nm and 645 nm for the highest and the lowest concentration respectively confirms that this particle size is sufficiently large for a good measurement.

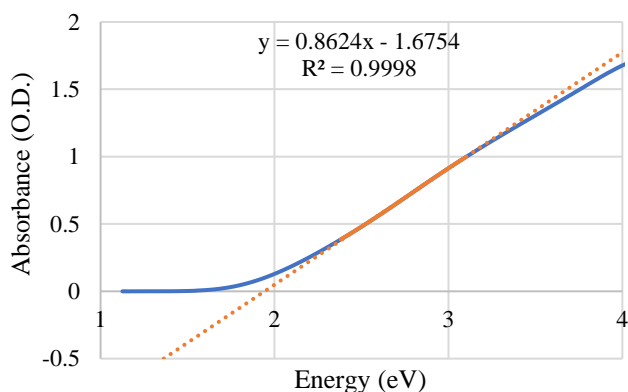


Figure 5: Determination of absorption threshold for 1.2 mM sulfide

## 5 CONCLUSION

A solution of bismuth ions, with poly(acrylic acid), a soluble polymer, can be used for the detection of H<sub>2</sub>S. The bismuth sulfide nanoparticles formed have limited quantum

confinement effects and have a maximum size of about 2.7 nm.

The optical density shows a linear relation with the sulfide concentration in the sample. The response is highly reproducible with less than 3% variation in sensitivity. The method is simple, and high-quality field measurements are feasible, reducing the need for sampling and lab measurements. It is demonstrated that the measurement range is at least 3 orders of magnitude between 0.04 mM to 60 mM with further extension feasible.

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