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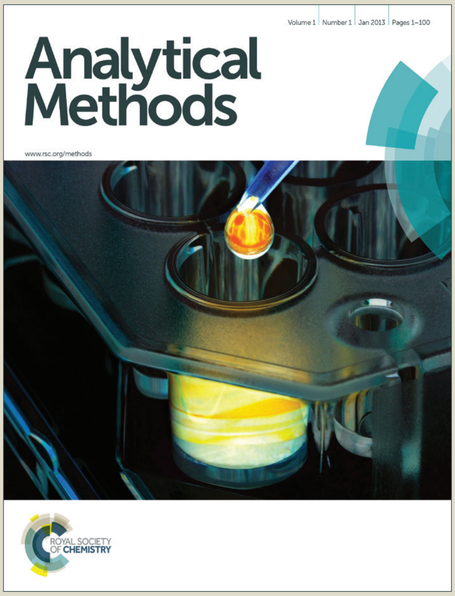

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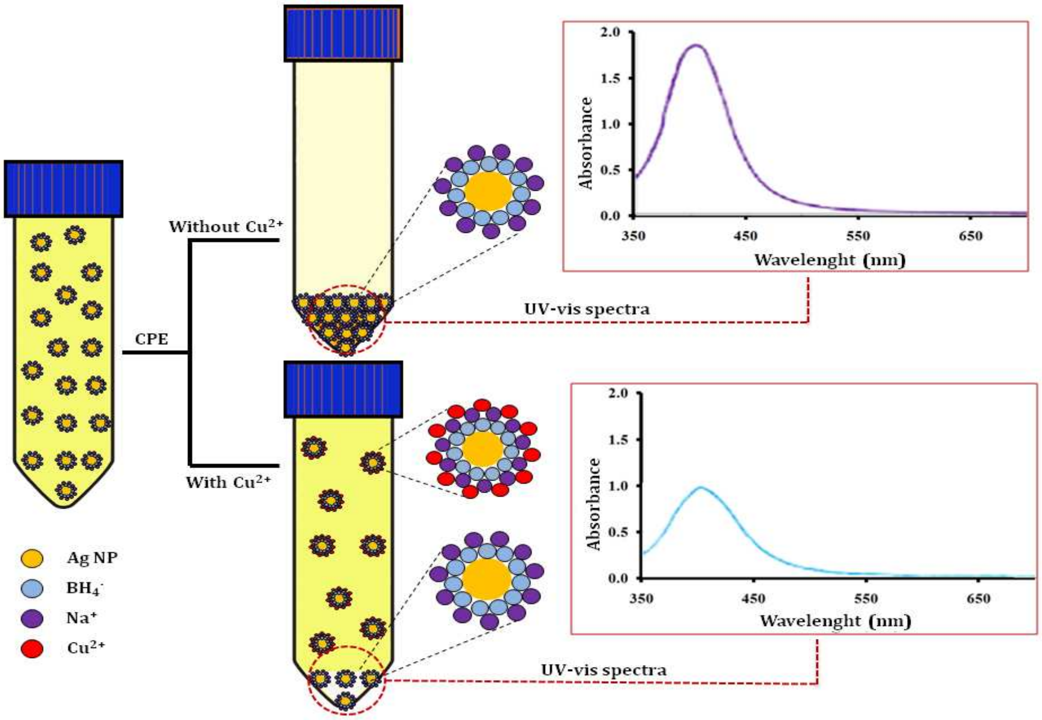

Colorimetric sensing of copper based on its suppressive effect on cloud point extraction of silver nanoparticle

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Abstract

Silver nanoparticles exhibit the optical properties of surface plasmon resonance (SPR). This paper describes a method based on both SPR and cloud point extraction of silver nanoparticles (AgNPs) for the determination of copper. Label free AgNPs are enriched into non-ionic surfactant phase and show strong SPR intensity. Copper(II) suppresses the transfer of AgNPs into surfactant and decreases the SPR intensity. The decrease in the absorbance of surfactant rich phase in the presence of Cu(II) was used as an analytical signal for the determination of copper. The influence of chemical variables such as pH of the sample solution, ionic strength, and concentration of AgNPs on the cloud point extraction was investigated. Under optimum conditions, the extent of decrease in SPR absorption intensity was linearly proportional to the concentration of Cu(II) in the range of 0.5-60.0 μg L^{-1} with a detection limit of 0.1 μg L^{-1}. The relative standard deviation for ten replicate measurements of 40 μg $L^{-1}$of Cu(II) was 3.7%. The proposed method was successfully applied to the determination of Cu(II) in food samples with satisfactory results.

