



Green colorimetric recognition of trace sulfide ions in water samples using curcumin nanoparticle in micelle mediated system



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ABSTRACT

In this paper, green curcumin nanoparticles (CURNs) are introduced for colorimetric sensing of sulfide using micelle mediated cloud point extraction for the first time. CURNs are transferred into non-ionic surfactant phase and show strong surface plasmon absorption intensity. The extraction of CURNs to the surfactant rich phase is suppressed in the presence of Cu^{2+} but upon addition of sulfide, the extraction of CURNs to the surfactant rich phase is increased again. This increase in the absorbance of surfactant rich phase is related to the sulfide concentration and was used as an analytical signal for the sensing of sulfide. The effect of chemical variables such as pH of the sample solution, concentration of Cu^{2+} , electrolyte and CURNs on the cloud point extraction was studied. Under optimum conditions, the change in absorption intensity was linearly proportional to the concentration of sulfide in the range of 0.5–200.0 ng mL^{-1} with a detection limit of 0.4 ng mL^{-1} . The relative standard deviations for 10 replicate measurements of 20 ng mL^{-1} and 175 ng mL^{-1} of sulfide were 4.1% and 1.4% respectively. The method was successfully applied to the determination of sulfide in different water samples.

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1. Introduction

The importance of sulfide monitoring in the environmental samples has been recognized because it is a toxic, harmful and corrosive anion even at low concentration. Sulfide is frequently present in various mediums such as industrial effluents, crude oil, gas extraction and refining units, as a byproduct of many industrial processes, and hot springs [1–4]. Sulfide has a lethal property at high concentration and it has an extreme action on the nerve system causing respiratory paralysis [5]. On the other hand, sulfide is a strong corrosive agent for many metals and alloys such as iron, brass, steel and copper. In aqueous medium sulfide is generally present in different forms such as H_2S , HS^- and S^{2-} which are in equilibrium in water [6]. Sulfide is released into the aquatic environments as the result of degradation of biological compounds or other organic compounds containing sulfur [7]. Various methods such as optical [2,4,8–11], electrochemical [12–16], chemiluminescence [17] and chromatography [18] have been reported for the determination of sulfide and its species. However, these methods have their own limitations and direct determination of trace amounts of analytes appears to be difficult due to matrix interferences and insufficient sensitivity of most of the analytical techniques. Therefore an initial sample pretreatment related to the

analyte extraction and preconcentration is considered as the most critical step [19]. As a result, a large number of research efforts have been devoted to the development of separation/preconcentration procedures such as cloud point extraction, solid phase extraction and liquid liquid microextraction prior to the analyte determination in recent years. Among these procedures the cloud point extraction using micellar systems have been exploited in different fields of analytical chemistry [20]. The cloud point is the temperature above which the aqueous solutions of non-ionic surfactants become turbid and above the cloud point temperature the solution is separated into two phases, a rich phase containing a high surfactant concentration in a small volume and a dilute phase with a surfactant concentration close to the critical micelle concentration (cmc). The small volume of the surfactant-rich phase obtained by using the cloud point methodology permits to design an extraction strategy presenting low cost and toxicity than those using organic solvents with higher extraction efficiency.

Recently, cloud point extraction of nanoparticles (NPs) with various sizes and different capping agents using non-ionic surfactants has been successfully evaluated. This methodology has been mostly utilized to concentrate and recycle the NPs from aqueous solutions [21]. Meanwhile, cloud point extraction of AuNPs has been employed for detection of Hg^{2+} in water samples [22].

Curcumin [(E, E)-1,7-bis (4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione] is a hydrophobic polyphenol compound which has been recognized as the active principle of turmeric. It is extracted from the dried root of the rhizome *Curcuma Longa*.

