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Research Paper

Spectrophotometric chemosensor for determination of sulfide in aqueous solution through ternary complex formation with eosin Y and lead (II)

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Abstract

A chemosensor based on eosin for sensitive and selective determination of S^{2-} in 100% aqueous solution was designed on the basis of the complex formation between eosin and lead. According to the method linear dynamic ranges between 3.831 $\times10^{-6}$ to 20.15$\times10^{-5}$ molL^{-1}. The calibration sensitivities were also estimated to 2.553 $\times10^{-6}$, with a detection limit of 1.414 $\times10^{-6}$ molL^{-1}. No serious interference was evaluated during the analysis of at least 100-fold excess of various anion species such as SO_3^{2-},SO_4^{2-},$S_2O_3^{2-}$,$S_2O_8^{2-}$,SCN^-, CN^-,PO_4^{3-} ,HPO_4^{2-} ,F^- ,Cl^- ,Br^-, I^- ,CH_3COO^- ,CO_3^{2-},NO^{3-}. The suggested method was applied for the determination of sulfide in various water samples. Which gave satisfactory results. This method based on the decrease of absorbance at 516 nm which related complex between of eosin-pb with addition S^{2-}.

Keywords: sulfide, eosin ternary complex, chemosensor.

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Introduction

Because the concentration of sulfide species in environmental waters can influence the survival, fertility, and distribution of aquatic organisms [1], the expansion of analytical procedure for selective and sensitive determination of these compounds in water samples is of momentousness. Up to now, numerous analytical procedures have been expanded for quantifying sulfide. These contain electrochemical [2-5], colorimetric [6-9], resonance light scattering [10], and fluorometric [11-17] methods, to name a few. Among them, chemosensor methods have the advantage of high sensitivity and selectivity, facile, cheap, and available which makes them appropriate for determining sulfide levels in aquatic samples. In this research, we employed the eosin-pb complex as spectrophotometric probes for sulfide analysis. In this work, we rely on the interaction of sulfide with an eosin-pb to form a stable product and the following change in the absorbance at 514 nm upon this interaction. The high selectivity of the method arises from the employment of tendency sulfide to formation ternary complex with eosin Y and lead, was having little tendency to react chemically to many potential interfering species.

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Experimental section and procedures:

2.1. Materials

Sodium sulfide nonahydrate ($Na_2S.9H_2O$), and all other chemicals were from Merck with analytical grade and used as received without purification.

Stock solutions (1.0×10^{-1} mol L^{-1}) SO_3^{2-},SO_4^{2-},$S_2O_3^{2-}$,$S_2O_8^{2-}$,SCN^-, CN^-,PO_4^{3-},HPO_4^{2-},F^-,Cl^-,Br^-,I^-, CH_3COO^-,CO_3^{2-},NO^{3-} ions were prepared by direct dissolution of appropriate amounts of sodium or potassium salts of anions in deionized water. The standard working solutions were prepared day-to-day by serial dilutions with doubly distilled deionized water from stock solutions. Deionized water was used throughout all the experiments unless otherwise mentioned.

2.2. Apparatus

UV-Vis absorption spectra were recorded utilizing a Shimadzu spectrophotometer and a quartz cell of 1 cm path length. A Jenway 3510 pH-meter calibrated with Merck standard buffer solutions were used for measuring the pH of the solutions. A Hamilton syringe (25 µL) was used to inject small volumes of reagent into the cell.

2.3. General procedure

The temperature for all titration experiments was room temperature (25 ^{0}C). The 1.0×10^{-3} mol L^{-1} stock solution of eosin was prepared in H_2O media and the 1×10^{-4} mol L^{-1} solution was obtained by dilution. The 1×10^{-3} mol L^{-1} lead nitrate solution added to 1×10^{-4} mol L^{-1} eosin solution and stirred at room temperature. The formation of the eosin/pb^{2+} complex was completed after 2 hours. Then 2.5 mL of this solution was transferred to the quartz cuvette to record the UV-Vis absorption spectra immediately. Then, a proper amount of sulfide with a microliter syringe was directly added to the complex solution, and the UV-Vis spectra and optical responses were evaluated instantly.