Keywords: Silver nanoparticles; Copper; Cloud point extraction; Surface plasmon resonance;

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1. Introduction

Copper is an essential element and an important bio-element present in animals, plants and microorganisms. However, copper at higher levels is toxic and severe oral intoxication will affect mainly the blood and kidneys. Above a healthy limit it accumulates in the liver, causing diarrhea, vomiting, transpiration and depending on its concentration, death from bleeding.[1,2] Pollution by heavy metals is also causing serious ecological problems in the world; therefore, the determination of trace heavy metals such as copper in the environmental samples is an important task in analytical chemistry and requires analytical methods exhibiting low detection limits for this toxic element. However direct determination of trace elements appears to be difficult as their concentration is close to or below the detection limits of the most analytical techniques and the real sample matrix may also cause serious interference during their determination process.[3] Therefore sample preparation in relation to analyte extraction and preconcentration is considered as the most critical step. The development of preconcentration procedures prior to the analyte determination has been extensively explored in recent decades. Among the techniques used are dispersive liquid–liquid extraction,[4] ion exchange,[5] coprecipitation,[6] solid phase extraction[7-10] and micellar systems.[11,12] The latter systems have been exploited in different fields of analytical chemistry, mainly those focusing on separation and preconcentration based on cloud point procedures.[13]

Aqueous solutions of nonionic and zwitterionic surfactants exhibit clouding phenomena when heated, which depends on the nature and concentration of the amphiphiles.[14] The cloud point is the temperature above which the aqueous solutions of non-ionic and zwitterionic surfactants become turbid. 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 poor phase with a surfactant concentration close to the critical micelle concentration (cmc). Hydrophobic species (organic compounds or metal ions after reaction with a suitable ligand) present in the samples are able to interact with the micelles, thus being concentrated in the small volume of the surfactant-rich phase.[15] Cloud point extraction using micelles has become a very popular methodology for the developments of new analytical procedures for various species[16-19] and metal ions.[20] Cloud point extraction procedure coupled to ICP-OES[21] has been developed for simultaneous determination of copper and mercury using 3-nitro benzaldehyde thiosemicarbazone (3-NBT) as complexing agent. Wen et al. have proposed an improved preconcentration method named as rapidly synergistic cloud point extraction (RS-CPE) for copper preconcentration and determination.[22]

Recently colorimetric method based on nanoparticles has been used to detect different analytes. Several researchers have applied modified AuNPs[25] and unmodified AuNPs[24] for developing colorimetric sensors for copper. A colorimetric sensor based on surface- enhanced Raman scattering (SERS) method using cysteine functionalized silver nanoparticles (AgNPs) attached with Raman-labeling molecules was developed for the detection of copper(II) and mercury(II).[25] A colorimetric method for the determination of Pb(II) based on the use of silver nanoparticles functionalizd with iminodiacetic acid (IDA-Ag NPs) have been reported.[26] Silver nanoparticles have been utilized for colorimetric sensing of copper by paper-based devices[27] and also for quantification of trace amounts of thrombin using aptamer-mediated detection.[28] For the first time Liu et al. reported the cloud point extraction of several nanomaterials with various sizes and different capping agents using non-ionic surfactant Triton X-114.[29] They have demonstrated that cloud point extraction (CPE), can be utilized to concentrate and recycle nanoparticles (NPs) in aqueous media. They also showed that cloud point extraction of AuNPs can be applied for the sensing of Hg^{2+} in water samples with high sensitivity and selectivity.[28] Cloud point extraction with mixed surfactants has also been employed for separation and recycling of nanoparticles from aqueous.[31,32]

This work presents the application of silver nanoparticles in cloud point extraction for the determination of copper. Label free AgNPs are extracted into Triton X-100 as a non-ionic surfactant. Strong surface plasmon resonance (SPR) intensity is observed for AgNPs enriched in surfactant phase. However in the presence of Cu(II), the intensity of SPR is decreased because of the interaction between silver nanoparticles and copper ions at the colloidal interface of the nanoparticles. The decrease in the absorbance of surfactant rich phase is proportional to Cu(II) concentration which was used as an analytical signal for the determination of Cu(II).

