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ORIGINAL PAPER

Spectrophotometric determination of hydrogen sulfide in environmental samples using sodium 1,2-naphthoquinone-4-sulfonate and response surface methodology

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Abstract A simple spectrophotometric method for determination of hydrogen sulfide in wastewater and hot spring samples was developed. The method is based on the reaction between hydrogen sulfide and sodium 1,2-naphthoquinone-4-sulfonate (NQS). The effect of various experimental factors on the reaction between hydrogen sulfide and NQS was investigated and optimized using central composite design. The optimal values of the factors were 5.00×10^{-4} mol L^{-1} for concentration of NQS and 1.00×10^{-2} mol L^{-1} for concentration of hydrochloric acid. The wavelength of the maximum absorption of the reaction product was 320 nm. Constructed calibration curve for hydrogen sulfide determination was linear in the range of 0.5–20.0 mg L^{-1} with the detection limit of 0.16 mg L^{-1}. The method was free from interferences. Percent relative errors below 2 % were obtained for determination of hydrogen sulfide in environmental samples.

Keywords Hydrogen sulfide · 1,2-naphthoquinone-4-sulfonate · Central composite design · Environmental

Introduction

Water pollutants are of great public concern, and removal of them is of great importance (Gupta et al. 2012, 2013; Gupta and Saleh 2013; Saleh and Gupta 2011, 2012a, b, c; Saleh 2011).

Hydrogen sulfide is gaseous molecule that accumulates in the environment from geothermal and anthropogenic sources (Watts 2000). In environmental waters, decomposition of organic matter and the activity of sulfate-reducing bacteria lead to the formation of hydrogen sulfide (Patnaik 1999; Yao and Millero 1996). This gas is a very important pollution index for water (Colon et al. 2008). It exists naturally in crude petroleum, natural gas, hot springs and foods. Furthermore, it is also produced in large quantity in industrial activities and places such as petroleum/natural gas drilling and refining, wastewater treatment, coke ovens, tanneries, Kraft paper mills and landfills (Kim et al. 2005, 2006). Exposure to this colorless, flammable gas can trigger eye and respiratory tract irritation (Evans 1967). Therefore, easy, inexpensive and convenient signaling of toxic hydrogen sulfide is very important for the rapid assessment of this widely used and environmentally important species. Various analytical techniques for the detection of hydrogen sulfide have been reviewed (Lawrence et al. 2000; Pandey et al. 2012).

A standard method for detection and determination of hydrogen sulfide is gas chromatography (Hannestad et al. 1989; Furne et al. 2008; Pandey and Kim 2009). However, application of these methods is not simple and includes several stages. Hence, relatively simpler methods such as titration (Balasubramanian and Pugalenthi 2000), spectrophotometry (Evans 1967; Ferrer et al. 2004; Silva et al. 2001, 2003; Rodriguez-Fernandez et al. 1999; Kuban et al. 1992; Siegel 1965; Fischer 1883) and spectrofluorimetry (Rodriguez-Fernandez et al. 1999; Choi and Hawkins 1997; Axelrod et al. 1969; Spaziani et al. 1997; Gohda et al. 1986; Yang et al. 2000) have been introduced for this purpose.

In these conditions, more advanced instrumental methods have also been developed for determination of hydrogen sulfide like inductively coupled plasma-atomic

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emission spectroscopy (Pouly et al. 1999), hydride generation-atomic fluorescence spectrometry (Jin et al. 2007), electrochemistry (Lawrence et al. 2004; Spilker et al. 2008; Tsai et al. 2006; García-Calzada et al. 1999; He et al. 2002; Doeller et al. 2005), ion chromatography (Giuriati et al. 2004; Divjak and Goessler 1999) and chemiluminescence (Lawrence et al. 2000; Huang et al. 2007; Maya et al. 2007; Safavi and Karimi 2002; Du et al. 2001). However, development of simple methods which does not require sophisticated instruments is a permanent requirement.

In the present work, a simple spectrophotometric method for determination of hydrogen sulfide is proposed. 1,2-Naphthoquinone-4-sulfonate was used as reagent in acidic medium. This reagent has functional groups (Quinone) which can be reduced by hydrogen sulfide. The factors influencing the reaction were explored by response surface methodology.