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Curcumin is a diferuloyl methane having two *o*-methoxy phenolic OH groups attached to the α,β -unsaturated β -diketone (heptadiene-dione) moiety, which can form chelates with copper, iron and other transition metals [23]. It shows keto–enol tautomerism [24,25] and in basic mediums, the enolate form is prevailed form of curcumin, which demonstrates its electron donor characteristic. The last property is mainly responsible for the scavenging activity of phenolic antioxidants. Curcumin exhibits the properties such as antioxidant, anti-inflammatory, anticarcinogenic, antibacterial and wound healing [26,27]. Despite having several benefits, curcumin suffers from low aqueous solubility. Nanonization is one of the processes that can help to overcome this drawback [24,25].

In the current paper, we present the application of cloud point extraction using curcumin nanoparticles for sensing sulfide in the aqueous solutions. CURNs are extracted into Triton X-100 as a non-ionic surfactant. Strong surface plasmon absorption intensity is monitored for CURNs enriched in surfactant phase. However in the presence of Cu^{2+} , extraction of CURNs to the surfactant rich phase is decreased but upon addition of sulfide, enrichment of CURNs to the surfactant rich phase is restored and consequently the absorption intensity of the surfactant rich phase is increased. The increase in the absorbance of surfactant rich phase in the presence of sulfide is proportional to its concentration and was employed as an analytical signal for monitoring sulfide concentration. Therefore the analytical signal (ΔA) was defined as the difference between absorption intensity of CPE-CURNs in the absence and presence of sulfide. In order to obtain the highest possible signal, the optimum conditions were established by studying the effects of various parameters on the method performance.

2. Experimental

2.1. Apparatus

Absorption spectra and absorbance measurements were made by a GBC UV–visible spectrophotometer model Cintra 101 (Australia) using 1 cm glass cells. TEM images were performed by a Zeiss-EM10C-80 KV transmission electron microscope (Germany). A digital pH-Meter model 632, Metrohm (Switzerland) with a combined glass electrode was used for pH measurements. A thermostat bath model Colora (England) maintained at the desired temperature was applied for the cloud point temperature experiments. An ultrasound bath DSA 100-SK₂, 100 W power, 40 kHz frequency (China) was utilized for the fabrication of nanoparticles. A rotary evaporator of Heidolph model Labrota 4000 (Germany) was used for the removal of solvent.

2.2. Reagents

All chemicals were of analytical grade and doubled distilled water was used throughout. A 1000 $\mu\text{g mL}^{-1}$ stock solution of sulfide was prepared by dissolving 0.75 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Merck, Germany) in water and diluting to 100 mL in a volumetric flask. This solution was standardized by the iodometric method [28]. This solution was prepared with degassed water on a daily basis to reduce the oxidation of sulfide during the preparation and storage of standards. A stock solution of 1000 mg L^{-1} of Cu^{2+} was prepared by dissolving 3.9270 g of the $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (Merck) in water and diluting to 1000 mL in a volumetric flask. 1.0 mol L^{-1} of NaCl was prepared by dissolving 5.844 g of sodium chloride (Merck) in water and diluting to 100 mL in a volumetric flask. A 5% (v/v) of Triton X-100 was prepared by diluting 5 mL of the reagent to 100 mL. An ammonium buffer pH 9 was prepared by the addition of HCl (0.1 mol L^{-1}) solution to 0.05 mol L^{-1} of ammonia and adjusting the pH to 9 using a pH meter.

2.3. Synthesis of curcumin nanoparticles

The CURNs were fabricated by modification of the technique described by Bhawana et al. [24]. A typical fabrication procedure was depicted as follows: the organic phase was prepared by dissolving 125 mg of curcumin in 25 mL of dichloromethane. For preparation of aqueous phase, 10 mL of Triton X-100 5% (v/v) was added to 90 mL of boiling water. Afterwards, 2 mL of organic phase was added dropwise to the aqueous phase (about 10 drops/min) under ultrasonic conditions, with an ultrasonic power of 100 W and a frequency of 40 kHz. Then the sonication was continued for 20 min. Following that, the contents were stirred at 1500 rpm by a magnetic stirrer at room temperature for 20 min until a yellow color was obtained. Eventually, this solution was placed in a rotary evaporator in order to ensure the complete removal of dichloromethane. This solution was then stored in a brown bottle. The total concentration of CURNs solution was 0.271 mmol L^{-1} . It was found that the prepared CURNs are stable for more than 6 months.