2. Experimental

2.1. Instruments

Absorption spectra and absorbance measurements were made by a GBC UV–visible spectrophotometer model Cintra 101 (Sidney, Australia) using 1 cm glass cells. TEM images were obtained with a Zeiss- EM10C-80 KV transmission electron microscope (Oberkochen, Germany). A digital pH-Meter model 632, Metrohm (Herisau, Switzerland) with a combined glass electrode was used for pH measurements. A thermostat bath model Colora (London, England) maintained at the desired temperature was used for the cloud point temperature experiments.

2.2. Reagents

All chemicals were of analytical grade and doubled distilled water was used throughout. A stock solution of 1000 mg L^{-1} of Cu(II) was prepared by dissolving

3.9270 g of the $CuSO_4.5H_2O$ (Merck, Darmstadt, Germany) in water and diluting to 1000 mL in a volumetric flask. 0.1 M of NaCl was prepared by dissolving 0.5844 g of sodium chloride (Merck) in water and diluting to 1000 mL in a volumetric flask. 5% (v/v) of Triton X-100 (Merck) was prepared by diluting 5 mL of the reagent to 100 mL. For preparation of Robinson buffer (pH 7.5), 2.473 g of boric acid, 20 mL of phosphoric acid (0.04 M) and 20 mL of acetic acid (Merck) were transferred to a 1 L volumetric flask and diluted to the mark with water. The pH of this solution was then adjusted to 7.5 by the addition 0.2 M of NaOH (Merck). 2×10^{-3} M of sodium borohydride (Merck) and 10^{-3} M of silver nitrate (Merck) were also prepared.

2.3. Synthesis of silver nanoparticles

The silver nanoparticles were synthesized using the following protocol: Aqueous solutions of sodium borohydride ($NaBH_4$, 2×10^{-3} M) and silver nitrate ($AgNO_3$, 10^{-3} M) were placed in an ice bath for 20 min without stirring as separately. Then, 10 mL of Triton X-100 was added to 100 mL of sodium borohydride, and was gently mixed to ensure homogeneous solution. Next, 33 mL of silver nitrate solution was added dropwise to this solution (about 1 drop/second) and the solution was stirred at 1500 rmp by a magnetic stirrer at room temperature, until it was all used up to obtain bright yellow AgNPs. The stirring was then stopped and 10 mL of Triton X-100 was added to this mixture and mixed. The solution was slightly shaken and kept away from heat and light.

2.4. Recommended procedure

A typical colorimetric analysis was carried out by following steps. 7 mL of synthesized AgNPs solution, 7 mL of Triton X-100 5%(v/v) 1.0 mL of Robinson buffer (pH 7.5), 2.5 mL of 0.1 M of NaCl and 40 μg L^{-1} of Cu(II) were placed in 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 20 min. The solution turns cloudy at this step. Then the solution was cooled in an ice-bath for 20 minutes. After decantation, the surfactant-rich phase was separated and in order to reduce the viscosity, it was diluted to 5 mL in a volumetric flask with doubled distilled water. A portion of this solution was transferred into a 1cm glass cell and its absorbance was measured at 402 nm. A blank solution was also prepared in the same way without adding Cu(II) solution.

2.5. Sample preparations

2.0 g of green tea, 2.0 g of black tea and 5.2 g of tomato sauce samples were precisely weighted and transferred to individual porcelain crucibles and burned on a flame. The crucibles were placed in a muffle furnace at 550 °C for 4 h. 10 mL of concentrated nitric acid was added to the residue and evaporated to dryness. Then 5 mL of hydrogen peroxide (30 %) was added and heated to dryness again. The pH of the samples was adjusted by dropwise addition of sodium hydroxide to about 7.5. These solutions were finally transferred to individual 25 mL volumetric flasks and made up to the mark with water. Aliquots of these solutions were subjected to the general procedure.