Materials and methods

Apparatus

Recording of the absorption spectra in the spectral range of 200–500 nm was performed by an Agilent 8453 UV–Vis spectrophotometer with diode array detector, equipped with 1-cm path-length quartz cells. A Huber polystat model CC3 thermostat was employed for temperature control. A JENWAY ion-meter, Model 3345 was employed for adjusting pH.

Reagents and solutions

All of the chemicals used including sodium 1,2-naphthoquinone-4-sulfonate (NQS) and hydrochloric acid (Merck, Darmstadt, Germany) and sodium sulfide (BDH chemicals Ltd Poole England) were of analytical reagent grade and used as received without any further purification. Aqueous solutions were prepared in deionized water.

A 1.0×10^{-3} mol L^{-1} stock solution of NQS was prepared by appropriate amount of solid in deionized water. NQS solutions were freshly prepared for experiment any stage. A 10 mL stock solution of sodium sulfide with concentration of 500.0 mg L^{-1} was prepared in deionized water. For preparation of acidic solutions, appropriate volume of the concentrated hydrochloric acid (12.7 mol L^{-1}) was diluted by doubly deionized water.

Response surface methodology

Experimental design is a strategy to gather empirical knowledge based on the analysis of experimental data and not on theoretical models. An effective experimental design technique commonly used for process analysis and modeling is central composite design (CCD). For a given number of factors (f), this design is a combination of a two-level full factorial design with 2^f points, $2f$ axial points and N0 central points.

The central point for each factor is assumed to be middle of the two levels of the full factorial points, around which the design is supposed to be symmetric. The factors considered for the studied system are concentration of NQS (x_1) and concentration of hydrochloric acid (x_2) in mol L^{-1}. The low and high levels of these factors are 0.0001 and 0.0005 mol L^{-1} for NQS and 0.001 and 1.000 mol L^{-1} for hydrochloric acid. For a system with two factors ($f = 2$), CCD can be represented by points on a square, in which each axis corresponds to a factor and consists of 13 points (four full factorial points, four axial points and five arbitrary central points). Values of the factors in these thirteen experiments and obtained responses are shown in Table 1.

Procedure for calibration

A volume equivalent to 2.50 mL of the stock solution of NQS, 0.50 mL of hydrochloric acid solution with concentration of 0.1 mol L^{-1} and different concentrations of sodium sulfide were transferred into 5-mL volumetric flasks. Then, the mixtures were completed to the mark with deionized water. The mixture was mixed well, and the reaction was allowed to proceed at room temperature (25.00 ± 1 °C) for 60 min. The absorbance of the resulting solutions was measured against a reagent blank prepared with the same reagents concentration, but no sodium sulfide.

Sample preparation for determination of hydrogen sulfide in different water samples

All of the analyzed water samples (wastewater and hot spring) were collected and were filtered through a Whatman No. 41 filter paper, and the filtrates were transferred into 100-mL volumetric flask without dilution. In the analysis of the hot spring samples, after sampling, zinc acetate was added to the sample to trap hydrogen sulfide as zinc sulfide precipitate. For the analysis and releasing hydrogen sulfide in hot spring samples, pH of the sample was adjusted to 1.0 by adding hydrochloric acid and the sample was filtered and transferred into a 100-mL volumetric flask without dilution.

For the analysis of the real samples, a volume equivalent to 2.50 mL of the stock solution of NQS and 0.50 mL of hydrochloric acid solution with concentration of 0.1 mol L^{-1} were transferred into 5-mL volumetric flasks. The mixture was then completed to the mark with the

Table 1 Experiments based on the central composite design with two factors

Experiment number	NQS concentration (mol L^{-1})	Concentration of hydrochloric acid (mol L^{-1})	Response (absorbance change at 320 nm)
1	0.00030	0.50050	0.579
2	0.00010	1.00000	0.327
3	0.00050	0.00100	0.682
4	0.00050	1.00000	0.604
5	0.00030	0.50050	0.468
6	0.00030	0.00000	0.357
7	0.00030	0.50050	0.421
8	0.00030	0.50050	0.480
9	0.00006	0.50050	0.254
10	0.00030	1.09990	0.469
11	0.00030	0.50050	0.564
12	0.00010	0.00100	0.000
13	0.00054	0.50050	0.411

above real samples, and after 60 min, its spectrum was recorded. For spiking, after addition of different concentrations of standard sodium sulfide solution, the real sample was added to the mixture.