2.4. Recommended procedure

The colorimetric analysis was carried out by performing the following steps. One milliliter of CURNs solution (0.271 mmol L^{-1}), 6 mL of Triton X-100 5% (v/v), 1.0 mL of ammonium buffer (pH 9), 2.0 mL of 1.0 mol L^{-1} of NaCl, 0.5 mL of 10 mg L^{-1} of Cu^{2+} and aliquots of sulfide (so that its concentration would be in the range of 0.5–200.0 ng mL^{-1}) were added to a 50 mL volumetric flask and diluted to the mark with water. This solution was transferred to a 50 mL conical centrifuge tube and placed in a thermostat water bath at 80 °C for 35 min. The solution turns cloudy at this step. Subsequently, the solution was cooled in an ice-bath for 5 min. After decantation, the surfactant-rich phase was separated and diluted to 5 mL in a volumetric flask with water and transferred into a 1 cm glass cell for absorbance measurement ($\lambda=423\text{ nm}$). A blank solution was also prepared in the same way without adding any sulfide solution.

2.5. Sample pretreatment

Water samples were collected from Mahshahr Petrochemical Refinery wastewater, Karoon River and Ahvaz tap water, stored in 1 L glass bottles and filtered through a filter paper (Whatman no. 40) before use.

3. Results and discussion

3.1. Sensing strategy

The preliminary investigation demonstrated that the absorption intensity of preconcentrated CURNs by CPE is decreased in the presence of Cu^{2+} but it is considerably increased upon the addition of sulfide due to strong interaction between sulfide ions with Cu^{2+} . Fig. 1 presents the UV–vis absorption spectra and TEM images of the corresponding CURNs after CPE. The absorption spectra of the extracted CURNs by cloud point extraction indicate that there is a significant change in the absorbance of (A) CURNs, (B) in the presence of Cu^{2+} and (C) in the presence of both Cu^{2+} and sulfide. The corresponding TEM images of (D) CURNs, (E) in the presence of Cu^{2+} and (F) in the presence of both Cu^{2+} and sulfide also presented in Fig. 1 show that the number of particles are different in each case. The interaction between curcumin and metal ions such as copper, iron and other transition metals has been recognized and implied in many studies [29,30] and 1:1 and 1:2 Cu(II)–curcumin complex have been synthesized and characterized [23]. Under the conditions in this procedure only a 1:2

