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Separation and flotation extraction of Cd(II) and Zn(II) traces using a new ligand 2-(4-choloro phenyl)–2,3-dihydroqinazoline(1H)–4-one(CPHQO), before their flame atomic absorption spectrometric determinations in colored hair and dryer agents of paint

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ABSTRACT

A simple, rapid and inexpensive method for separation and pre-concentration of some traces of hazardous elements is presented prior to their flame atomic absorption spectrometric determinations. At pH 9.0±0.1; cadmium(II) and zinc(II) were separated simultaneously with 2-(4-Choloro Phenyl) –2,3 Di Hydro Qinazoline (1- H) – 4 one (CPHQO) as a new complexing agent and floated after adding sodium dodecyl sulfate (SDS) as a foaming reagent. The floated layer was then eluted by concentrated nitric acid in methanol and introduced to the flame atomic absorption spectrometer (FAAS). These ions can be eluted quantitatively with 0.5 ml1.0M HNO_3 in methanol. The linear range of the determination is between 0.03-1.5 $\mu g\ mL^{-1}$ for Cd^{2+} and 0.02-1.7 $\mu g\ mL^{-1}$ for Zn^{2+} with a detection limits for Cd^{2+} and Zn^{2+} were 0.9 ng mL^{-1} and 1.2 ng mL^{-1}, respectively. The method has been successfully applied for determination of those heavy metals in colored human hair and dryer agents of paint samples.

Keyword: Trace; flotation; separation; Flame atomic absorption spectrophotometry (FAAS) ; dryer agent; colored hair.

INTRODUCTION

The determination of trace metals in the environmental samples including natural waters have been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated [1–3]. The importance of heavy metals and their complex roles in biological systems come from their diverse functions and low level of existence. For instance, some of the trace heavy metals are essential to life while others are toxic even at very low concentrations. However, some of these heavy metals are of particular concern because of their toxicities to humans [4-7], These problems can be overcome by replacement of filtration or centrifugation by flotation. The major advantages of the flotation pre-concentration method are the rapidity in addition to excellent recoveries of investigated trace elements. The equipments necessary for flotation pre-concentration are simple and inexpensive. The small amount of a surfactant and the tiny air bubbles require to perform the proper flotation prevent serious contamination risks, which could be manifested by the high blank value. one of the most important advantages of the flotation method is the ability to analyze a large volume of sample solution and to obtain a greater pre-concentration factor. on the other hand, because the physical and chemical properties of aragonite aqueous solution are similar to those of the natural waters with higher water hardness, a method of flotation is applied as the second way to eliminate the calcium matrix effects [8-11]. Flotation has been used for the recovery of valuable substances from ores and minerals in the mining industry since this century began [12و13]. Step by step, this technique has found applications in different fields of chemical engineering as well as analytical chemistry[14]. Ion flotation, as a flotation subgroup, is a pre-concentration technique known since the early 1960s[15]. It is a simple and inexpensive method for effective removal of ionic species from dilute aqueous solution[16و17]. The major advantages of this method are the rapidity and high recoveries of the trace elements investigated[18]. Several methods have been developed for the flotation of cadmium and zinc ions as trace elements [19-21].

The purpose of this work is pre-concentration by flotation of Cd^{2+} and Zn^{2+} using CPHQO (figure 1) [22]. The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

Mp: 206-208 ºC (Lit. 198-200 ºC) ; ^{1}H NMR (DMSO-d_6, 400 MHz) δ : 5.77 (s, 1H), 6.68 (dt, 1H, J_1= 7.4 Hz, J_2= 0.5 Hz), 6.75 (d, 1H, J= 8.1 Hz), 7.15 (s, 1H), 7.25 (dt, 1H, J_1= 7.8 Hz, J_2= 1.5 Hz), 7.46 (d, 2H, J_1= 8.6 Hz), 7.51 (d, 2H, J= 8.8 Hz), 7.61 (dd, 1H, J_1= 7.8 Hz, J_2= 1.7 Hz), 8.34 (s, 1H). ; ^{13}C NMR (DMSO-d_6, 100 MHz): 65.7, 114.4, 114.9, 117.3, 127.3, 128.3, 128.7, 132.9, 133.9, 140.6, 147.6, 163.5. ; IR (KBr) (cm^{-1}): 3270, 3125, 1650, 1600, 1505, 1485, 1427, 1378, 1485, 1147, 1094, 1008, 827, 796, 750, 662, 500.