For each sample, five replicates were measured and mean of the predicted concentrations was reported. Based on these replicates, standard deviation was calculated and divided by mean of the results to yield percent relative standard deviation (RSD%) after multiplication by 100. Percent relative error (RE%) was obtained by dividing the difference between the predicted amount and actual amount to the actual amount multiplied by 100. Multiplication of the ratio of predicted amount to the actual amount by 100 will give percent recovery.

Results and discussion

Due to the leachability of sodium sulfide as hydrogen sulfide with time, the reagent grade sodium sulfide must firstly be standardized. In the second step, the condition of the reaction between NQS and hydrogen sulfide should be optimized. In the optimal conditions, the reaction was employed to build a relation between the signal and hydrogen sulfide concentration.

In the next step, the constructed calibration was used to determine hydrogen sulfide in the environmental samples. In the last part of the work, the characteristics of the method were compared with the related published works.

Standardization of sodium sulfide stock solution

A volume equivalent to 2.0 mL of freshly prepared sodium sulfide reagent solution with concentration of 500.0 mg L^{-1} was transferred into a conical flask. After adding 5.0 mL of a standard iodate solution (0.005 mol L^{-1}), and 0.291 g potassium iodide (KI), the solution was acidified with 0.5 mL of sulfuric acid, the solution was allowed to stand for 10 min, and excess of the iodine was titrated by standard sodium thiosulfate solution. Starch solution was added when the color of the solution became pale straw. After addition of starch solution, immediately the color was changed to deep blue-black. The titration was continued until the color changes from deep blue-black to colorless. Similarly, the blank titration was performed. The difference between titration values of the blank and sample was used for calculation of sodium sulfide contents in stock solution. Calculations based on the results of titration revealed that the purity of the reagent sodium sulfide solution is 28.8 %.

Reaction between hydrogen sulfide and NQS

In acidic media, sulfide is considerably in the form of hydrogen sulfide. It can be simply realized from the pKa_1 and pKa_2 values of hydrogen sulfide (7.02 and 13.88, respectively). In a solution with concentration of hydronium ion close to 0.1 mol L^{-1}, more than 99.99 % of the sulfide is in the form of hydrogen sulfide.

In the reaction with NQS, hydrogen sulfide reduces the carbonyl groups of NQS to hydroxyl ones. To prove this change, FTIR spectrum of NQS and the product of its reaction with hydrogen sulfide were recorded (Fig. 1). As can be seen in the spectrum of the product (Fig. 1b), broad band at 3505 cm^{-1} has been evolved. This band is the characteristics of the stretching of the O–H bond (Gupta et al. 2011a, b; Saleh 2015a, b; Saleh et al. 2014). It can be noted that this band cannot be seen in the FTIR

