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Cloud Point Extraction and Spectrophotometric Determination of Sulfide in Water Samples using Ethylene Blue Formation Reaction

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Abstract: A rapid, selective, and sensitive cloud point extraction process using mixed micelle of a nonionic surfactant, Triton X-114, and an anionic surfactant, SDS, to extract sulfide from aqueous solutions was investigated. The method is based on the color reaction of sulfide with N,N-diethyl-*p*-phenylenediamine (DPD) in the presence of suitable oxidizing reagent (Fe^{3+}) in acid media and cloud point extraction of ethylene blue (EB) dye. Various factors and optimal extraction and reaction conditions like: acid, Fe^{3+}, reagent, and surfactant concentration were studied and the analytical characteristics of the method (e.g., limit of detection, linear range, RSD%) were obtained. Linearity was obeyed in the range of 1–100 ng mL^{-1} of sulfide ion. The detection limit of the method is 0.5 ng mL^{-1} of sulfide ion. The interference effect of some anions, cations, and neutral species was also tested. The method was applied to the determination of sulfide in spring, river, and waste water samples.

Keywords: Cloud point extraction, ethylene blue, spectrophotometry, sulfide determination

INTRODUCTION

Sulfide is formed in waste waters by the action of anaerobic sulfate reducing bacteria on organic matter. Moreover, sulfide can be introduced into the environment through industrial processes which require the use of sulfide as a reagent or generate it as a by-product, for example, in

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the paper, petrochemical and leather industries. From the environmental point of view, hydrogen sulfide is one of the most important parameters to monitor in water matrices due to its high toxicity for aquatic organisms. Also, hydrogen sulfide controls the bioavailability of heavy metals in anoxic environments due to the low solubility of sulfide salts (1). At low concentrations, H_2S can produce personal distress while at higher concentrations, it can result in loss of consciousness, permanent brain damage, or even death through asphyxiation (2,3). Thus the detection of sulfide has gained significant importance within the analytical chemistry and the potential hazards of sulfide-contamination have meant that there is a pressing need for the development of selective and sensitive detection techniques.

Several methods have been reported for the determination of sulfide including spectrophotometry (4–11), cold vapor atomic absorption spectrometry (12,13), and electrochemical methods (14). Methylene blue (MB) formation reaction is one of the most successful and frequently used methods for sulfide determination (4–7). Ethylene blue (EB) formation reaction has also been used as a successful method for sulfide determination (8–11). The ethylene blue (EB) method has the advantage of the higher molar absorptivity of EB than the classical methylene blue method and the greater stability of the 4-*N*,*N*-diethylaminoaniline reagent.

However, due to the presence of sulfide in environmental samples at low levels, its separation from other elements present and also the use of a preconcentration is usually necessary. Cloud point extraction (CPE) has been used in several different matrices for preconcentration of trace amounts of organic and inorganic species determinations (15–22). CPE offers many advantages over traditional liquid-liquid extraction. Compared with traditional solvent extraction, CPE uses water and avoids the use of large amounts of toxic and flammable organic solvents. In addition, CPE can lead to higher recovery efficiency and a large preconcentration factor because the presence of the surfactant can minimize losses of analytes due to their adsorption onto the container.

The cloud point phenomenon is generally observed in nonionic surfactant micellar solutions when the temperature of the system is raised to a certain value. It was reported that the CP of Triton X-114 increased on adding small amounts of either cationic surfactant cetyltrimethylammonium bromide (CTAB) or anionic surfactant sodium dodecyl sulfate (SDS) (23). Mixed surfactants of different charges have been used for extraction and preconcentration in order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions. Mixed micelle-mediated extraction (mixed-MME) was used for the preconcentration of organic compounds (24) and metal cations (25,26).

The effect of electrolytes on the cloud point while using ionic–nonionic surfactant solutions (mixed-MME) has been investigated (27,28). When small amounts of electrolytes are added to Triton X-100 in the presence of lower SDS concentrations, the cloud point decreases in a ratio dependent on the electrolyte concentration and the nature of the counterion (27).

The purpose of this study is to propose a method for the spectrophotometric determination of sulfide after preconcentration in a simple CPE process. The method is based on the color reaction of sulfide with N,N-diethyl-*p*-phenylenediamine (DPD) in acid media and micelle-mediated extraction of the produced dye. A mixed micelle of a nonionic surfactant, Triton X-114, and an anionic surfactant, SDS, was chosen as the extraction agent. To the best of our knowledge, this is the first report on the preconcentration of sulfide by CPE method.