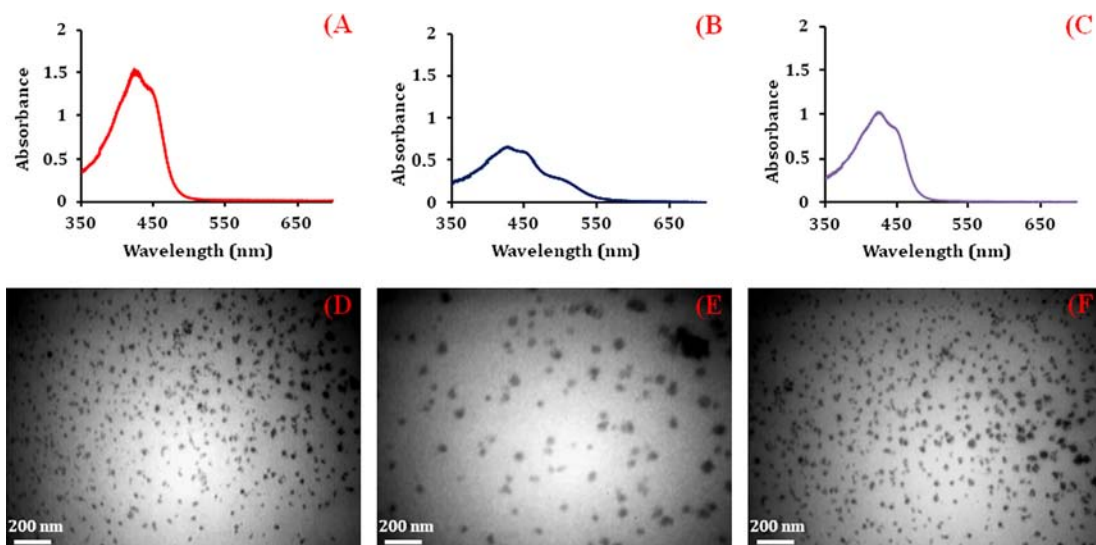
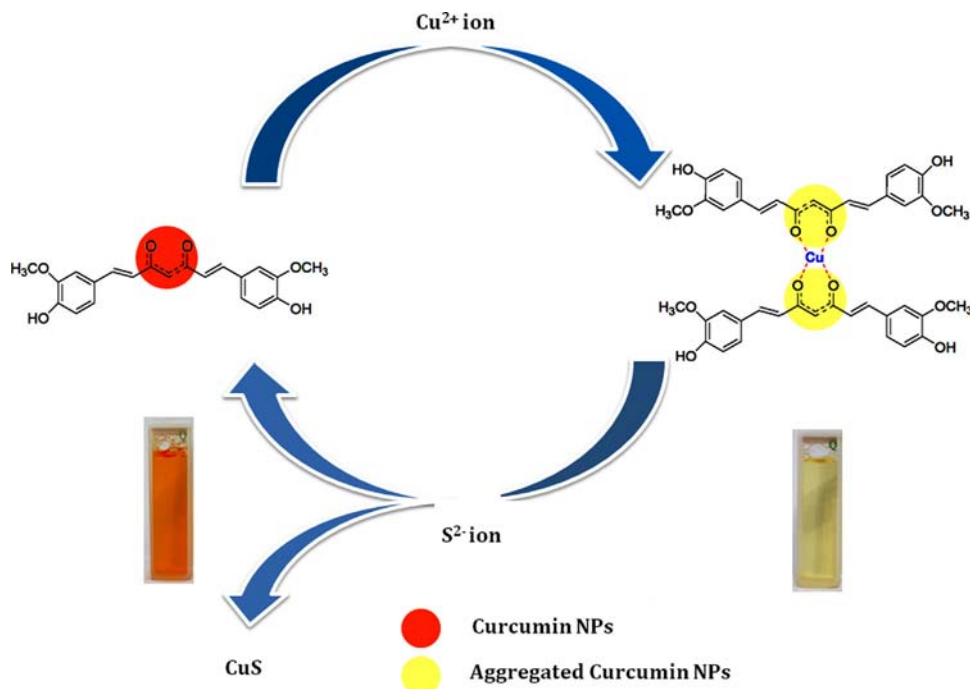


Fig. 1. UV-vis spectra of the extracted CURNs by CPE: (A) in the absence of sulfide and Cu^{2+} , (B) in the presence of Cu^{2+} and (C) in the presence of both sulfide and Cu^{2+} and the corresponding TEM images of CURNs after cloud point extraction, (D) in the absence of Cu^{2+} and sulfide, (E) in the presence of Cu^{2+} and (F) in the presence of both sulfide and Cu^{2+} .



Scheme 1. Schematic representation for the colorimetric sensing of sulfide ions using CPE-CURNs in the presence of Cu^{2+} .

complex $\text{Cu}(\text{CUR})_2^{2+}$ is probably formed since 1:1 complex is formed in the presence of acetate as an auxiliary ligand [23].

Based on the above observations, the probable determination mechanism for sulfide based on CPE-CURNs is shown in Scheme 1. In the absence of both sulfide and copper ions, CURNs are enriched into non-ionic surfactant phase and exhibits high surface plasmon absorption intensity. The copper ions, when present bind to the CURNs, hence the surface charge of CURNs becomes positive and it is not extracted into surfactant phase and consequently the absorption intensity is decreased. On the other hand, a complex is formed between electron rich CURNs and Cu^{2+} as an electron deficient compound. As a consequence of this reaction, CURNs undergo aggregation and a color change from orange-red to yellow occurs in the presence of Cu^{2+} in basic solution. Therefore, in

a system containing both sulfide and Cu^{2+} , CURNs are also enriched into surfactant phase as a result of sulfide action as a preventing agent on Cu^{2+} due to the strong interaction of sulfide with Cu^{2+} ($K_{\text{sp}} \text{CuS} = 10^{-40}$).