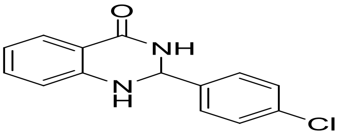

Figure1: ligand 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinazoline (1- H) – 4 one (CPHQO)

MATERIALS AND METHODS

2. Experimental

2.1. Instruments

All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the equipment were established according to the manufacturer's recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements.

2.2. Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of cadmium, zinc, mercury, cobalt, iron, nickel, copper, Lead, silver, magnesium, calcium, strontium, barium, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. The ligand 2-(4-Choloro Phenyl) – 2,3 Di Hydro Qinazoline (1- H) – 4 one (CPHQO) was synthesized according to literature [22].

2.3. Spectrophotometric titrations

Standard stock solutions of CPHQO (10^{-5} M) and the metal ions (3.0×10^{-5} M) were prepared by dissolving appropriate and exactly weighed (accuracy of ± 0.0001 g) amounts of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks, and diluting to the mark with MeOH. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of 2.6 mL of CPHQO 3.5×10^{-5} M solution was carried out by the addition of micro-liter amounts of a concentrated standard solution of the metal ion ($1.0\text{-}7.5 \times 10^{-5}$ M) using a pre-calibrated micro-syringe, at 25.0 $^{\circ}$C, with the spectrum subsequently recorded.

2.4. Flotation-separation procedure

A separation funnel with sidelong tube was used for flotation-separation. The separation funnels a sample solution containing 0.20 µg mL^{-1} of each ion, 0.5 mL 1.0 M of HNO_3 solution. 0.25 mL of 0.5% (w/w) solution of SDS and 0.35mL of 10^{-5} M of CPHQO were added, the pH of medium was carefully adjusted to 9.0±0.1 with nitric acid or sodium hydroxide solution . The mixture was diluted to 10 mL and after stirring for 20 min. then an air stream (10 mL min^{-1}) was kept flowing for 2-4 min to raise the foam layer to the water surface. A foamy layer was thus obtained and the aqueous solution in the cell became clear. Then the aqueous solution in the cell became clear was ousted of separation funnel and the foam layer was dissolved in 0.5 mL 1.0 M HNO_3 in methanol and then the metal ions content was readily evaluated by FAAS.

2.5. Application to real samples

Two kinds of naphthenates, cadmium naphthenate and zinc naphthenate, were selected among the various types of dryer agents. These kinds of paint additives are some resistant soap prepared from naphthenic acid, a sort of acid which is found naturally in raw oil, and they widely are used in the paint technology as the catalysts in drying process of the paint film[23]. Analysis of the both samples was performed as the following: A sample of the dryer containing 5 mg of the metal was piped into a 100 mL beaker and 2 mL concentrated nitric acid was added. The mixture was boiled for about 3 minutes on a hot plate with rapid stirring. When the hydrolysis was completed, the naphthenic acids along with the solvent present separated as a clear light yellow layer. The contents of the beaker were cooled and transferred to a separating funnel and 10 mL of ethyl acetate was added to it. The lower aqueous layer containing the metal was drawn off into a 250 mL beaker. The organic layer was then washed twice with 10 mL DDW and the washing was added to the beaker each time[24]. The medium was diluted to 250 mL. After adjustment of pH to desired value, 1mL of the solution was used for flotation procedure given in section 2.4.

The determination of cadmium and zinc in colored hair samples of human was performed as the following: prior to analysis, each individual hair sample was cut into a size less than 1cm and mixed tomake a representative hair sample. After washing, the sample was dried in an oven at 50 °C for 5 minutes. 100 mg of the sample was heated in the presence of 10 mL concentrated nitric acid on a hot plate for about 20 minutes. After a clear solution was formed, 1 mL of H_2O_2 30% was added and again heated to one-fourth volume[25]. Then its pH was adjusted and the procedure in section 2.4 was repeated.

