



NOVEL SELECTIVE SPECTROPHOTOMETRIC METHOD FOR HYDROSULFIDE (HS⁻) IONS ASSESSMENT USING VITAMIN B₁₂ PRECURSOR, AQUACYANOCOBYRINIC ACID HEPTAMETHYL ESTER

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A simple spectrophotometric method with good selectivity and high sensitivity towards sulfide ions has been introduced. The method is based on the replacement of the axial water molecule of the aquacyanocobyrinic acid heptamethyl ester (ACCbs) reagent after the reaction with HS⁻ ions, and forming stable complex. ACCbs reagent is characterized with three distinguishable absorption bands with absorption maxima at 353, 497 and 527 nm. After adding HS⁻, a new absorption band at 582 nm has been obtained. The decrease of the absorption bands of the reaction product at 353, 497 and 527 nm and the enhancement of the band at 582 nm are quantitatively linear to HS⁻ concentration over the concentration range 0.02-1.543 μg mL⁻¹ with lower limit of detection 0.019 μg mL⁻¹. No noticeable interferences are caused by most common ions. Suitability for the assessment of HS⁻ in complex matrices without prior treatment was shown after validation of the method according to the standards of quality assurance. The results compare fairly well with data obtained using the standard method.

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can be also present in hydrogen sulfide pretreated fruits and vegetables. Therefore, rapid detection of hydrogen sulfide and its existing forms in aqueous media (total sulfides) has been gaining a great interest from researchers. In addition, to assure the quality control of manufactured products, a sensitive and selective method for sulfide determination is required.

Introduction

Sulfides (H₂S, HS⁻, and S²⁻) have been found in anoxic environments including natural water, wastewater, crude petroleum, natural gas and volcanic gases.¹ Hydrogen sulfide is a colorless gas that can exist naturally in groundwater. It is corrosive and can leach metals from plumbing systems into the water. Corrosion of metals by hydrogen sulfide forms a black precipitate that can stain laundry and bathroom fixtures, darken silverware, and discolor copper and brass utensils. Water that is giving off a distinctive smell is most likely contaminated with hydrogen sulfide.² It is also can enter a groundwater through sulfur-reducing bacteria present in groundwater well. These bacteria use sulfur as an energy source to chemically change sulfates to hydrogen sulfide. They can also use sulfur from decaying plants and other organic matter in oxygen-deficient environments. They can occur in deep or shallow wells, and reside in plumbing systems.³ In the human body, mercaptans are readily oxidized to their respective sulfides and, consequently, sulfide can be founded in animal halite. Animals showing signs of liver cirrhosis produce more sulfides in their bloodstream and halite. Thus, determination of sulfide could be used as a marker of liver diseases.⁴ Environmental sulfide concentration has been usually found in concentrations of μmol L⁻¹. For example, the recognition threshold range which hydrogen sulfide odor can be detected by humans is 0.30-90 μmol L⁻¹.⁵ Thus, the determination of sulfide is necessary in different human activities, but continues to present challenges due to the complexity of samples, and the necessity to determine low concentrations of sulfide. In addition to the above, sulfides

Various analytical methods for hydrogen sulfide quantification and monitoring have been reported. These include simple titrimetry.^{6,7} However, this method is not useful for measurement of low concentrations, not selective and requires sample pre-treatment. Other techniques and methods have been developed including electrochemistry,⁸⁻¹⁰ chromatography,¹¹⁻¹³ inductively coupled plasma-atomic emission spectroscopy,^{14,15} fluorimetry,¹⁶⁻¹⁸ and capillary electrophoresis.¹⁹

Many spectrophotometric methods have been reported in the literature for monitoring sulfide. Some of these methods are based on the inhibitory effect of sulfide ion on the reactions of peroxidase/pyrogallol and H₂O₂ system,²⁰ reducing effect on Fe³⁺/phenthroline complex,²¹ 2,6-dichlorophenolindophenol (DCPI),²² N,N-dimethyl-*p*-phenylenediamine/Fe³⁺,^{23,24} production of phenothiazine dyes,²⁵ nitroprusside,²⁶ 2-naphthoquinone-4-sulfonate,²⁷ and phenylseleno-nitrobenzoxadiazole derivative.²⁸

In this work, a novel spectrophotometric method is introduced for sulfide assessment. The method is based on the selective axial coordination of sulfide ion to the central cobalt atom in aquacyanocobyrinic acid heptamethyl ester (ACCbs) to cause significant changes in the spectrum of ACCbs reagent. The method offers a very high selectivity, sensitivity and accuracy for assessment of sulfide ions as compared with many of those previously reported methods. Application for determining sulfide in domestic wastewater and ground water samples gives precise results that agree fairly well with those obtained by the official method.