2.4. Real sample analysis using the eosin-pb chemosensor assay

The empirical applicability of the eosin-pb chemosensor assay was appraised by analysis of sulfide in mineral water, and an industrial wastewater sample (collected from a food products company). The mixture was then centrifuged at 3900 rpm for 5 min to separate any precipitate. An appropriate volume of the supernatant was then added to a solution containing eosin-pb complex. The samples were analyzed utilizing the standard addition procedure.

Result and discussion:

3.1. The UV-visible response of eosin-pb to sulfide ions

The interaction of the eosin-pb complex with sulfide was studied in H_2O, through the UV-Vis absorption method under optimized experimental conditions. As can be seen in Figure 1, the eosin-pb solution absorption band dominated at 514 nm. The addition of sulfide ion causes increased to peak at 514 nm. Upon the successive addition of an incremental amount of sulfide to eosin-pb complex in H_2O, the maximum absorption at 514 nm started decreasing, and two isobestic points were observed at 545 nm and 451 nm. (Figure 1).

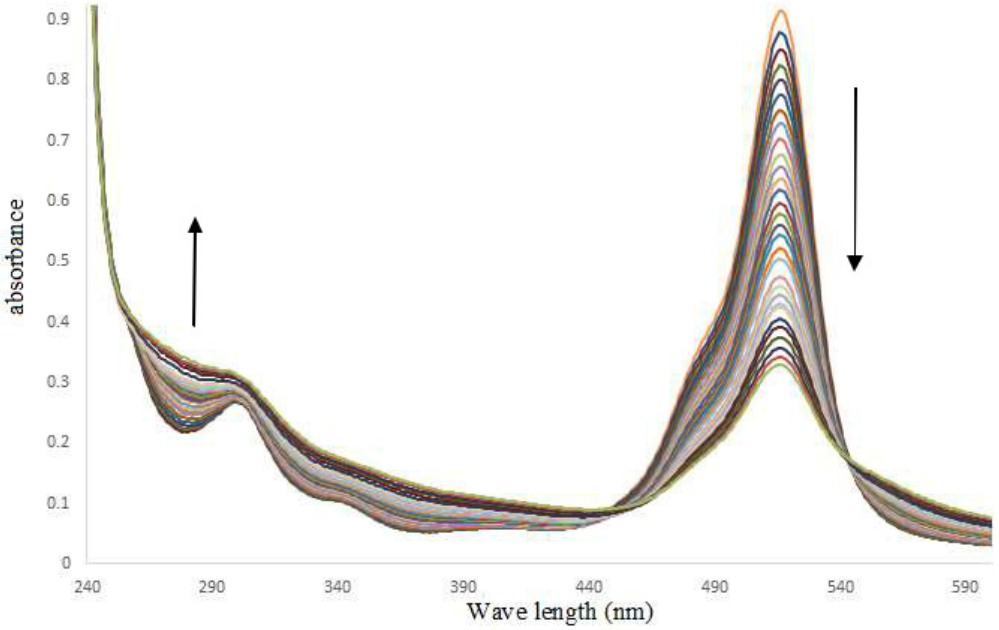

Fig 1: UV–Vis spectra of eosin-pb upon gradual addition of sulfide ion (3.831×10^{-6} to 20.15×10^{-5} $molL^{-1}$)

The binding affinity of eosin-pb to an equal amount of different anions (SO_3^{2-},SO_4^{2-},$S_2O_3^{2-}$,$S_2O_8^{2-}$,SCN^-, CN^-,PO_4^{3-} ,HPO_4^{2-} ,F^- ,Cl^- ,Br^- ,I^- ,CH_3COO^- ,CO_3^{2-} ,NO^{3-}) was also examined using the UV-Vis absorption changes and naked-eye detection. The addition of the mentioned anions did not cause any significant changes even up to 100.0 fold excess amount (Figure 2).