EXPERIMENTAL

Reagents and Apparatus

All chemical reagents used were of analytical reagent grade, and double distilled water (DDW) was used throughout the experiments. Stock sulfide solution (100 mg L^{-1}) was prepared daily by dissolving an appropriate amount of $Na_2S \cdot 9H_2O$ in DDW and standardized iodimetrically (29). N,N-diethyl-*p*-phenylenediamine sulfate (molecular formula $C_{10}H_{16}N_2H_2SO_4$, molecular weight 262.32) solution (0.1 mol L^{-1}) was prepared daily in 3 mol L^{-1} sulfuric acid. EDTA solution 1000 mg L^{-1} was prepared by dissolving its disodium salt in DDW. Fe^{3+} solution (2 mol L^{-1}) was prepared by dissolving $FeCl_3 \cdot 6H_2$ O in DDW. SDS and Triton X-114 stock solutions (2% w/v) was prepared by dissolving an appropriate amount of solid and concentrated solution, respectively in hot distilled water. A single beam WPA model Lightwave II UV/Vis spectrophotometer with 1 cm quartz cell (0.5 mL) was used to record absorption spectra and absorbance measurements at λ_{max}. A centrifuge with 10 mL calibrated tubes (Superior, Germany) was used to accelerate the phase separation process.

Procedure

An aliquot of the sulfide solution (so that its final concentration would be in the range of 1.00–100.00 ng mL^{-1}), 0.5 mL of 0.1 mol L^{-1} DPD reagent in 3 mol L^{-1} sulfuric acid, 0.1 mL EDTA solution and 0.2 mL of 2 mol L^{-1} Fe^{3+} solution was transferred into a 10-mL tube and mixed immediately by inverting the tube slowly. Color (ethylene blue dye) formed and completed in about 1 min. The solution was diluted to approximately 7 mL with water and allowed to stand for 5 min. After that, 1.5 mL of 2% (w/v) Triton X-114 and 0.5 mL of 2% (w/v) SDS solutions was added and made up to the mark with double distilled water. Separation of two phases was accelerated by centrifugation for 10 min at 3500 rpm. The mixture was cooled in a salt bath to increase the viscosity of the surfactant-rich phase, and the aqueous phase was easily decanted by simply inverting the tube. The surfactant-rich phase of this procedure (about 0.25 mL) was dissolved and diluted to 0.5 mL with ethanol and transferred into a 0.5 mL quartz cell to measure its absorbance at 667 nm against a reagent blank as the reference. The blank solution was prepared as sample solution except that DDW was used instead of sulfide solution.

RESULTS AND DISCUSSION

In the acidic media and in the presence of an appropriate oxidizing agent the condensation reactions of sulfide with N,N-diethyl-*p*-phenylenediamine produces colored product EB dye (Scheme 1).

Colored product shows an absorption spectrum with maximum absorbance at 667 nm in micellar media (Fig. 1). It was observed that with the addition of mixed micelle the neutral surfactant, Triton X-114, and anionic surfactant, SDS, is suitable for separation and preconcentration of the produced dye by the CPE method.

Optimization of the System

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain the optimized system.

The concentration of the surfactant that is used in CPE is an important factor. In CPE the hydrophobic compounds initially present in the solution and bound to the micelles are extracted to the surfactant-rich phase, leaving only a very small portion in the water phase. As the charge of the ethylene blue is positive, in order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions within the same extraction system, a mixed micellean anionic surfactant and a nonionic surfactant should be used for extraction. To obtain the optimal concentration of TritonX-114, the effect of surfactant concentration on the absorbance

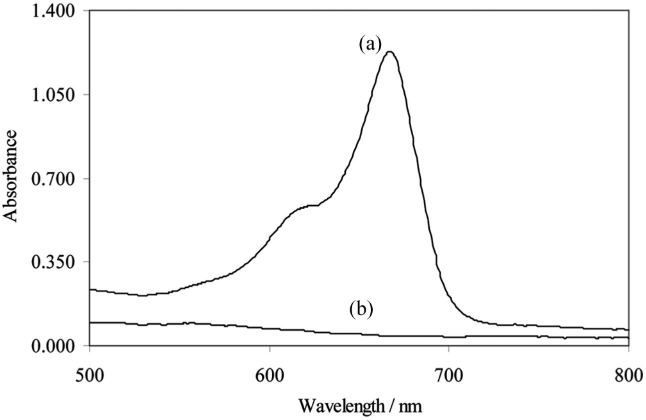

Figure 1. Spectra for (a) produced EB dye and (b) blank solution against water after CPE. Conditions: sulfide, 50 ng mL^{-1}; sulfuric acid, 0.15 mol L^{-1}; Triton X-114, 0.3% (w/v); SDS, 0.1% (w/v); DPD, 0.005 mol L^{-1}; Fe^{3+}, 0.04 mol L^{-1}.