RESULTS AND DISCUSSION

The aim of this work was to develop a simple, sensitive and available method for the pre-concentration and determination of trace amounts of Cd^{2+} and Zn^{2+} ions in various real samples using flame atomic absorption spectrometry coupled with Flotation. In this regard, the influence of various effective parameters including, pH, surfactant and CPHQO concentrations, heating time and temperature, centrifuge time and rate, as well as the effect of electrolyte on absorbance, were optimized. The complexation study yields important information about the interaction between the ligand and metal ions. Recently, we have used the spectrophotometric method for this purpose [26], before using CPHQO for the flotation of the metal ions.

3.1. Spectrophotometric investigation

The spectra of CPHQO with the addition of Cd^{2+} and Zn^{2+} ions, corresponding mole ratio plot and curve fitting at wavelengths of 498 or 495 nm, are depicted in Figures 2 and 3, respectively. complexation occurs through binding of Cd^{2+} and Zn^{2+} ions to nitrogen atoms, leading to the ML, or ML, ML_2 models. Formation constants and stoichiometries of complexes were calculated using the Kinfit program [27,28] and results are shown in Table 1.

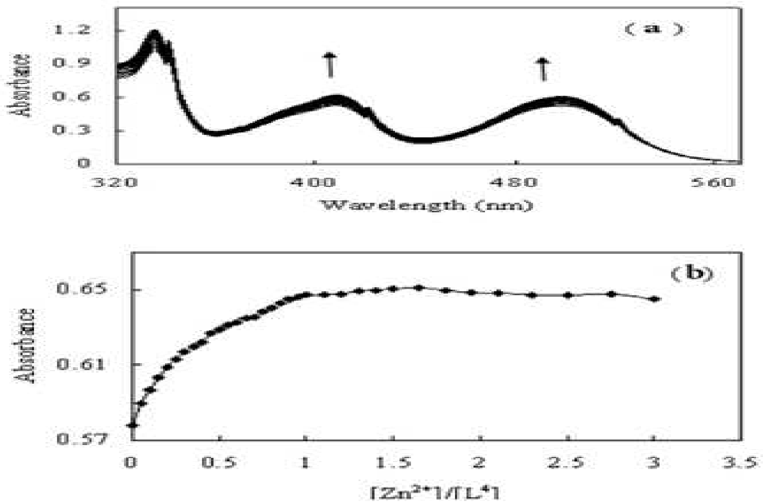

Figure 2. U.V- Visible spectra for titration of CPHQO (3.5 × 10^{-6}mol/L) with Zn^{2+} (5.o × 10^{-5}mol/L) in MeOH (T = 25^{0C}) and I = 0.05 M) (a) and molar ratio plot at 495 nm (b)

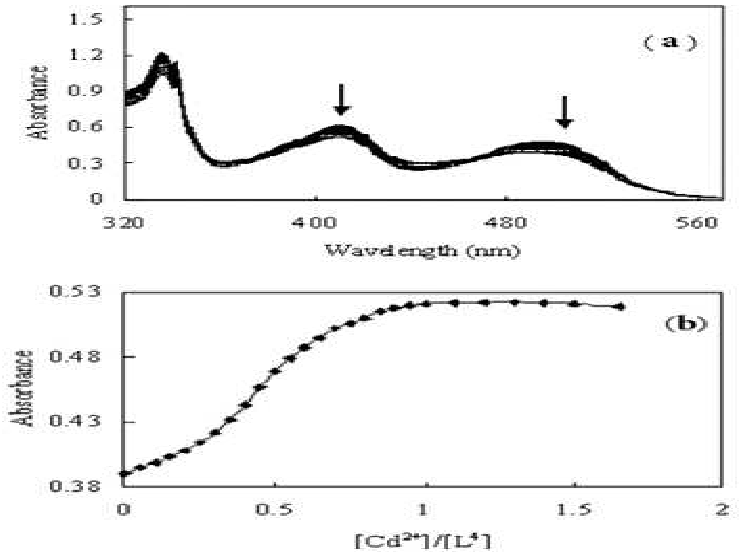

Figure 3. U.V- Visible spectra for titration of CPHQO (3.5 × 10^{-6}mol/L) with Cd^{2+} (5.o × 10^{-5}mol/L) in MeOH (T = 25^{0C}) and I = 0.05 M) (a) and molar ratio plot at 495 nm (b)