Experimental

Apparatus

All absorbance measurements were carried out using Shimadzu UV-vis spectrophotometer (Model UV-1601) with 1.0 cm light path length matched quartz cells. For all pH measurements, Orion digital pH/mV meter (Model SA 720) and an Orion combined glass pH electrode (Model 80-02) were used.

Reagents

All Chemicals and reagents used were of analytical grade and deionized water was used throughout. Sodium sulfide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, was purchased from Sigma-Aldrich. Phosphoric acid 85%, acetic acid (glacial) and boric acid were obtained from Fluka. Aquacyanocobester (ACCbs) was prepared as described previously.^{29,30} In brief, vitamin B_{12} was dissolved in methanol solution containing $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and was refluxed under nitrogen atmosphere for 4 days. The reaction mixture was then diluted with deionized water, neutralized with NaHCO_3 and treated with solid NaCN to produce dicyanocobester (DCCbs; violet color). The product is then extracted firstly with CCl_4 followed by CH_2Cl_2 . The solid is then collected after solvent removal. The purity of DCCbs was checked with HPLC using 4.6 mm x 256 mm column filled with TSK-Gel silica-60 stationary phase, dichloromethane (97.3 %) as a mobile phase and a 1 mL min^{-1} elution rate. Aquacyanocobester (ACCbs) was prepared by adding CH_3COOH to methanolic solution of DCCbs and adjusting the pH at 3. Formation of ACCbs was detected by the appearance of a characteristic absorption band at 353 nm. Universal buffer solutions were prepared by mixing 0.04 mol L^{-1} phosphoric, acetic and boric acids as reported³¹ followed by pH adjustment with $0.2 \text{ mol L}^{-1} \text{ NaOH}$.

Calibration curve and analytical procedure

A 2.5 mL of ACCbs ($3.5 \times 10^{-5} \text{ mol L}^{-1}$) working reagent solution, buffered with 0.04 mol L^{-1} universal buffer of pH 9, was transferred into 1.0 cm path light length spectrophotometer quartz cell (4 mL total capacity) then titrated with small aliquots of HS^- solution to obtain series of solutions containing 0.02 - $1.55 \text{ } \mu\text{g mL}^{-1}$ of HS^- ion and the absorbance was measured after 1 min at 353, 497, 527 and 582 nm, against a blank containing universal buffer adjusted to the same pH. The calibration plots between the absorbance changes at each wavelength against the sulfide concentration were constructed. All spectrophotometric measurements were in triplicate.

Determination of sulfide in wastewater samples

Domestic sewage water samples were collected and were filtered through Whatman filter paper no. 41 prior to analysis. A 2.5 mL portion of ACCbs reagent buffered with 0.04 mol L^{-1} of universal buffer (pH 9) was introduced in a 1.00 cm light path length cuvette and placed in the thermostated cell block of the spectrophotometer. A $100 \text{ } \mu\text{L}$ of the test sample was introduced to the cuvette, shaken and the absorbances at 353, 497, 528 and 582 nm were recorded.

Sulfide concentration was calculated from the calibration graph.

Wastewater samples were collected from sugarcane refinery factory, power plant and petrochemical industry, and filtered prior to analysis. A known volume, 1 mL of the effluent was introduced to a 10 mL volumetric flask and diluted to the mark with buffer at pH 9. For Power plant and petrochemical industry samples, 0.5 mL of the sample was diluted to 1 L with buffer at pH 9.