3. Results and Discussion

Our investigation showed that SPR absorption intensity of enriched AgNPs after CPE is considerably decreased upon the addition of Cu(II) without any wavelength shift. Fig. 1 demonstrates the UV-Vis absorption spectra and TEM images of the corresponding AgNP after CPE. The TEM images show that there is a significant change between the extracted AgNPs by CPE in the (b) absence and (d) presence of Cu(II) which indicates less AgNPs are transferred into Triton X-100 in the presence of copper ions. The UV-Vis spectra (Fig. 1) show that λ_{max} of the enriched AgNP in Triton X-100 is at 402 nm. Fig. 1 also shows the decrease in the absorbance of the corresponding spectra in the (a) absence and (c) presence of Cu(II). The decrease in the absorption intensity was proportional to Cu(II) concentration. As can be deduced from TEM images, here no significant aggregation of AgNPs was observed because aqueous micellar solutions such as non-ionic surfactant Triton X-100 are known as colloidal self-assembly fluids for stabilization of NPs and can acts as a molecular spacer which could prevent the aggregation of AgNPs. Triton X-100 is also known to form the hexagonal phase in aqueous solution which could restrict the aggregation of AgNPs to some extend.[32] Therefore despite most reported methods that use the aggregation or accumulation property of SPR nanoparticles for analyte determination, here no aggregation has occurred. The reason for this phenomenon is dispersion of AgNPs in surfactant-rich phase as a dispersing agent that prohibits the AgNPs from aggregation.[33] In this work the Cu(II) measurement strategy is related to its inhibitory effect on transfer of AgNPs to surfactant-rich phase and not its effect on size or shape of AgNPs. This phenomenon distinguishes this study from previous studies in which AgNPs have been used for analytical purposes. Thereupon, for this work, the analytical signal (ΔA) was defined as the difference between SPR absorption intensity of AgNPs-CPE in the absence and presence of Cu(II).

The change in SPR absorption intensity in the presence of different concentrations of Cu(II) is also shown in Fig. 2. As can be observed the dimensions of the nanoparticles in the surfactant-rich phase were preserved, and there was no shift in the wavelength.

In order to obtain the best results, the optimum conditions were established by studying the influence of various parameters including the effects of pH, buffer, electrolyte concentration, surfactant types and concentrations, AgNPs concentration, and equilibrium temperature and time on the method performance.

3.1. Influence of pH

The pH is an important analytical parameter because; it has a major effect on the CPE-AgNPs spectral characteristics. Hence, the effect of pH on the SPR absorption intensity of CPE-AgNPs was investigated in the range of 4-11 to obtain an optimum pH for the determination of Cu(II). The pH of the solution was adjusted by dilute NaOH and HCl solutions using pH meter. As can be seen from Fig. 3 the maximum of analytical signal for the determination of 40 μg L^{-1} of Cu(II) was appeared at pH 7.5. Therefore, pH 7.5 was chosen for further experiments. Different buffer solutions with pH 7.5 such as phosphate, citrate, maleate, carbonate and Robinson were examined for the adjustment of pH of the CPE-AgNPs solution. All the buffers except Robinson buffer decreased the analytical signal, thus, Robinson buffer with pH 7.5 was selected for further studies and 1 mL of Robinson buffer (pH 7.5) was added to the solutions for maintaining pH at 7.5.

3.2. Influence of electrolyte

The study of the effect of electrolytes on the cloud point extraction using ionic-nonionic surfactants has been reported before.[34] It has been shown that the cloud point of micellar solutions can be controlled by the addition of salts, alcohols and some organic compounds (salting-out effects).[35] For this purpose the impact of electrolytes on this work was evaluated by adding different salts to the solutions before CPE. It was found that among the salts tested i.e. NaCl, KCl, $NaNO_3$, Na_2SO_4 and NaF, the NaCl was better electrolyte for this system with respect to viscosity of coacervate phase. Therefore, the influence of NaCl concentration on the analytical signal was evaluated by adding different concentrations of NaCl. It was found that by increasing the concentration of NaCl, the extent of SPR absorption intensity ascends rapidly. In the absence of NaCl and Cu(II) ions, surface charge of AgNPs is negative (AgNPs are surrounded by BH_4^-), thus it is not enriched into surfactant phase. By adding Cu(II) to the system without adding NaCl, Cu(II) ions are binding to the negative AgNPs so that the surface charge of AgNPs is neutralized and it can be enriched into surfactant phase and SPR absorption intensity is increased. On the other hand, in a system containing NaCl but without Cu(II), AgNPs are also enriched into surfactant phase as a result of electrolyte surrounding the negative AgNPs, meaning that it also neutralizes the surface charge of AgNPs (high SPR absorption intensity). But in a system containing both Cu(II) and NaCl, both ions compete for neutralization of AgNPs and at lower concentration of NaCl negative ΔA is obtained (Fig. 4). However at the higher concentration of NaCl where AgNPs are surrounded by Na^+, the presence of Cu(II) inhibits the transfer the AgNPs to surfactant phase (Low SPR absorption intensity) by making the surface more positive this time.