Table 1. Stepwise stability constsnts of complexation between metal ions and CPHQO in MeOH

Metal ion	Log K_1	Log K_2	M/L
Zn^{2+}	4.46 + 0.33	_	1:1
Cd^{2+}	5.70 + 0.23	1.24 + 0.39	1:1 , 1:2

3.2. Influence of pH

The formation of the metal–chelate and its chemical stability are two important factors influencing flotation. The pH plays a unique role in metal–chelate formation and subsequent extraction, proving to be the main parameter for flotation. extraction yield depends on the pH at which complex formation is carried out. Thus, a set of similar experiments in the pH range 2.0-12.0 was conducted according to the described procedure described in the experimental section with respective results illustrated in Figure 4. The maximum sensitivity by flotation was obtained at pH 9.0±0.1; In more acidic solutions, deterioration of the signal occurs due to protonation of CPHQO, while at pH > 9.0±0.1, the signal decreases and recovery is reduced due to precipitation of Cd^{2+} and Zn^{2+} ions in the form of hydroxides or ternary complexes. Consequently, pH = 9.0±0.1; was selected for the subsequent studies.

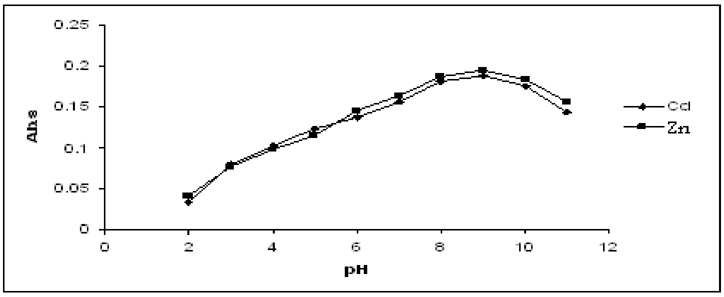

Figure4. Effect of pH on ions recoveries

3.3. Influence of CPHQO concentration

The evaluation of the concentration of complexing agent on the recoveries of the analytes in the floated layer was performed in the range of 1.0 × 10^{-6} to 3.5 × 10^{-5}mol/L of CPHQO. At pH = 9.0±0.1;, 25 mL of a sample solution containing 3.5 × 10^{-6} mol/L of each of the metal ions and 4 mLthe perfect flotation separation of the metal ions was achieved at CPHQO concentration greater than 3.5 × 10^{-6} mol/L Figure 5. Thus, the solution of CPHQO with concentration of 3.5 × 10^{-6} mol/L was used for subsequent experiments. Since the separation efficiency remained constant in the presence of excess amounts of CPHQO, this ligand could easily be used for investigation of the samples containing unknown amounts of the analytes.

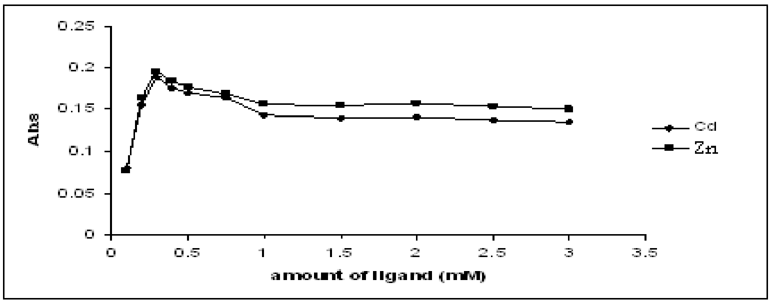

Figure 4. Effect of CPHQO on ions recoveries

3.4. Selection of surfactant

To select the most effective tenside among several cationic, anionic and non-ionic surfactants, a number of tests under previously optimized conditions were carried out and respective results are presented in Table 1. The flotation by use of TX-100 and TX-114 was also ineffective. The anionic surfactants were more effective. The ions flotation recoveries obtained by SDS within the optimal pH range 9.0±0.1; were greater than 98.2 – 98.8%. The anionic surfactant SDS was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost.