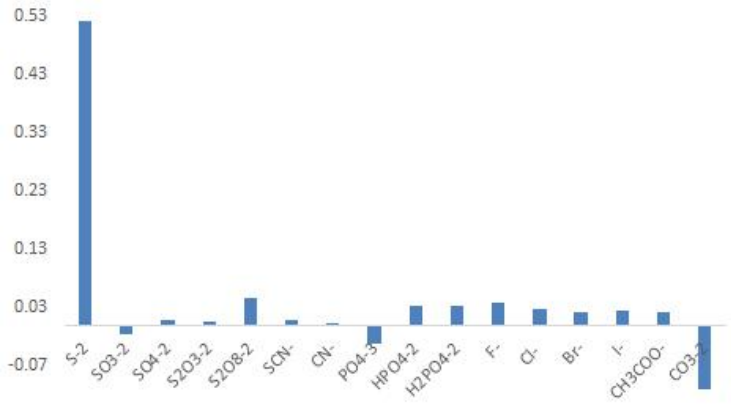

Fig 2: The UV-Vis absorption changes eosin-pb in H_2O media in the presence of 20.15×10^{-3} mol L^{-1} of different anions (SO_3^{2-},SO_4^{2-},$S_2O_3^{2-}$,$S_2O_8^{2-}$,SCN^-, CN^-,PO_4^{3-} ,HPO_4^{2-} ,F^- ,Cl^- ,Br^- ,I^- ,CH_3COO^- ,CO_3^{2-},NO^{3-}) and sulfide (20.15×10^{-5} mol L^{-1}).

These results are supported by the Benesi-Hildebrand plot analysis (Figure 3) where, according to the Benesi-Hildebrand equation (Equation 1), $1/(A-A_0)$ is plotted against$1/[S^{2-}]$ at λ_{max} = 514 nm.

$$\frac{1}{(A-A_0)} = \frac{1}{(A_{max}-A_0)}\left[\frac{1}{Kass[S^{2-}]^n}+1\right]$$

Equation 1. The Benesi-Hildebrand equation: A_0 is the absorbance of the receptor without analyte; A is the absorbance of the receptor with analyte; Amax is the saturated the absorbance of the receptor in the presence of an excess amount of analyte.

The linear relationship between $1/(A-A_0)$ and $1/[S^{2-}]$ affirms the 1:1 stoichiometry of the receptor and analyte.

The association constant, K_{ass}, is calculated to be $2.67(\pm 0.14)\times10^3$ mol L^{-1}.

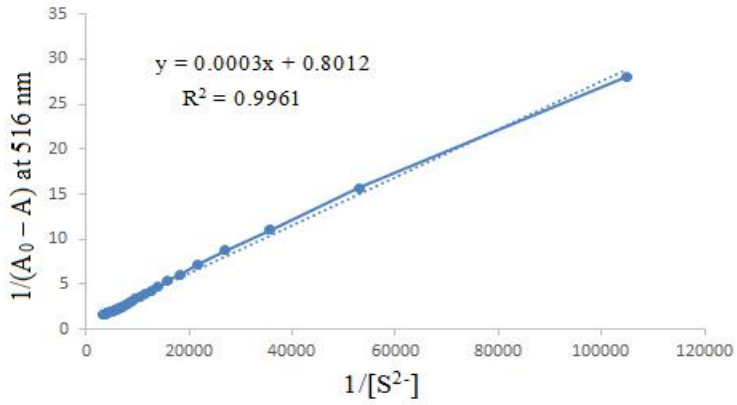

Fig 3: Benesi-Hildebrand plot of eosin-pb (the variation of $1/(A-A_0)$ at 514 nm versus the function of $1/[S^{2-}]$) based on 1:1 binding stoichiometry with sulfide ions

3.2. Optimizing pH of the solution

For the purpose of finding the suitable pH range, the effect of pH on the absorbance of eosin-pb and in the presence of sulfide ion was studied by UV-Vis spectroscopy. The pH range of 2.65 to 11.53 was selected for taking the measurements. The spectra were recorded before and after the insertion of S^{2-} (20.15×10^{-5} mol L^{-1}). As demonstrated in Figure 4, the addition of S^{2-} ion has the highest impact on the absorbance intensity in the pH close to 5.34. Hence, further studies of

UV-Vis spectroscopy were carried out at a pH equal to 5.34.