Results and Discussion

Characteristics of the absorption spectra

As previously reported,³² aqueous solution of ACCbs exhibits three distinct absorption bands with absorption maxima at 353, 497 and 527 nm. After the addition of HS^- , a new absorption band at 582 nm and three isobestic points at 365, 440 and 554 nm have been also obtained as shown in figure 1. In alkaline solutions (pH 9), the reaction of ACCbs with hydrogen sulfide is not straightforward. HS^- can act as both ligands and reducing agents in which coordination (thermodynamic factor) and reduction (kinetic factor) can occur.³³ It reacts with ACCbs in three consecutive and rapid steps at pH 9.0. The first is the formation of $(\text{HS})(\text{CN})\text{Cbs}^{(\text{III})}$ complex between aquacyanocobester and hydrogen sulfide ion. The second step is a short-lived intermediate via inner-sphere electron transfer with to form reduced cobester $[(\text{HS})\text{Cbs}^{(\text{II})}]$ or even super reduced cobester (+1 oxidation state). The third is the addition of a second HS^- ion to the already reduced cobester. Kinetics and mechanism of the reaction of hydrogen sulfide with cobalamin in aqueous solution have been previously described.³⁴ The equilibrium established between HS^- ion and ACCbs can be simplified and represented as shown in figure 2.

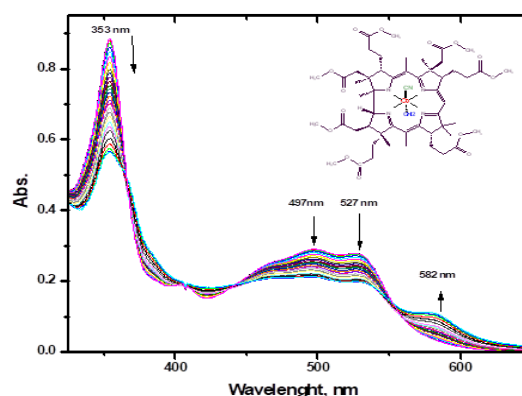


Figure 1. Absorption spectra of $[\text{ACCbs}]^+$ reagent ($3.5 \times 10^{-5} \text{ mol L}^{-1}$) of pH 9 with different concentrations of HS^- ion (0.02 - $5.5 \text{ } \mu\text{g mL}^{-1}$).

Optimum reaction conditions

The effect of pH on the stability of HS^-/ACCbs system was investigated by measuring the decrease of the absorbances at 353, 497 and 527 nm and the increase of the absorbance at 582 nm for a series of solutions containing $0.5 \text{ } \mu\text{g mL}^{-1} \text{ HS}^-$ ion and $2.6 \times 10^{-5} \text{ mol L}^{-1} [\text{ACCbs}]^+$.

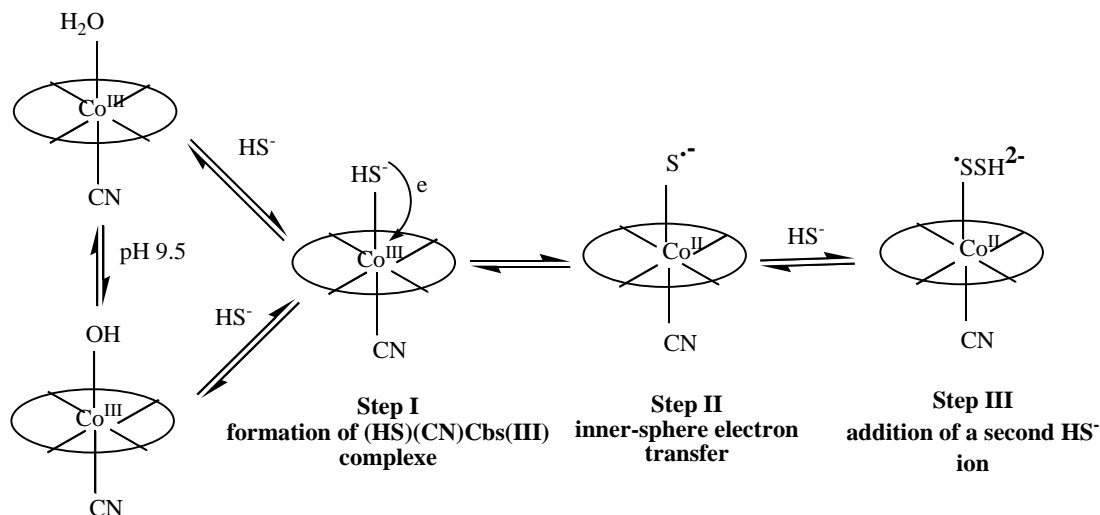


Figure 2. Schematic representation of the interaction of hydrosulfide ion with ACCbs.