As illustrated in Fig. 4 analytical signal of AgNPs-CPE in the presence of Cu(II) was increased by increasing the NaCl concentration and reached a maximum at 5×10^{-3} M concentration and it was descended again. Hence, the final concentration of 5×10^{-3} M of NaCl was selected for further experiments and 2.5 mL of 0.1 M NaCl was added to 50 mL solutions in order to achieve this concentration.

3.3. Surfactant selection and influence of its concentration

AgNPs have a strong tendency to agglomerate and aggregate, hence a stabilizing agent is often used to prevent this. Therefore, in this method, a non-ionic surfactant was used as a dispersing and stabilizing agent for AgNPs and also for cloud point extraction process. In order to investigate the effect of non-ionic surfactants types on the system, surfactants such as Triton X-114 and Triton X-100 and mixture of both were studied. In this case, Triton X-100 gave slightly better phase separation. Triton X-100 5%(v/v) was chosen and the effect of its volume was investigated in the range of 5-15 mL. The highest analytical signal was observed in a volume of Triton X-100 5%(v/v) equal to 7 mL. Thus, this volume was selected as optimum for further experiments.

3.4. Influence of equilibrium temperature and time

It is most desirable to employ 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 AgNPs were investigated in the range of 60-90 °C and 15-45 min, respectively. The results showed that maximum analytical signal was obtained at 80 °C and an equilibration time of 30 min was adequate for the analysis. Based on the results obtained in this study the standing time of surfactant enriched phase in the ice bath has no significant effect on the extraction efficiency. Hence, 20 min was chosen as the standing time in ice bath for all experiments.

3.5. Influence of AgNPs concentration

The effect of the AgNPs concentration on the analytical signal was studied by using different volumes of the synthesized AgNPs. It was observed that the analytical signal was increased by increasing AgNPs concentration. Although by increasing the AgNPs concentration, SPR absorption intensity is increased, transfer of AgNPs to surfactant phase is difficult and higher surfactant amounts is needed. As was stated in the above sections, SPR absorption intensity of enriched AgNPs-CPE decrease considerably upon addition of Cu(II). Therefore 7 mL of synthesized AgNPs was added to 50 mL solutions for high ΔA for Cu(II) and ease of extraction into surfactant for further experiments.

3.6. Analytical performance and validation

The analytical figures of merit of the proposed method were evaluated with the recommended procedure under the optimum conditions. The method exhibited a linear range from 0.5 to 60 μg L^{-1} and with a correlation coefficient (r) of 0.9992. The linear regression equation for Cu(II) was $\Delta A = 0.027C + 0.010$. The relative standard deviation for ten replicate measurements of 40 μg L^{-1} of Cu(II) was 3.7%. The limit of detection was determined as a concentration giving a SPR peak with a signal to noise ratio of (3:1) and found to be 0.1 μg L^{-1}. The molar extinction coefficient of the method was found to be 1.7×10^{6} L mol^{-1} cm^{-1}.

3.7. Interferences

The influence of common anions and cations on the analytical signal of Cu(II) in binary mixture system under the optimum experimental conditions stated above was investigated. Any relative error equal or greater than ±5% from the analytical signal value of the Cu(II) was considered as an interference. The assays were operated by fixing the concentration of Cu(II) at 40 μg $L^{-1}$and then measuring the analytical signal before and after adding the interfering ion. The results of this investigation are represented in Table 1. Fluoride and oxalate ions did not interfere even at 500-fold of

Cu(II); hence they were applied as a masking agent for Cd^{2+} to 10-fold and Ni^{2+}, Mn^{2+}, Co^{2+} to 25-fold respectively.

3.8. Application of AgNPs-CPE to determination of Cu(II) in food samples

In order to assess the potential application of the proposed method, it was applied to determination of Cu(II) in food samples such as tomato sauce, black and green tea under optimum conditions. These samples were spiked with two concentration levels of Cu(II) and analyzed. The results of this 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 added and found value of the analyte and recoveries were in the range of 96.3-105.0%. Tomato sauce and black tea samples were also analyzed by ICP-OES method for comparison and the results are given in Table 3. The values obtained by both methods show that there is a good agreement between the results and there was no significant difference between them by performing a t-test at 95% confidence limit.