of the surfactant rich phase was investigated (Fig. 2). As Fig. 2 shows, the absorbance of the solution increased by increasing Triton X-114 concentration up to 0.25% (v/v) and then remained constant. Therefore, 0.3% (v/v) of Triton X-114 concentration was used as the optimal

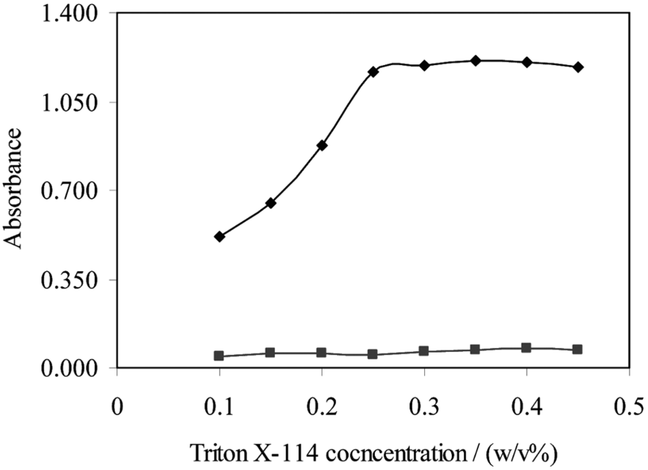

Figure 2. Effect of Triton X-114 concentration on the CPE preconcentration and determination of (◆) sample and (■) blank. Conditions: sulfide, 50 ng mL^{-1}; DPD, 0.005 mol L^{-1}; Fe^{3+}, 0.06 mol L^{-1}; sulfuric acid, 0.225 mol L^{-1}.

concentration. It was observed that using a mixed micelle of Triton X-114 and SDS caused an increase in the absorbance of the surfactant rich phase. Therefore, the effect of SDS was also studied. The results showed that at a concentration of 0.1% SDS an increase of about 5% in the absorbance of surfactant rich phase was observed.

The effect of Fe^{3+} concentration on the absorbance of surfactant rich phase in the range 0.005–0.08 mol L^{-1} was studied. As Fig. 3 shows, the absorbance of the solution increased by increasing Fe^{3+} concentration up to 0.02 mol L^{-1} and then remained nearly constant. Therefore, a concentration of 0.04 mol L^{-1} of Fe^{3+} was used as optimal.

The color formation reaction takes place in acid media. In this work sulfuric acid was used. The effect of the concentration of sulfuric acid on the absorbance of the surfactant rich phase in the range 0.0075–0.30 mol L^{-1} was also studied. As can be observed from Fig. 4, the absorbance of the solution increased by increasing the sulfuric acid concentration up to 0.045 mol L^{-1} and remained nearly constant at higher concentrations. Therefore, 0.15 mol L^{-1} sulfuric acid was used as the optimal acid concentration.

The effect of the DPD reagent concentration on the absorbance of the system in the range 0.0005–0.01 mol L^{-1} was investigated. The results showed that the absorbance of the solutions increased by increasing DPD concentration up to 0.004 mol L^{-1}, remained nearly constant between

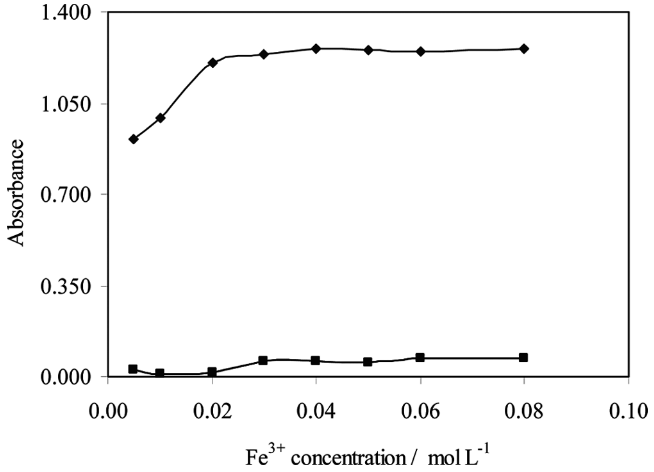

Figure 3. Effect of Fe^{3+} concentration on the CPE preconcentration and determination of (◆) sample and (■) blank. Conditions: sulfide, 50 ng mL^{-1}; sulfuric acid, 0.225 mol L^{-1}; Triton X-114, 0.3% (w/v); SDS, 0.1% (w/v); DPD, 0.006 mol L^{-1}.