3.2. Influence of pH

The pH of the sample solution is often considered as an important analytical parameter that affects CPE-CURNs spectral characteristics. Therefore, the effect of pH on the absorption intensity of CURNs extracted into non-ionic surfactant was evaluated in the range of 5–11 in order to obtain an optimum pH for sensing of sulfide ion. The pH was adjusted to the desired value by the addition of dilute NaOH and HCl to the test solutions and using

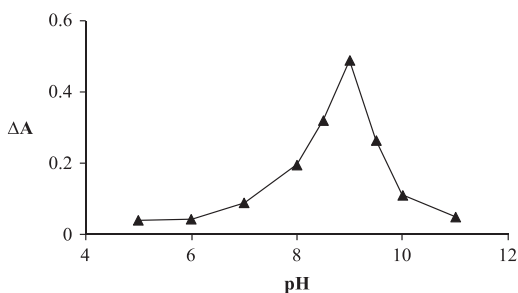


Fig. 2. Influence of pH on determination of 200 ng mL^{-1} of sulfide by CPE of CURNs. Each number is average of three determinations.

a pH meter. The result of this investigation presented in Fig. 2 indicates that the maximum analytical signal for determination of 200 ng mL^{-1} of sulfide is appearing at pH 9. Hence, pH 9 was selected for further experiments. Different buffer solutions with pH 9 such as phosphate, ammonium, carbonate and Robinson were examined for adjustment of the pH of the CPE of CURNs solution. Among the tested buffers, ammonium buffer exhibited the highest analytical signal, thus, ammonium buffer with pH 9 was chosen for further studies and 1.0 mL of this buffer was added to the solutions for maintaining pH at 9.

3.3. Influence of electrolyte

The influence of electrolytes on the cloud point extraction using ionic–nonionic surfactants has been previously investigated [31]. It has been shown that the cloud point of the micellar solutions can be affected by the addition of salts, alcohols and some organic compounds (salting-out effects) [32]. To assess the effect of the electrolytes impact on this work, the experiments were carried out by adding different salts to 200 ng mL^{-1} of sulfide solutions before CPE. Different salts such as NaCl, KCl, NaNO_3 , KNO_3 , Na_2SO_4 and NaF were investigated and it was observed that NaCl was a better electrolyte for this system with respect to viscosity of coacervate phase. Hence, the effect of NaCl concentration on the analytical signal was assessed by adding different concentration of NaCl. As the results revealed the maximum analytical signal was achieved at $4 \times 10^{-2} \text{ mol L}^{-1}$ of NaCl. Therefore, NaCl concentration of $4 \times 10^{-2} \text{ mol L}^{-1}$ was chosen for the following experiments and 2 mL of 1.0 mol L^{-1} of NaCl was added to 50 mL solutions in order to achieve this concentration.

3.4. Influence of Cu^{2+} concentration

The principle of this work is the transfer of CURNs into surfactant rich phase by the CPE method which is suppressed in the presence of copper ions and restored again by adding sulfide ion. Therefore, the effect of Cu^{2+} concentration was investigated. Different concentrations of Cu^{2+} ranging from 25 to 300 ng mL^{-1} were added to the sample solution. According to the results shown in Fig. 3, the highest signal is obtained when Cu^{2+} concentration is 100 ng mL^{-1} in the final solution. Therefore this concentration was chosen as optimum and 0.5 mL of $10 \text{ mg L}^{-1} \text{ Cu}^{2+}$ was added to 50 mL solutions to fulfill this concentration.