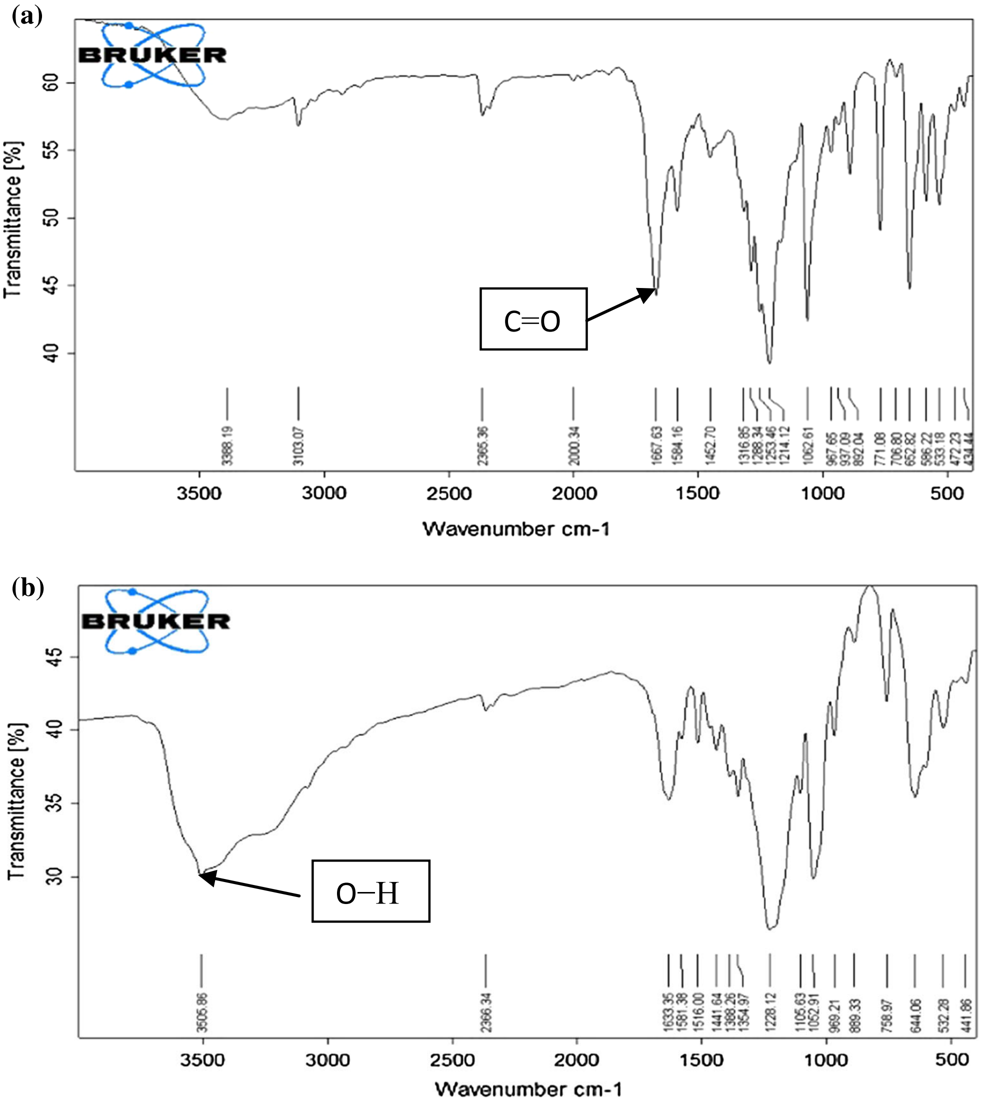
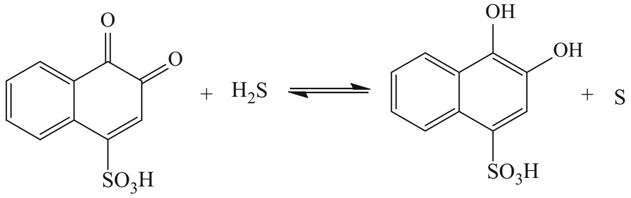


Fig. 1 FTIR spectrum of **a** NQS in hydrochloric acid medium and **b** NQS in the presence of hydrogen sulfide

spectrum of NQS (Fig. 1a). In aryl ketones, the stretching of the C=O occurs at 1680–1700 cm^{-1} (Saleh 2015a, b; Saleh et al. 2011). For NQS, this band has been shifted to the lower wavelengths and can be seen at 1668.64 cm^{-1} (Fig. 1a). However, as can be seen in Fig. 1b, the intensity of this band has been decreased. Moreover, diketones have characteristics at 1540–1640 cm^{-1} (Gupta et al. 2011a, b) which can be simply observed in Fig. 1a. It can clearly be observed in Fig. 1 that the peak located at 1668.64 cm^{-1} decreases in intensity accompanying by the evolving the band at 3505 cm^{-1} assigned to O–H bond. This indicates the reaction between NQS and hydrogen sulfide.



Scheme 1 Proposed reaction between NQS and hydrogen sulfide

Based on the inspection of the FTIR spectra, the reaction between hydrogen sulfide and NQS can be shown as in Scheme 1. Hydrogen sulfide acts as a reducing agent, and carbonyl groups are reduced to hydroxyl groups. Sulfur can be considered as another product of the reaction.

Absorption spectra

In Fig. 2, the absorbance spectra of NQS in acidic medium and in the presence of hydrogen sulfide in optimal

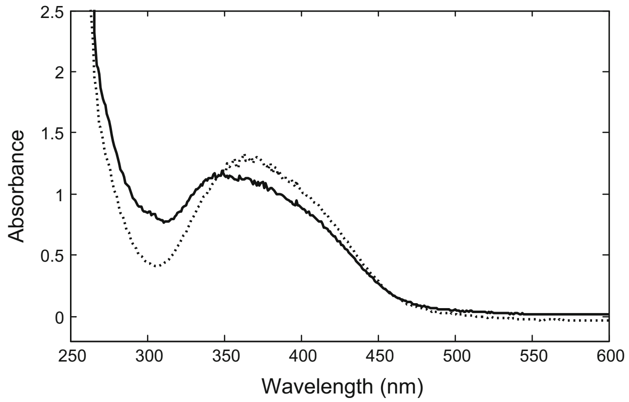


Fig. 2 Absorbance spectrum of NQS (5.00×10^{-4} mol L^{-1}) in hydrochloric acid (1.0×10^{-2} mol L^{-1}; *dotted line*) and NQS (5.00×10^{-4} mol L^{-1}) in hydrochloric acid (1.0×10^{-2} mol L^{-1}) in the presence of hydrogen sulfide (5.00 mg L^{-1}; *solid line*)

conditions are shown. Wavelength of the maximum absorption of the product is located at 320 nm.