4. Conclusions

This research has demonstrated the application of silver nanoparticles (AgNPs) in non-ionic micellar systems, here Triton X-100, for developing a method for sensitive determination of copper using cloud point extraction. The AgNPs are label free and no reagent is used for the modification of AgNPs. Despite previously reported methods the dimensions of the nanoparticles in the surfactant-rich phase were preserved, and there was no shift in the SPR wavelength due to entrapment of AgNPs in hexagonal phase formed by nonionic surfactant Triton X-100 as a colloidal self-assembly fluid.[32] The advantage of this method is that it is cost-effective, requiring commercially available and relatively cheap surfactants. The methodology is simple and relatively selective for Cu(II) and does not require sophisticate instrumentation. A significant advantage of this method over other attempts is its low detection limit (0.1 µg L^{-1}) which is comparable or better than some of the previously reported methods in the literature. A more detailed comparison with some of the previously reported methods for copper determination is provided in Table 4.

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Table 1

The effect of interfering ions on the determination of 40 μg L^{-1} of Cu (II).

Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) 1.0 mL of Robinson buffer (pH 7.5) and NaCl (5×10^{-3} M).

Interfering	Tolerance ratio [Ion]/[Cu^{2+}]
SO_4^{2-}, Cl^-, Borate	1000
NO_3^-, $C_2O_4^{2-}$, F^-, K^+, Citrate	500
CO_3^{2-}, HCO_3^-, Br^-, PO_4^{3-}	250
Pb^{2+}	100
Al^{3+}, Bi^{3+}	50
Hg^{2+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}	25
Cd^{2+}	10
I^-	5
Cr^{3+}	3
Zn^{2+}	1

Table 2

Determination of Cu(II) in food sample solutions.

Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) 1.0 mL of Robinson buffer (pH 7.5) and NaCl (5×10^{-3} M).

Sample	Cu(II) added (μg L^{-1})	Cu(II) found[a] (μg L^{-1})	Recovery (%)
Tomato sauce	-	17.1±1.0	-
	10	26.9±0.4	98.0
	30	48.2±0.3	103.6
Green tea	-	6.6 ±0.5	-
	10	17.1±1.0	105.0
	30	36.2±2.1	98.7
Black tea	-	11.2±0.6	-
	10	21.4±1.0	102.0
	30	40.1±2.2	96.3

a) x ±ts/√n at 95 % confidence (n=5)

Table 3

Determination of Cu (II) in food samples and comparison by ICP-OES

Sample	Proposed method[a] ($\mu g\ g^{-1}$)	ICP-OES[a] ($\mu g\ g^{-1}$)
Tomato sauce	3.3±0.2	3.4±0.2
Black tea	27.9±1.7	27.2±2.2

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

Table 4
Comparison of the proposed method with some of the previously reported methods for copper determination in literature

System	DL (μg L^{-1})	RSD (%)	Ref
SPE-FAAS	1.0	2.4	[1]
Solidified floating drop microextraction	0.18	2.7	[2]
SPE-FAAS, nano material (ZrO_2/B_2O_3	3.3	3.0-4.0	[3]
Liquid–liquid microextraction	0.5	1.4	[4]
SPE-FAAS coprecipitation by zirconium(IV) hydroxide	1.55	3.9	[6]
CPE-FAAS	0.5	2.7	[11]
CPE-ICP	0.48	3.2	[21]
Synergic CPE	0.4	3.7	[22]
Paper-based devices	0.5	-	[27]
SPR-CPE	0.1	2.3	This work

Figure captions

Fig. 1 UV-Vis spectra of AgNPs after CPE (a) in the absence and (c) in the presence Cu(II), together with the corresponding TEM images (b) and (d) in the absence and presence of Cu(II), respectively. Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) 1.0 mL of Robinson buffer (pH 7.5) and NaCl (5×10^{-3} M).

Fig.2. The UV–vis spectra and colorimetric detection of Cu(II) at different final concentrations utilizing the CPE-AgNPs. Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) 1.0 mL of Robinson buffer (pH 7.5) and NaCl (5×10^{-3} M).

Fig. 3. Influence of pH on determination of Cu(II) with CPE-AgNPs. Each number is average of three determinations. Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) and NaCl (5×10^{-3} M).