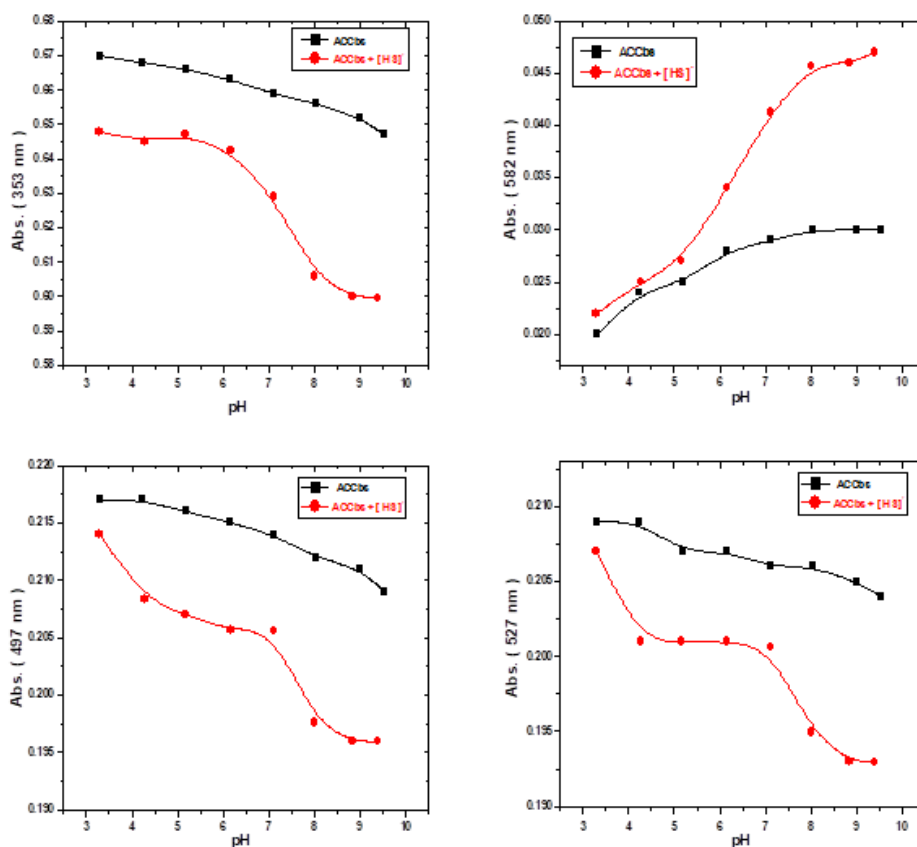


Figure 3. Effect of pH on the absorbance of $(2.6 \times 10^{-5} \text{ mol L}^{-1})$ $[\text{ACCbs}]^+$ reagent in absence and presence of $0.5 \mu\text{g mL}^{-1}$ hydrosulfide ion at different wavelengths.

The pH of each solution was adjusted at values ranging from pH 3-9.5 using 0.04 mol L^{-1} universal buffer. The absorbance-pH profiles reveal good response of the system at pH 9 as shown in figure 3. At $\text{pH} > 9$, OH^- interference takes place due to the formation of cyanohydroxocobester $[\text{HO}(\text{CN})\text{Cbs}]$ species. All subsequent measurements were made at pH 9.0.

Selectivity measurements

The selectivity of $[\text{ACCbs}]^+$ reagent towards HS^- ion was studied by measuring the absorbance of solutions containing fixed concentration of HS^- concentration ($0.72 \mu\text{g mL}^{-1}$), in the presence of a series of varied concentrations of different anions such as SCN^- , I^- , Br^- , Cl^- , NO_3^- , NO_2^- , HSO_3^- , SO_4^{2-} , HPO_4^{2-} , CN^- , oxalate, citrate and tartrate. The tolerance limit was taken as the amount