Table2. Effect of type of surfactant on sensitivity for 0.2 μg mL^{-1} of interest ion, pH 9.0±0.1, CPHQO(3.5 × 10^{-6}mol/L) and 0.5 % (w/v) of each surfactant

Surfactant t	Cd %	Zn %
Triton X-114	48.7	53.7
SDS	98.2	98.8
Triton X-100	56.7	49.8
No surfactant	25.9	30.4

The flotation efficiency was evaluated using SDS concentrations ranging from 0.05% to 1.0% (w/v). The highest cadmium and zinc ions recovery was obtained with 0.5% (w/v) SDS. By decreasing the surfactant concentration to 0.5% (w/v) the recovery was reduced. The cadmium and zinc ions recovery also decreased for a higher SDS concentration (0.5% w/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [29-31]. At lower SDS concentrations (below 0.5% w/v), the pre-concentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex and float the complex [32,33]. Since, 0.5% (w/v) of SDS showed the highest cadmium and zinc ions recovery; a surfactant concentration of 0.5% (w/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration.

3.5. Effect of ionic strength

It is known that ionic strength of the solution is one of the effective factors in flotation. In this work, the effect of KNO_3 salt as an electrolyte in the range 0.01-0.5 mol L^{-1} on the process was investigated. It is observed that increasing concentration of salt to 0.1 M exerts no effect on the process, but higher concentrations caused a decrease in absorbance of extracted surfactant-rich phase. This effect might be explained by the additional surface charge when the salt concentration is very high.

3.6. Calibration, precision and detection limits

Calibration graphs were obtained by pre-concentration of 25 mL of several solutions under optimum conditions, containing various concentrations of each analyte, with the process performed according to the General procedure section where the absorbance of the final solution was measured by FAAS. A linear relationship between the measured absorbance and concentration of Cd^{2+} and Zn^{2+} ions in the Linear Range 0.03-1.5µg mL^{-1} and 0.02-1.7µg mL^{-1} was obtained(Table 3). shows the calibration parameters for the proposed flotation method including the linear ranges, the relative standard deviation obtained for two analyte samples subjected to the complete procedure, volume ratio and the limit of detection. Also, a calibration graph was obtained without pre-concentration in order to calculate the enrichment factor. The enrichment factor was calculated as the ratio of the slopes of the calibration curve with and without pre-concentration, and Detection limit for Cd^{2+} and Zn^{2+} ions were 0.9 (ng mL^{-1}) and 1.2 (ng mL^{-1}), respectively.

Table 3. Specification of presented method at optimum conditions for each element

Parameters	Cd	Zn
Linear Range (µg mL^{-1})	0.03-1.5	0.02-1.7
Detection Limit (ng mL^{-1})	0.9	1.2
RSD %	1.4	1.7
Recovery%	98.5	99.4

3.7. Flotation mechanism

There are in fact two main types of interactions involved in the process of flotation, namely physical and electrostatic interactions [34,35]. The predominance of the electrostatic mechanism is mainly governed by such important factors as the size and charge of ionic species involved, the presence of electronegative atoms capable of forming hydrogen bonds in the ligand structure, and charged sites on the solid species and precipitates. Based on the existence and observation of some experimental factors in the present work, it seems reasonable to assume the redominance of an electrostatic mechanism for the proposed flotation system. which possess high tendencies for forming H-bonds with the surfactant; the inability of SDS as a ionic surfactant for flotation of the metal ions complexes involved.