Fig. 4. Effect of electrolyte concentration on the determination of Cu(II) with CPE-AgNPs. Each number is average of three determinations. Conditions: 7 mL of AgNPs solution, 7 mL of Triton X-100 5%(v/v) and 1.0 mL of Robinson buffer (pH 7.5)

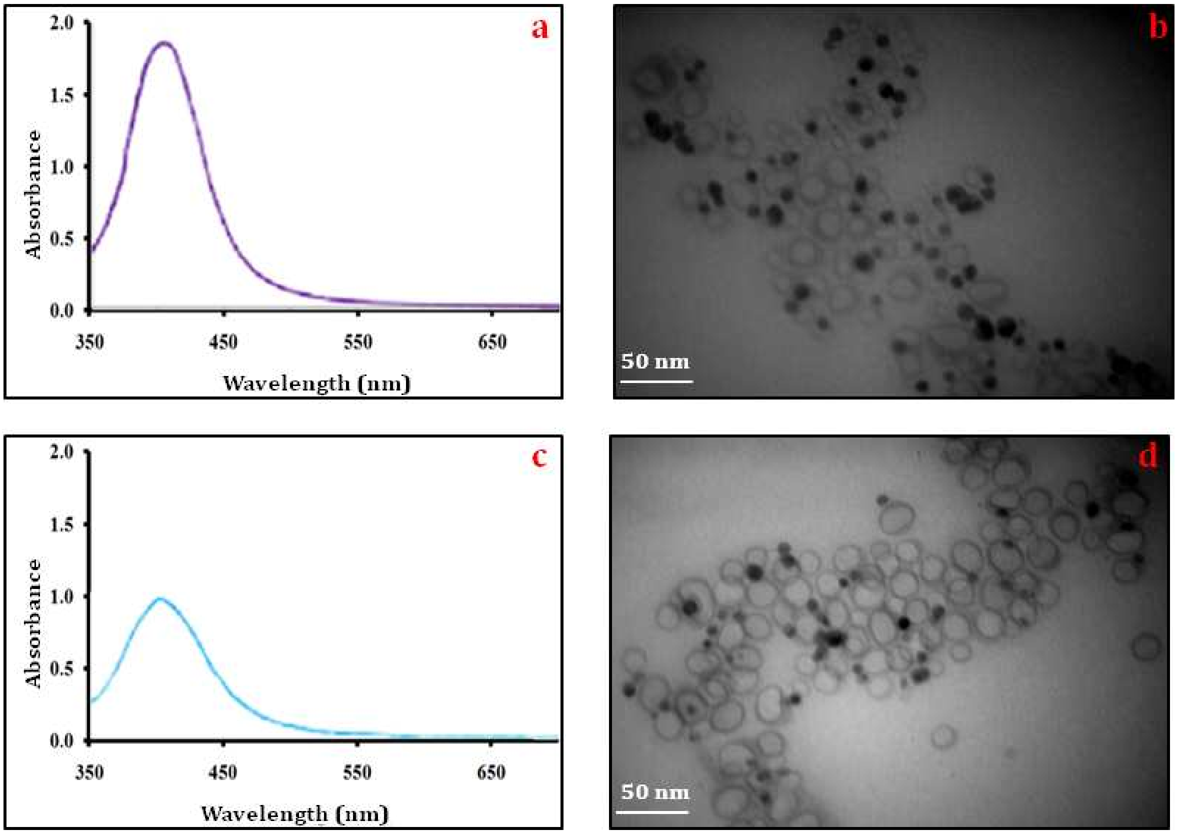
a
2.0
1.5
1.0
0.5
0.0
Absorbance
350
450
550
650
Wavelength (nm)
b
50 nm
c
2.0
1.5
1.0
0.5
0.0
Absorbance
350
450
550
650
Wavelength (nm)
d
50 nm