3.5. Surfactant selection and influence of its concentration

Like most nanoparticles, CURNs have a strong tendency to agglomerate and aggregate also. Hence a stabilizing agent is often employed to hinder this phenomenon. Therefore, in this work, a non-ionic surfactant was used as a dispersing and stabilizing agent for CURNs and also for the cloud point extraction process. In order to investigate the effect of non-ionic surfactant types on the

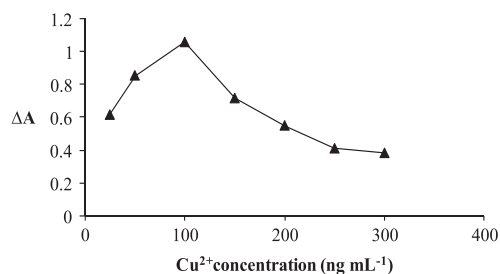


Fig. 3. Influence of Cu^{2+} concentration on determination of 200 ng mL^{-1} of sulfide by CPE of CURNs. Each number is average of three determinations.

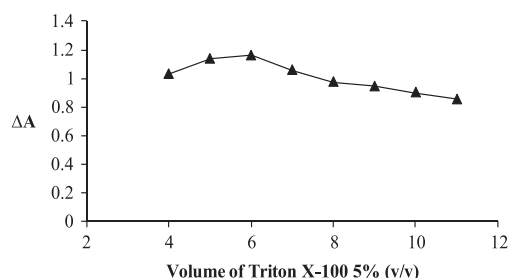


Fig. 4. Influence of volume of Triton X-100 (5% v/v) on determination of 200 ng mL^{-1} of sulfide by CPE of CURNs. Each number is average of three determinations.

system, surfactants such as Triton X-114 and Triton X-100 and a mixture of both were investigated. The results revealed that Triton X-100 shows the highest analytical signal. Subsequently, a Triton X-100 (5% v/v) was selected and the effect of its volume in the range of 4–11 mL on the extraction efficiency and subsequent measurement was investigated. The obtained results in Fig. 4, demonstrated that the highest analytical signal was observed when 6 mL of Triton X-100 (5% v/v) was used. Thus, this volume was selected as optimum for the following studies.

3.6. Influence of equilibrium temperature and time

Equilibrium temperature and time play important roles in cloud point extraction. It has been shown that increased temperature and prolonged reaction time result in more satisfactory extraction. However it is most desirable to use the lowest possible equilibration temperature and shortest equilibration time as a compromise between completion of extraction and efficiency of phase separation. Therefore the effects of equilibration temperature and incubation time on CPE of CURNs were evaluated in the range of 60–90 °C and 15–45 min, respectively. The results indicated that the maximum absorption signal was obtained when the solution was equilibrated at 80 °C for an equilibration time of 35 min. The results also showed the standing time of surfactant enriched phase in the ice bath had no significant effect on the extraction efficiency. Thus, 5 min was chosen as standing time in the ice bath for all experiments.

3.7. Influence of CURNs concentration

The influence of CURNs concentration on the analytical signal was also studied. As the results in Fig. 5 demonstrates the analytical signal was increased by increasing CURNs concentration. Although the increase in the CURNs concentration enhances the absorption intensity, transfer of CURNs to surfactant phase is less effective and higher surfactant amounts should be used. Thus in this study, the CURNs concentration of $5.4 \mu\text{mol L}^{-1}$ was chosen in order to achieve high ΔA for sulfide and ease of extraction into surfactant for further experiments. Therefore 1 mL of CURNs

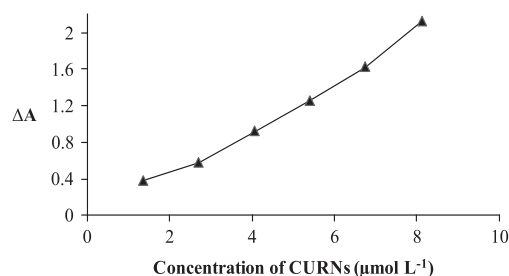


Fig. 5. The effect of CURNs concentration on determination of 200 ng mL⁻¹ of sulfide by CPE of CURNs. Each number is average of three determinations.

Table 1

The effect of interfering ions on the determination of 200 ng mL⁻¹ of sulfide.