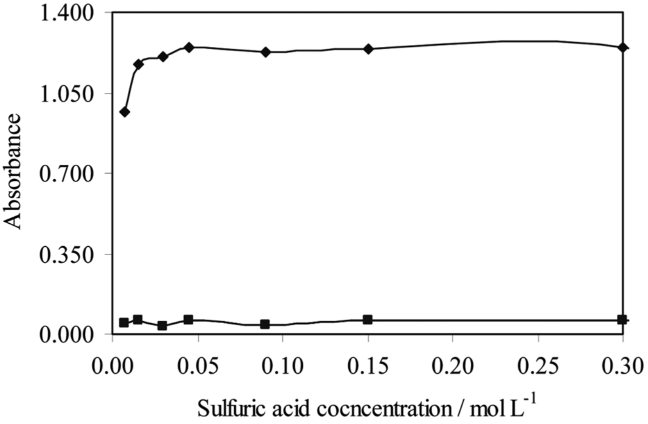

Figure 4. Effect of sulfuric acid concentration on the CPE preconcentration and determination of (◆) sample and (■) blank. Conditions: sulfide, 50 ng mL^{-1}; Fe^{3+}, 0.06 mol L^{-1}; Triton X-114, 0.3% (w/v); SDS, 0.1% (w/v); DPD, 0.006 mol L^{-1}.

0.004 and 0.006 mol L^{-1} and then decreased at higher concentrations (Fig. 5). The decrease in the absorbance may be due to the competition of the unreacted DPD reagent with the product in CPE. Therefore, 0.005 mol L^{-1} DPD reagent was applied in the proposed method.

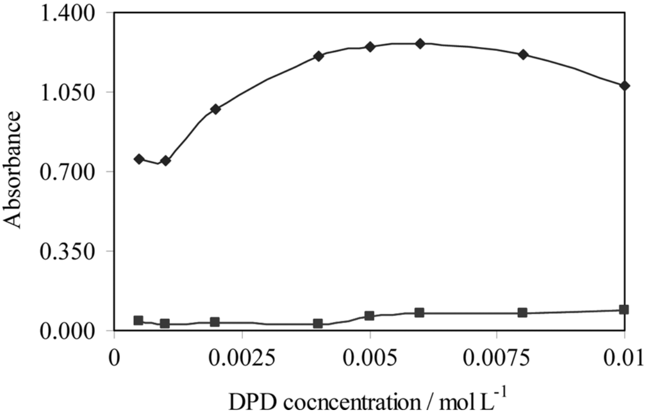

Figure 5. Effect of DPD reagent concentration on the CPE preconcentration and determination of (◆) sample and (■) blank. Conditions: sulfide, 50 ng mL^{-1}; Fe^{3+}, 0.004 mol L^{-1}; sulfuric acid, 0.15 mol L^{-1} Triton X-114, 0.3% (w/v); SDS, 0.1% (w/v).

As Figs. 2–5 show change in the concentrations of Triton X-114, Fe^{3+}, sulfuric acid and DPD had no considerable effect on the signal of the blank solutions.

The effect of time on reaction steps (dye formation) as well as on the CPE procedure, was investigated. The results showed that oxidation and the coupling reaction were completed in 1 min at room temperature. Also 10 min centrifugation and 10 min in ice-salt bath was found to be enough for successful CPE of formed dye.

Because the surfactant-rich phase was very viscous, ethanol was added to the surfactant-rich phase after CPE to facilitate its transfer into a spectrophotometric cell. The extractaed phase was diluted to 0.5 mL with ethanol.