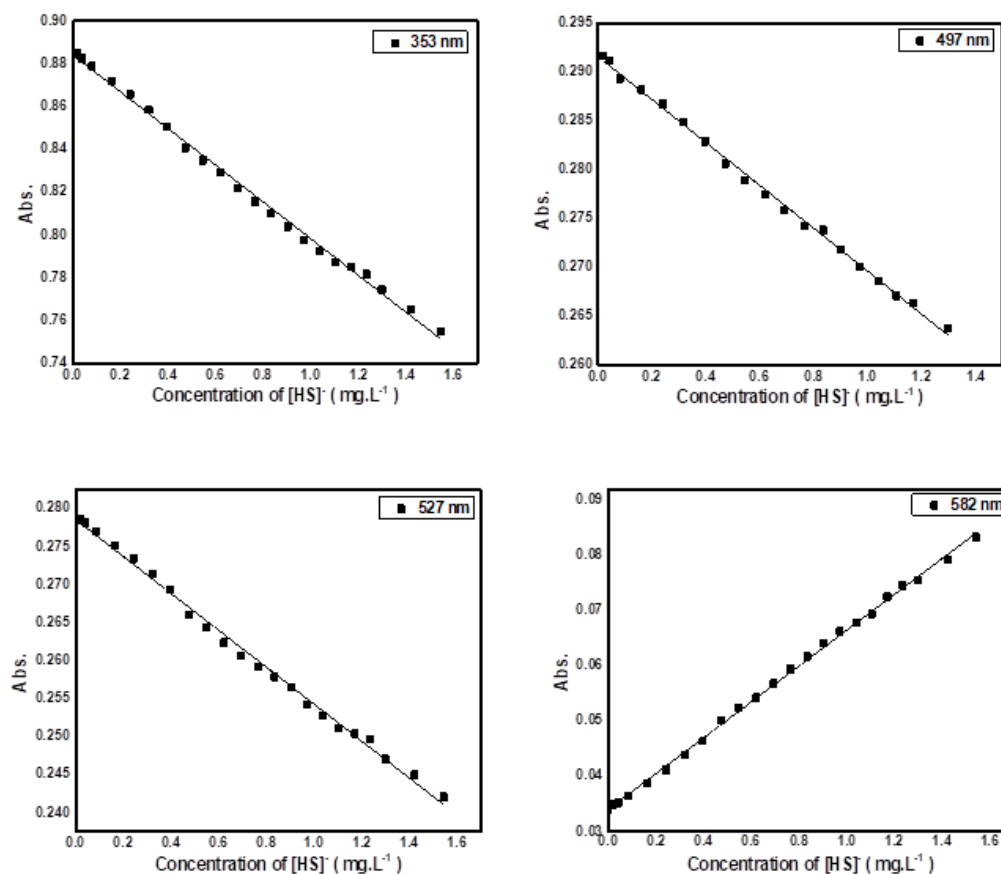


Figure 4. Calibration curves at different wavelengths of $(3.5 \times 10^{-5} \text{ mol L}^{-1})$ $[\text{ACCbs}]^+$ with HS^- ion (0.02 - $1.55 \mu\text{g mL}^{-1}$).

that causes $\pm 5\%$ error in the analytical signal at 353, 497, 527 and 582 nm for the formed HS/ACCbs complex. All anions used in selectivity measurements were in the form of sodium or potassium salts. As shown in (Table 1) that summarizes the tolerance limits of the tested anions, it was found that the method displays good selectivity towards HS^- in the presence of many common anions. The method, however, suffers from slight interference by iodide ion especially at 353 nm (γ -band). High interference from CN^- and SO_3^{2-} was also observed. This can be attributed to the high affinity of both cyanide and sulfite ions for coordination with cobalt atom in the axial position of the complex. Sulfite interference was eliminated by the addition of 1 mL of 0.1 % formaldehyde to 3 mL of test solution prior to each measurement.

Batch determination of hydrosulfide ion and calibration curves

Under optimized conditions, validation of the proposed spectrophotometric method for HS^- determination was done by measuring linearity range, lower limit of detection (LOD), accuracy (recovery), precision or repeatability (within-batch variability CV_w), between-batch variability (CV_b), standard deviation and sensitivity (slope). Six batches (six determinations each) were examined at each wavelength according to the quality assurance standards³⁵ and the results are given in Table 2.

Table 1. Tolerance limits (change in absorbance $\leq 5\%$) of some diverse ions on the reaction of aquacyanocobester with hydrogen sulfide ion ($0.72 \mu\text{g mL}^{-1}$).