NQS possess a broad absorption peak with maximum located at about 360 nm (Fig. 2). In the presence of hydrogen sulfide, maximum of this absorption peak shifts to 345 nm. Moreover, a new peak at about 320 nm appears. Upon addition of hydrogen sulfide to the solution of NQS in optimal conditions, a decrease in absorbance at 360 nm and an increase in absorbance at 320 nm can be seen.

Response surface methodology (RSM) and optimization of factors

Response surface methodology (RSM) is a method of experimental design used for the optimization of chemical reactions and/or industrial processes. Whenever several factors influence the response, RSM can be utilized to assess the relationship between dependent (response) and independent variables (factors) as well as to optimize the relevant processes. Experimental design methodology involves simultaneous changing the level of all the factors from one experiment to the next because the factors can influence each other, and the optimal value for one of the factor might be related to the values of the others. CCD as a response surface method was originally developed by Box et al. (1951) and later on improved upon by Box and Hunter (1957).

In Table 1, the responses of the experiments designed based on CCD have been included. The closeness of the responses of the replicate experiments (experiments 1, 5, 7, 8 and 11 in Table 1) is the sign of the precision of the experiment process. The relation between the response and the factors can be shown by the following polynomial equation:

Table 2 Results of ANOVA for the experiments and responses reported in Table 1

Term	Coefficient	p^{a}	F^{b}
Constant	0.494	0.000	
x_1	0.167	0.004	17.11
x_2	0.056	0.210	1.91
x_1x_1	−0.086	0.127	2.99
x_2x_2	−0.031	0.556	0.38
x_1x_2	−0.101	0.096	3.69
Regression		0.025	5.25
R	0.888		

[a] Probability value

[b] *F* statistics

$$\text{Response} = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1x_1 + b_{22}x_2x_2 + b_{12}x_1x_2$$

where b_0 is the average of the results of the replicated center point. The coefficients b_1 and b_2 are the main half-effects of the variables x_1 and x_2, respectively. b_{11} and b_{22} are the squared effects, and b_{12} is the two-factor interaction effect.

Analysis of variance (ANOVA) of the experiments (Table 1) is given in Table 2. The regression between the response and factors (model) is reliable due to the high correlation coefficient ($R = 0.888$) and very low p value (0.025) of the regression. This p value indicates that the variation in the response is mainly (about 88.8 %) due to the variation in the factor levels. Among the linear terms, the concentration of NQS (x_1) is highly significant. This is reflected in the very low calculated p value (0.004) and high F statistics (17.11). Interaction between the studied factors is relatively important. This can be realized from the calculated p value for the term x_1x_2 in Table 2. None of the squared terms is significant at the 95 % confidence level since corresponding p values are high.

After performing ANOVA, the response surface of the full quadratic model was depicted. Via the surface, the relations between the response and the effective factors are graphically shown. The surface is shown in Fig. 3. The surface shows that for maximizing response, in the low levels of x_2 (concentration of hydrochloric acid), higher amounts of x_1 (concentration of NQS) is needed. On the other hand, when concentration of hydrochloric acid increases, the response is higher at moderate levels of concentration of NQS. This is the concept of the interaction between the factors which was realized by considering p values in the preceding paragraph. The optimal value for each factor which leads to the best response (the highest absorbance intensity) can be extracted from response surface. The response optimizer was used to give the values of the factors for which the response is higher. The result is