Analytical Characteristics

Table 1 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, and repeatability. The limit of detection, defined as $C_L = 3\ S_b\ /m$ (30), where C_L, S_b and m are the limit of detection, standard deviation of the blank, and the slope of the calibration graph, respectively, was 0.5 ng mL^{-1}. Because the amount of sulfide in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.5 mL the solution is concentrated by a factor of 20. The improvement factor, defined as the ratio of the slope of the calibration curve for the CPE method to that of the calibration curve without preconcentration, was 25.

Common Ion Effect

To study the common ion effect or selectivity of the proposed method, the effect of various species (anions, cations and neutral species) on the determination of 50 ng mL^{-1} sulfide was tested under the optimum

Table 1. Analytical characteristics of the proposed method

Regression equation (n = 9)	$A = 0.0228X - 0.0026$, $R^2 = 0.9976$
Linear range (ng mL^{-1})	1.0–100.0
Limit of detection (ng mL^{-1})	0.5 (3σ blank) (n = 5)
Repeatability (RSD, %) (n = 4)	1.77 (for 50 ng mL^{-1} sulfide)
Maximum preconcentration factor	20
Improvement factor	25

Table 2. Tolerance ratio of diverse species on the determination of 50 ng mL^{-1} sulfide ion

Species	Tolerance ratio ($w_{ion}/w_{sulfide}$)
Ca^{2+}, Mg^{2+}, Ni^{2+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Na^{+}, K^{+}, NH_4^{+}, NO_3^{-}, Citrate, Acetate, HCO_3^{-}, CO_3^{2-}, ClO_4^{-}, SO_4^{2-}, Cl^{-}	1000
F^{-}, MoO_4^{2-}	100
SCN^{-}	50
Cu^{2+}, Hg^{2+}, CrO_4^{2-}	20[a]
SO_3^{2-}	10(20[a])
Thiourea, Thioacetamide	Interfere

[a] After removal as described in the text.

conditions. The tolerance limit was defined as the concentration of added species caused less than ±5% relative error on the preconcentration and determination of sulfide. The results are summarized in Table 2. It was found that most of the investigated ions did not interfere even when present 1000-fold excess over sulfide. Cu^{2+}, Hg^{2+}, $Cr_2O_7^{2-}$, thiourea and thioacetamide interfered. The interfering effect of Cu^{2+}, Hg^{2+}, $Cr_2O_7^{2-}$ up to 20 fold excess over sulfide ion was completely removed in the presence of 1.0×10^{-4} mol L^{-1} EDTA. Presence of 5.0×10^{-4} mol L^{-1} formaldehyde removed the interfering effect of sulfite ion up to 20 fold excess over sulfide.

Table 3. Determination of sulfide ion in spring and river water samples

	Sulfide/ng mL^{-1}		
Sample	Added	Found	Recovery (n = 3) (%)
River water	0.00	ND[a]	—
	25.00	25.25	101 ± 1.7
	50.00	48.50	97.0 ± 1.9
	100.00	102.00 ± 2.2	102.0
Spring water	0.00	ND	—
	25.00	26.00	104.0 ± 3.0
	50.00	48.80	97.0 ± 1.6
	100.00	98.00	98.0 ± 2.0
Waste water	0.00	23.32	—
	10.00	33.42	101 ± 2.6
	20.00	44.38	105 ± 2.4

[a] ND: not determined.

Application

In order to test the reliability of the proposed method, it was applied to the determination of sulfide ion in spring and river water samples, and a sugar manufacturing waste water sample. For this purpose, 7 mL of each of the samples was treated under the general procedure. The amount of sulfide in the waste water sample was found as 23.32 ng mL^{-1} and 23.10 ng mL^{-1} by the proposed method and standard method (31), respectively. The spring and river water samples were found to be free from hydrazine and so synthetic samples were prepared by adding known amounts of sulfide to the water samples. The results are presented in Table 3. The recoveries are in the range 97–104% and indicate that the proposed method is helpful for the determination of sulfide in the natural water samples.

CONCLUSION

The proposed method gives a very rapid, simple, sensitive, and low-cost spectrophotometric procedure for determination of sulfide ion. The surfactant has been used for preconcentration of sulfide ion, and thus toxic solvent extraction has been avoided. A mixed micelle of Triton X-114 and SDS was chosen for the formation of the surfactant rich phase at room temperature; and better separation and rapid association of the surfactant-rich phase in tube bottom. High density of the surfactant-rich phase facilitates phase separation easily. The proposed method is simple, rapid, low cost, safe, and nontoxic and can be applied to the determination of sulfide in water and waste water samples.

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