Diverse ion	Tolerance ratio [DI : $[\text{Ag}(\text{CN})_2]$], w/w at λ			
	353	497	527	582
NO_2^-	180	120	280	380
NO_3^-	120	160	160	200
Cl^-	70	80	80	105
Br^-	60	90	80	80
I^-	20	22	22	22
SO_3^{2-}	0.65	0.9	0.8	1
SCN^-	75	85	85	120
SO_4^{2-}	100	110	110	110
Oxalate	160	220	180	240
Citrate	250	290	290	350
Tartarate	190	210	210	230
HPO_4^{2-}	150	160	160	160
CN^-	0.8	0.2	1.2	0.05

For HS^- determination, the absorbance change was linearly proportional to the HS^- concentration at 353, 497, 528 and 582 nm. Beer's law is obeyed over the concentration ranges of 0.04 - 1.543 , 0.04 - 1.3 , 0.04 - 1.543 and 0.02 - $1.543 \mu\text{g mL}^{-1}$ with a detection limit of 0.035 , 0.027 , 0.037 and $0.019 \mu\text{g mL}^{-1}$ at 353, 497, 527 and 582 nm, respectively (Figure 4).

Table 2. Performance characteristics of the proposed colorimetric method for measuring the concentration of HS⁻ ion.

Parameter	$\lambda_{\max}= 353 \text{ nm}$	$\lambda_{\max}= 497 \text{ nm}$	$\lambda_{\max}= 527 \text{ nm}$	$\lambda_{\max}= 582 \text{ nm}$
Linear range ($\mu\text{g mL}^{-1}$)	0.04-1.543	0.04-1.3	0.04-1.543	0.02-1.543
Detection limit ($\mu\text{g mL}^{-1}$)	0.035	0.027	0.037	0.019
Sensitivity ($\text{mL } \mu\text{g}^{-1}$)	0.086	0.022	0.024	0.032
Molar absorptivity ($\text{mol}^{-1}\text{cm}^{-1}\text{L}$)	9.43×10^4	2.41×10^4	2.66×10^4	3.55×10^4
Correlation coefficient (r^2)	0.996	0.997	0.996	0.999
Optimum pH	9	9	9	9
Standard deviation (σ %)	0.4	0.9	1.1	1.2
Between-batch variability (CVb %)	0.3	0.5	0.8	0.8
Within-batch repeatability (CVw %)	0.6	1.1	0.9	1.2
Accuracy (%)	99.5	98.7	98.4	99.1

Table 3. Spectrophotometric determination of [HS⁻] test solutions at different wavelengths in the same run.

Taken $\mu\text{g mL}^{-1}$	Recovery, %* at λ_{\max} nm			
	353	497	527	582
0.1	99.1±0.3	98.5±0.1	97.9±0.7	98.6±0.5
0.4	98.9±0.1	97.8±0.5	97.5±0.4	98.3±0.6
0.8	98.7±0.7	98.9±0.6	99.8±0.1	99.4±0.4
1.0	99.4±0.2	98.9±0.2	99.4±0.2	99.6±0.1

*Average of six measurements.

According to the IUPAC recommendations,³⁶ the lower detection limit was calculated as: $\text{LOD} = 3\sigma/S$ where σ is the standard deviation of the blank measurements ($n = 6$), S is the slope of the calibration curve. As shown in Table 3, it presents results obtained for assessment of internal quality control HS⁻ test solutions ($0.1\text{-}1.0 \mu\text{g mL}^{-1}$) by absorbance measurements at four different wavelengths in the same run.

A relative standard deviation of 0.3% and a mean average recovery of 98.7% were obtained. These data obtained support the application of this proposed method for quality control assessment of HS⁻ in various matrices.

Table 4. Sulfide assessment in real wastewater samples.

Wastewater sample	Sulfide content, $\mu\text{g mL}^{-1}$		Error (%)
	Proposed method	Standard method	
Sample 1	1.1±0.08	1.05±0.05	+4.51
Sample 2	0.81±0.04	0.84±0.03	-3.57
Sample 3	0.3±0.02	0.29±0.01	+3.33
Sugarcane refinery effluent	9.3±0.6	9.81±0.3	-5.14
Power plant	191.3±2.1	195.2±2.1	-2.03
Petrochemical industry	878.4±4.5	869.6±6.3	+1.01

Analytical applications

The proposed method was tested for the determination of sulfide in some domestic sewage water samples and an effluent formed from sugarcane factory. The results obtained for the analysis by the proposed spectrophotometric and the standard method,³⁷ are shown in Table 4.

The calculated Student means (t -test) from each method at 95% confidence level do not exceed the tabulated values. An F -test, show no significant difference at 95 % confidence level between the means and variances of the two sets of results.