Interfering species	Tolerance mass ratio interference/analyte
Cl ⁻ , borate, Ca ²⁺ , NO ₃ ⁻ , K ⁺ , PO ₄ ³⁻ , NH ₄ ⁺	1000
C ₂ O ₄ ²⁻ , citrate, Mg ²⁺	500
CO ₃ ²⁻ , HCO ₃ ⁻ , Br ⁻ , SO ₄ ²⁻ , tartarate, I ⁻	250
SCN ⁻ , F ⁻	100
Pb ²⁺ , Cd ²⁺ , Ni ²⁺ , Sn ²⁺ , Mn ²⁺ , Cr ³⁺ , Zn ²⁺	50
CN ⁻	10
Co ²⁺ , S ₂ O ₅ ²⁻ , S ₂ O ₃ ²⁻	5
Fe ³⁺	3
SO ₃ ²⁻	1

(0.271 mmol L⁻¹) was added to 50 mL solutions to obtain this concentration.

3.8. Analytical performance

The analytical characteristics of the proposed method were evaluated using the recommended procedure under the optimum conditions. The calibration curve was linear in the range of 0.5–200.0 ng mL⁻¹ with a correlation coefficient (*r*) of 0.9992. The linear regression equation for sulfide was $\Delta A = 0.0062C + 0.0254$ where *C* is the concentration of sulfide in ng mL⁻¹. The limit of detection was determined as a concentration giving an absorption peak with a signal to noise ratio of (3:1) and found to be 0.4 ng mL⁻¹. The relative standard deviation for 10 replicate measurements of 20 ng mL⁻¹ and 175 ng mL⁻¹ of sulfide was 4.1% and 1.4% respectively.

3.9. Interference studies

The effect of common anions and cations on the analytical signal of sulfide in the system under the optimum experimental conditions mentioned above was investigated. The experiments were performed at a fixed concentration of sulfide (200 ng mL⁻¹) and then measuring the analytical signal before and after adding the possible interfering ion. A relative error higher than $\pm 5\%$ in the analytical signal value of the sulfide was considered interference. The results of this study are represented in Table 1. It was observed that most of the ions normally present in the water samples do not interfere under the experimental conditions applied.

3.10. Application of CPE-CURNs for the determination of sulfide levels in water samples

The performance of the method was investigated by the determination of sulfide concentration in Mahshahr refinery wastewater, Karoon River and Ahvaz tap water samples. These samples were spiked with two concentration levels of sulfide and

Table 2

Determination of sulfide in water samples.

Sample	Sulfide added (ng mL ⁻¹)	Sulfide found ^a (ng mL ⁻¹)	Recovery (%)
Mahshahr refinery wastewater	–	96.6 ± 0.9	–
	20	117.7 ± 0.3	105.5
	100	199.8 ± 1.7	103.2
Karoon river water	–	ND ^b	–
	20	19.5 ± 1.1	97.5
	100	101.1 ± 1.6	101.1
Tap water	–	ND	–
	20	21.4 ± 1.0	102.0
	100	98.4 ± 1.9	98.4

^a $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence (*n*=5).

^b ND, not detected.

analyzed. The results of these determination and the recoveries for the spiked samples are listed in Table 2. Five measurements were performed at each concentration. A good agreement was obtained between the added and found and the value of the analyst and recoveries were in the range of 97.5–105.5. The obtained results show the applicability of the method to matrices such as water samples.

4. Conclusions

The investigation carried out illustrates the high potential and feasibility of using the CURNs in cloud point extraction for the determination of analytes. This study proposes a method for the sensitive determination of sulfide based on its effect on CPE of CURNs. To the best of our knowledge this is the first application of cloud point extraction CURNs for the determination of an analyte. The CURNs are label free and no reagent is used for its modification. The methodology is simple and relatively selective for sulfide with a low detection limit and does not require sophisticated instrumentation. The limit of detection achieved is better than some of the previously reported methods in the literature. As can be ascertained, analytical characteristics of the recommended CPE-CURNs method for sulfide sensing are significantly improved over some of the previously reported methods [2,4,6,7,11,13–17]. The noteworthy advantage of the proposed method is using the CURNs as a green nanoparticle in cloud point extraction as a green method for determination of sulfide.

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