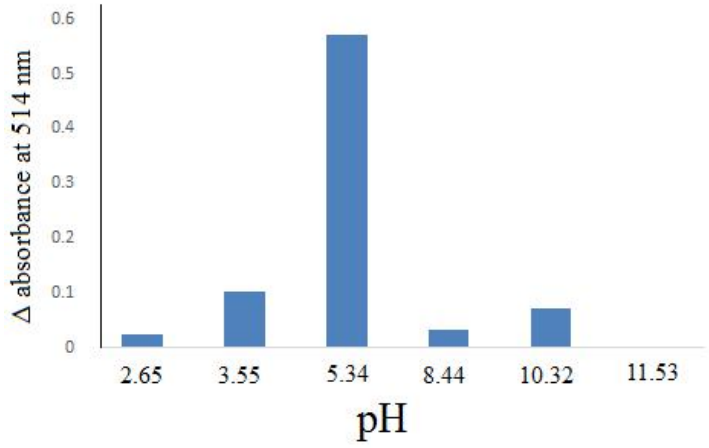

Fig 4: Effect of the pH on the absorbance changes of eosin-pb in the presence of sulfide ion (20.15×10^{-5} mol L^{-1}) at 514 nm in H_2O media.

3.3. Analytical figures of merit

As can be noticed from the plotted calibration curve (Figure 5), in the range of 3.831×10^{-6} to 20.15×10^{-5} molL^{-1} of sulfide, a good linear relationship is attained between the absorbance intensity and the concentration of sulfide, with the Coefficient of Determination, R^2, of 0.9962.

The Limit of Detection and the Limit of Quantification at λ_{max} = 514 nm were determined mathematically to be 1.414×10^{-6} and 3.715×10^{-6} mol L^{-1}, respectively. The repeatability of the method was evaluated by calculating the RSD from 10 replicates at the carbonate concentration levels of 13.33×10^{-5} mol L^{-1} and 37.04×10^{-6} mol L^{-1} and the obtained values were 1.05 % and 0.54 %, respectively.

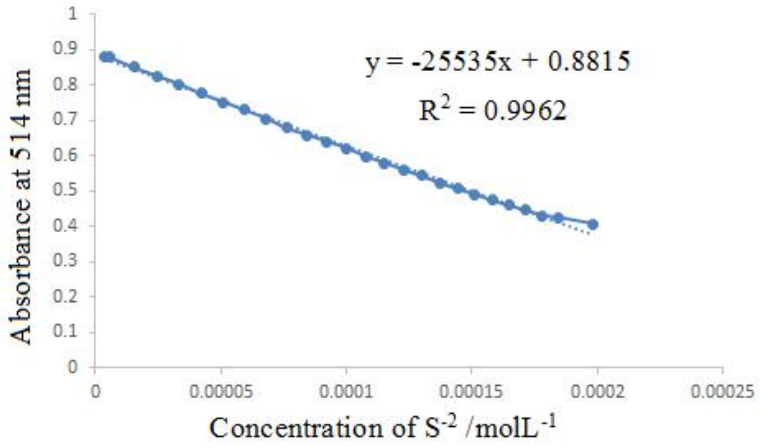

Fig 5: The linearly proportional relationship between the absorbance of the eosin-pb solution at 514 nm and the concentration of sulfide in H_2O

3.4. Analysis of real samples

In order to examine the practical applications, mineral water, and an industrial wastewater sample were analyzed for determining their sulfide ions content by the presented method. The samples were analyzed using the method of standard additions, in which known and different amounts of the analyte were added to the samples. As recapitulate in Table 1, good spike recoveries of 92.8–125 % were obtained for all of the samples. The results indicated no detectable sulfide in samples. To further assess the reliability of the method in determining sulfide in complex matrices, we spiked several mM sulfides into the sulfide-free industrial wastewater sample and analyzed the obtained sample with our chemosensor method. These results demonstrate the reliability of the proposed chemosensor assay to analyze sulfide in environmental samples.

Table 1: Determination of sulfide in real samples using the proposed chemosensor method

Sample	Added (μM)	Found (μM)	Recovery (%)
mineral water	0	0	----
industrial wastewater	0	0	----
industrial wastewater	4	5	125
industrial wastewater	7	7.5	107
industrial wastewater	14	12	92.8
industrial wastewater	25	25.4	101.6

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