Conclusion

Novel sensitive and selective spectrophotometric method is presented for sulfide determination in domestic sewage water samples. The method is based on the substitution of axial ligands of [ACCbs]⁺ reagent by HS⁻ ion for determination of HS⁻ ion with insignificant interference with most common ions. The reaction of HS⁻ with [ACCbs]⁺ is reversible reaction with stoichiometric ratio (2:1) at pH 9. Changes of the absorbances at 353, 497, 528 and 582 nm are linearly related to HS⁻ concentrations over the range of $0.04\text{-}1.543$, $0.04\text{-}1.3$, $0.04\text{-}1.543$ and $0.02\text{-}1.543 \mu\text{g mL}^{-1}$ with a detection limit of 0.035, 0.027, 0.037 and 0.019 $\mu\text{g mL}^{-1}$ for the previously shown wavelengths, respectively.

This recommended technique is distinguished by obtaining satisfactory results with simple and available reagents and it is simple, cheap, selective and highly sensitive technique for determination of traces of HS⁻ ion in aqueous solutions.

Advantages offered by the proposed method, compared with those previously suggested (Table 5) are the lower detection limit,^{23-25,27,28} the wider working range of measurements,^{20-24,27,28} the faster reaction time^{20-25,27,38} and less color reagent used.²⁰⁻³⁸

Table 5 Comparison of the recommended colorimetric method for determination of [HS]⁻ ion with other spectrophotometric methods

Reagents	λ_{\max} , nm	Linear range, $\mu\text{g mL}^{-1}$	Detection limit ($\mu\text{g mL}^{-1}$)	Major interferents	Working pH	Reaction time	Ref.
Peroxidase/pyrogallol and H ₂ O ₂	420	0.02 – 0.23	0.013	CN ⁻ , I ⁻ , Fe ³⁺ , Cd ²⁺ , Co ²⁺	6.5	4 min.	[20]
Fe ²⁺ /HS ⁻ / catechol/ p,toluidine	510	0.035 – 1.4	Not mentioned		0.1 M HCl		[21]
Fe ³⁺ / HS ⁻ /1,10-phenanthroline complex	510	0.035 – 1.4		NO ₂ ⁻ , NO ₃ ⁻ , SO ₂ , Fe ³⁺ , V ⁵⁺		Few minutes	
Mn ³⁺ /HS ⁻ /diphenylamine	570	0.14–1.40			5 M H ₂ SO ₄		
Mn ³⁺ /HS ⁻ / barium diphenylamine sulfonate	540	0.14–1.40					
2,6-dichlorophenolindophenol (DCPI)	520	0.01- 1.0	0.01	10% EtOH, used in halitosis treatments (Halita and Perio-Aid solutions)	12	2 min	[22]
N,N-dimethyl-p-phenylenediamine/Fe ³⁺	745	0.4 - 2.0	0.4	Not mentioned	Not mentioned	3 min	[23]
	745	0.17 - 1.0	0.04	Not mentioned	0.1 mol L ⁻¹ HCl	95 s	[24]
Production of phenothiazine dyes	520	0.25–3.0	0.033	I ⁻ , F ⁻	0.1 mol L ⁻¹ H ₂ SO ₄		[25]
	664	0.05–1.5	0.024				
	677	0.04–0.75	0.018				
	590	0.05–1.0	0.051				
Sodium nitroprusside	558	5000 - 15000	Not mentioned	Not mentioned	Not mentioned	30 s	[26]
Sodium 1,2-naphthaquinone-4-sulfonate (NQS)	320	0.5 - 20	0.16	CN ⁻ , SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , HCO ₃ ⁻ , IO ₃ ⁻ , PO ₄ ³⁻ , C ₂ O ₄ ²⁻ , CH ₃ COO ⁻	0.1 M HCl	60 min	[27]
Phenylselenonitrobenzoxadiazole derivative	551	0.33 – 3.30	0.069	-	4.8	-	[28]
Magenta	540	0.025 – 2.50	0.015	IO ₃ ⁻ , SO ₃ ²⁻ , Hg ²⁺ , Hg ⁺ , Pb ²⁺ , Cu ²⁺ , Ag ⁺	7	2.5 min	[38]
[ACCbs]+		0.02 – 1.543	0.019	CN ⁻ , SO ₃ ²⁻	9	1 min	This work

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