3.8. Interference study

With a view to obtaining high selectivity by the FAAS method, the interferences were studied. These interferences constitute special ions which are related to the pre-concentration step, *i.e.* those that may react with CPHQO and decrease the pre-concentration and extraction efficiency (Table 4). The study of possible interferences was conducted for Li^+, K^+, Na^+, Ni^{2+}, Pb^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, NO_3^-, SO_4^{2-}, ClO_4^-, Cl^- and Cd^{2+} or Zn^{2+} ions under the experimental conditions (at a fixed concentration of 66.7 or 133.3 µg L^{-1} of Cd^{2+}or Zn^{2+}, respectively). There was no significant interference at a 1:1000 ratio of Cd^{2+}or $Zn^{2+}$with Li^+, K^+, Na^+, Ni^{2+}, Pb^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cr^{3+} , NO_3^-, ClO_4^-, Cl^- and SO_4^{2-} ions, and also for the same condition at a ratio of 1:500 Zn^{2+}or Cd^{2+} with Cu^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, and Cd^{2+} or Zn^{2+} ions.

Table 4. Effects of the matrix ions on the recoveries of the examined metal ions (N=5)

Analyte	Ions	Interference/ analyte ratio(µg L^{-1})	Recovery (%)
Cd^{2+}	Li^+, K^+, Na^+, NO_3^-, Cl^-	1000	101.2
	Ca^{2+}, Mg^{2+}, Ba^{2+}	1000	100.3
	Zn^{2+} , Cu^{2+}, Mn^{2+}	500	99.1
	Fe^{3+}, Al^{3+}	500	99.3
	Cr^{3+}	1000	98.9
	Ni^{2+}, Pb^{2+},CO^{2+}	1000	100.2
	SO_4^{2-}, CLO_4^-	1000	99.8
Zn^{2+}	Li^+, K^+, Na^+, NO_3^-, Cl^-	1000	100.1
	Ca^{2+}, Mg^{2+}, Ba^{2+}	1000	101.0
	Cd^{2+}, Cu^{2+}, Mn^{2+}	500	99.8
	Fe^{3+}, Al^{3+}	500	99.4
	Cr^{3+}	1000	100.1
	Ni^{2+}, Pb^{2+},CO^{2+}	1000	100.4
	SO_4^{2-}, CLO_4^-	1000	99.7

3.9. Real samples – evaluation of method

The proposed procedure was applied to dryer agents and colored human hair samples for the cadmium and zinc determination. Two usual kinds of dryers, cadmium and zinc naphthenates containing known amounts of cadmium and zinc metals, were treated by the flotation after the digestion procedure. The accuracy of the method is confirmed by making a comparison between the certified and found data given in (Table 5). On the other hand, due to the lack of a certified reference material to evaluate the recoveries of the analytes, the method of standard addition (simple spiking/ recovery tests) was used for the analysis of the hair sample and the results are presented in (Table 6). The relative standard deviations for five replicate measurements of the sample in each investigation, all below 2%, revealed that the precision and the reproducibility of the technique are acceptable.

Table 5. Determinations of cadmium and zinc in certified dryer agent samples submitted to the flotation procedure

Sample	Analyte	Found (µg/g)a	Certified (µg/g)
Cadmium naphthenate	Cd	0.262 ± 0.003	0.267
Zinc naphthenate	Zn	0.262 ± 0.004	0.267

Table 6. Determinations of cadmium and zinc in female human colored hair submitted to the flotation procedure

Analyte	Added(µg/g)	Found(µg/g)	RSD %	Recovery %
Cd	0	0.87	1.4	---
	10	11.10	1.0	102.3
	20	21.23	0.8	101.8
Zn	0	17.64	1.9	---
	10	27.42	1.7	97.8
	20	37.11	1.4	97.4

CONCLUSION

The proposed flotation of cadmium and zinc ions with CPHQO as a stable and fairly selective complexing agent offers a simple, rapid, inexpensive and environmentally benign method to pre-concentrate and separate Cd^{2+} and Zn^{2+} in aqueous solutions. This method has a very low limit of detection (LOQ), good relative standard deviation (RSD) and was applied to determine trace amounts of Cd^{2+} and Zn^{2+} ions in various real samples. In a full comparison of the results presented in this paper with those using similar methods reported in literature[36-38], revealed that, on key measurements, the proposed method proved comparable or superior to the reported methods.

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