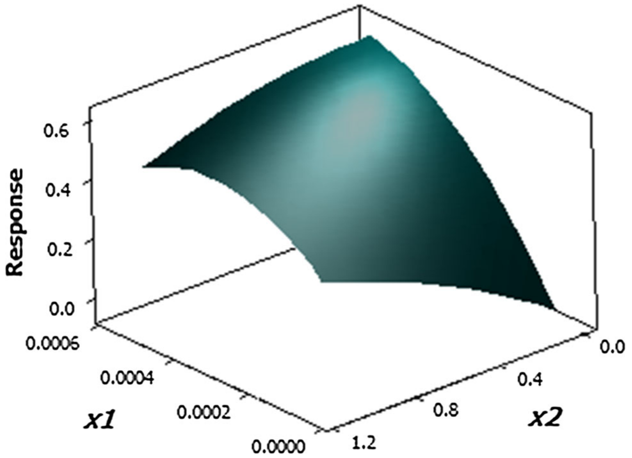


Fig. 3 Response surface obtained by the model with coefficients reported in Table 2 and factors x_1 (concentration of NQS) and x_2 (concentration of hydrochloric acid)

Table 3 Statistical results of the calibration of hydrogen sulfide using the proposed method

Parameters	Characteristic
Color changes	Yellow to colorless
Wavelength (nm)	320
Molar absorptivity (L mol^{-1} cm^{-1})	1.4×10^3
Linear range (mg L^{-1})	0.50–20.00
Number of samples	11
Intercept of calibration curve	0.0114
Slope of calibration curve	0.0456
Correlation coefficient	0.997
F statistic of the model	1642.68
Limit of detection (mg L^{-1})[a]	0.16

[a] Calculated as DL $= 3s_B/m$, s_B is the standard deviation of the blank and m is the slope of the calibration curve

5.00×10^{-4} mol L^{-1} for x_1 and 1.00×10^{-2} mol L^{-1} for x_2.

The coefficient of the concentration of NQS (x_1) is positive (Table 2), and it is the largest coefficient in Table 2 except for the constant term. This indicates the importance of the concentration of NQS in the studied reaction. From Fig. 3, the significant effect of concentration of NQS (x_1) on the response is clearly observed. The coefficient of concentration of hydrochloric acid (x_2) is positive, but it is smaller than the coefficient for x_1. Therefore, x_2 is not as important as the concentration of NQS in the studied reaction. This can be simply inferred from Fig. 3.

Analytical data

In order to examine the applicability of the recommended method for determination of hydrogen sulfide, the absorbance of a series of solutions containing varying concentrations of hydrogen sulfide in the optimal conditions was recorded against the corresponding reagent blank at 320 nm. The univariate calibration curve was linear in the range of 0.50–20.00 mg L^{-1}. The statistical parameters of the constructed calibration curve are summarized in Table 3. As data in Table 3 show, the linear range of the method for determination of hydrogen sulfide is relatively wide.

Application to the real samples

Before application of the proposed method for determination of hydrogen sulfide in real environmental samples, leachability tests were done for hydrogen sulfide. For this purpose, different 10.0 mg L^{-1} solutions of hydrogen sulfide were prepared and after times 0, 1, 2, 3 and 4 h, in optimal conditions, corresponding spectra were recorded. Based on the absorbances and calibration curve, the concentration of hydrogen sulfide was calculated. The results showed that in average, 11.8 % of the hydrogen sulfide is lost per hour.

In order to examine the suitability of the recommended method for determination of hydrogen sulfide in real samples, it was applied to wastewater and hot spring samples. Application of the method showed that the examined samples have amounts of hydrogen sulfide. However, the hot spring sample has considerable amounts of hydrogen sulfide. Accuracy was evaluated as the percent relative error in prediction (RE%), and precision was evaluated by percent relative standard deviation (RSD%). The results of the analyses have been collected in Table 4. As can be inferred from data in Table 4, the method for determination of hydrogen sulfide in different samples is very accurate (RE% values are below 2 %). Moreover, this indicates that the method is very selective.

Interference study

Validity of the method was assessed by examining the effect of various anions and cations at mg L^{-1} levels on the determination of hydrogen sulfide using the recommended method. These studies were performed in the optimal values of the factors. The results have been collected in Table 5. The anions were used as sodium and potassium salts, and the cations as chlorides and nitrate. As can be seen from Table 5, most of the common anions do not interfere in determination of hydrogen sulfide. Among

Table 4 Application of the recommended method for determination of hydrogen sulfide in various samples

Sample	Hydrogen Sulfide added (mg L^{-1})	Hydrogen Sulfide found (mg L^{-1})	RSD(%)[a]	RE(%)[b]	Recovery(%)[c]
Wastewater	0.00	2.62			
	2.00	4.61	5.5	−0.51	99.5
Hot spring	0.00	14.55			
	2.00	16.52	3.3	1.85	98.1