Fig. 1

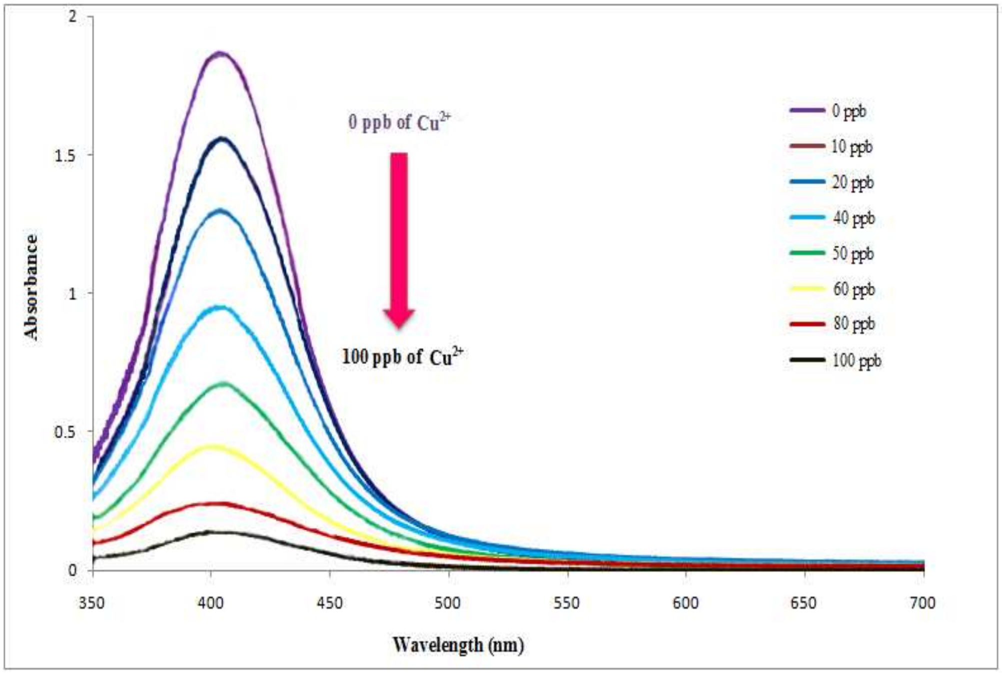
2
1.5
1
0.5
0
Absorbance
350
400
450
500
550
600
650
700
Wavelength (nm)
0 ppb of Cu^{2+}
100 ppb of Cu^{2+}
0 ppb
10 ppb
20 ppb
40 ppb
50 ppb
60 ppb
80 ppb
100 ppb

Fig. 2

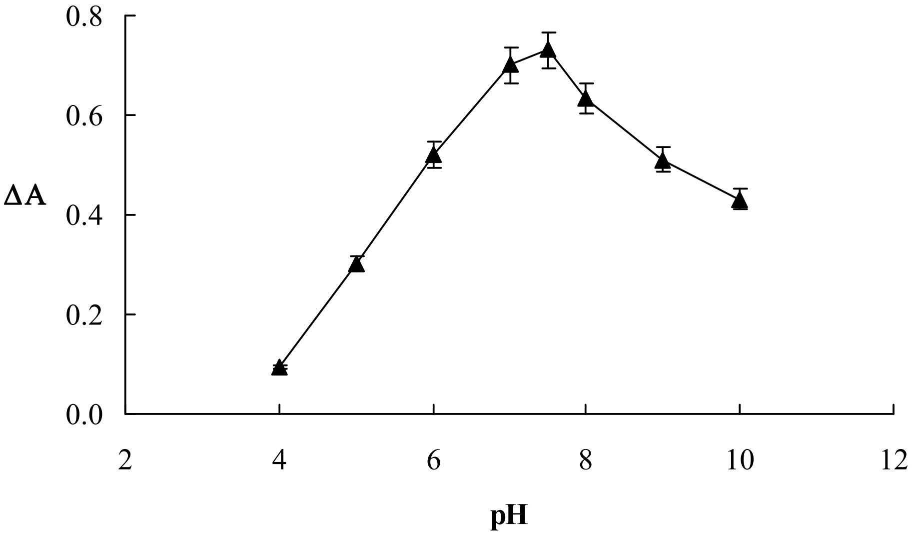

Fig. 3

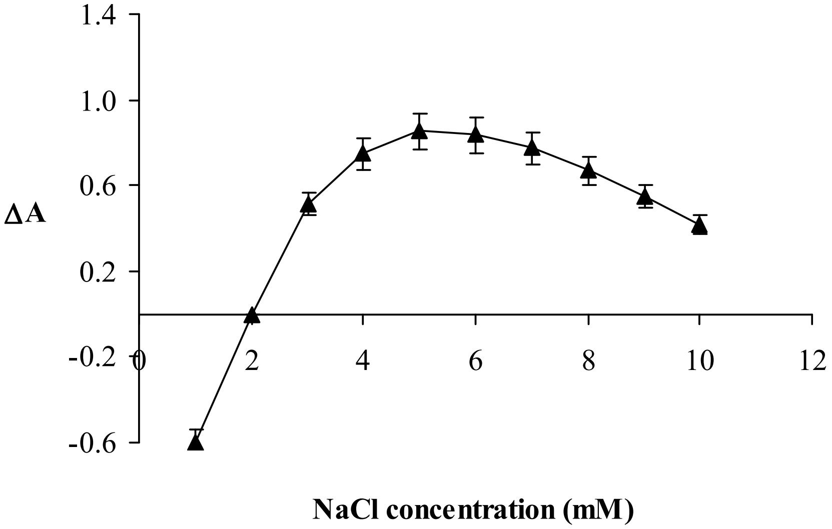

Fig. 4