Number of replicates for calculation of RSD% and RE% is five

[a] Percent relative standard deviation (RSD%) was calculated by dividing the standard deviation of the five repetition to the mean value of the predicted amount multiplied by 100

[b] Percent relative error (RE%) was calculated by dividing the difference between the predicted amount and the actual amount to the actual amount multiplied by 100

[c] Percent recovery was obtained by dividing the predicted amount to the actual amount multiplied by 100

Table 5 Effect of interfering ions on the determination of hydrogen sulfide

Foreign ions	Added as	Error	Tolerance limit (mg L^{-1})
CN^-	KCN	−13.2	5
CH_3COO^-	$CH_3COONa \cdot 3H_2O$	−11.2	5
SO_3^{2-}	Na_2SO_3	−13.2	10
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	−8.8	10
HCO_3^-	$NaHCO_3$	−15.3	20
$C_2O_4^{2-}$	$Na_2C_2O_4$	9.2	30
PO_4^{3-}	$K_3PO_4 \cdot 3H_2O$	9.3	50
IO_3^-	KIO_3	−9.5	50
$H_2PO_4^-$	KH_2PO_4	10.6	80
SO_4^{2-}	Na_2SO_4	−10.1	100
NO_3^-	KNO_3	5.3	200
NO_2^-	KNO_2	−5.6	200
CO_3^{2-}	Na_2CO_3	3.9	250
Cl^-	LiCl	−2.3	400
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	−10.2	15
Fe^{2+}	$Fe(NO_3)_2 \cdot 6H_2O$	7.1	60

Table 6 Comparison of the spectrophotometric methods for determination of hydrogen sulfide with the recommended method

Instrumental methodology	Reagents	Determination range (μ mol L^{-1})	Detection limit (μ mol L^{-1})	References
Spectrofluorimetry	2,4-Dinitrobenzenesulfonyl	0.05–1	0.0043	Yang et al. (2009)
Spectrophotometry	Hydrogen peroxide	0.6–7.0	0.4	Ghadiri et al. (2013)
Spectrofluorimetry	Dansyl azide	0–100	As low as 1	Peng et al. (2011)
Kinetic spectrophotometric	Magenta	0.735–73.52	0.441	Safavi and Ramezani (1997)
Spectrofluorimetry	Iminocoumarin benzothiazole scaffold	0–100	0.15	Zhang et al. (2015)
Colorimetry	Nitrobenzoxadiazole moiety	10–100	2.1	Bae et al. (2013)
ICP-OES	–	1.764–647	0.882	Cmelik et al. (2010)
UV spectrophotometry	Silver nitrate	14.7–441.17	14.7	Evans (1967)
Spectrophotometry	*N*,*N*-dimethyl-*p*-phenylene diamine hydrochloride	1.47–58.82	1176.47	Silva et al. (2001)
Spectrophotometry	NQS	15.6–625.0	5.0	This work

the examined species, very reactive anions such as CN^-, IO_3^-, $S_2O_3^{2-}$ and NO_2^- can be seen. As the results collected in Table 5 show, in most cases, the tolerance limit is high which indicates that the method is selective.

Comparison with the published results

We compared the results of some of the spectrophotometric methods (Yang et al. 2009; Ghadiri et al. 2013; Peng et al. 2011; Safavi and Ramezani 1997; Zhang et al. 2015; Bae et al. 2013; Cmelik et al. 2010; Evans 1967; Silva et al. 2001) for determination of hydrogen sulfide (Table 6). The linear range of the method presented here is satisfactory and relatively wide. We used simple and available reagents, and in this method we broadened the linear range of the calibration. The upper limit of the linear range of this method is better than other methods.

A method with a wide linear range is preferred. This is because it can be applied to different samples with a wide range of concentrations of the analyte (here hydrogen sulfide). Moreover, the method is simple which can be employed in most of the libraries.

Conclusion

Sodium 1,2-naphthoquinone-4-sulfonate (NQS) was introduced as a reagent for determination of hydrogen sulfide. The developed method is simple for determination of hydrogen sulfide. Hydrogen sulfide in acidic conditions reduces NQS which results in the changing color from yellow to colorless. The method was successfully applied to determine hydrogen sulfide in environmental water samples with very low relative errors. The most distinctive characteristic of the method is its wide linear range which makes it suitable for determination of hydrogen sulfide in various samples.

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