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Cloud Point Extraction, Preconcentration and Spectrophotometric Determination of Co (II) and Cu (II) using 15-Crown-5

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Abstract

In the current study, a cloud point extraction (CPE) with UV-vis spectrometry for detection of Cu (II) and Co (II) ions with 15-crown-5 as a chelating agent was developed to be more selective and sensitive. The CPE method is improving the analytical signal and permits the preconcentration of metals ions. After phase separation induced by change temperature to become higher more than the temperature of the cloud, the point is performed with centrifugation. The Co (II) and Cu (II) ions are determined in the enriched phase by UV-vis spectrometry. Several factors affecting the extraction efficiency were optimized, e.x. pH, the concentration of the chelating agent, non-ionic surfactant concentrations, and cloud point temperature. Under optimum conditions, a linear calibration graph in the range of 0.5-5 µg mL^{-1} of Co (II) in the initial solution with r^2 = 0.9994 (n=8) and 0.2–7µg of Cu

(II) in the initial solution (mL-1) with r^2 = 0.9991 (n=8) were obtained. Detection limits of 0.4and 0.1µg are for Co(II) and Cu(II) along with preconcentration factors (66 and 50) for these ions, respectively. The method was used for detection of Co(II) and Cu(II) in some food samples.

Keywords: *Cloud point extraction, preconcentration, spectrophotometric*

Introduction

CPE Cloud Point Extraction method which is interest with the separation method metal ions field by forming small volume of the surfactant-rich phase (colloidal system) as a result of heating non-ionic aqueous solution of surfactant to a certain temperature at which the solution become turbid ,then the colloidal solution is separated into a small volume of surfactant-rich phase and an aqueous phase(1-6) .A list of advantages of this method than other analytical methods because of i-it green method to avoid hazardous solvents ii- its selectivity for obtaining high coefficient of preconcentration iii- its economic for capital cost iv- its rapidity for reduce the time(7-9) iiv-simplicity application for separation and purification of a variety samples of pharmaceutical products, vital and solid,and enviromental(10-16).

A previous study used CPE methodology coupled with flame atomic absorption,(17-22) high performance liquid chromatography,(23)Ultrasonically modified Amented,(24-25)Ultrasound,(26-27) atomic absorption spectrometry,(28)spectrophotometric technique(29)and total reflaction X-ray fluorescence(30).

Supramolecular chemistry are strong linked to molecular recognition chemistry ,which investigates now host molecules that do the recognizing quests molecules that are recognized ,although molecular recognition chemistry is sometimes called host-guest chemistry ,the main concept associated with molecular recognition is the “Lock and Key “concept proposed by Email Fisher at the end of the nineteenth century [31]. According to the structures and sizes of various crown ethers are forming stable and selective complexes with metal ions including alkali and alkali earth metal catoin ,although ability of these macro cyclic ligands as electron pair molecules towards neutral molecular iodine and with δ- or π- acceptors(35-37).In this present work we report the formation of complex 15Crown5 with copper and cobalt in ethanol solution. This work focused on the suitability of CPE combination with UV-Visible spectrophotometr

The experimental

The apparatus

Spectrophotometer (A Shimadzu UV–vis 2101) was used for making experiment studies. Determinations of pH were measured using a (Wellhem, Model 7110) (Germany) digital pH meter. The water bath is used for studying temperature (OPTIMA co, made in Japan). A centrifuge (Hettich co., made in Germany) was used to the separation.

Reagents and Solutions:

Doubly Distill water was used in the study. The nitrate salts of cobalt and copper (Merck) solution of 1000 µg. mL^{-1} were prepared by dissolving the appropriate amount of nitrate salt. The solutions were produced by dilution by doubly distil water. The nonionic surfactant Triton X-114 was provided (Acros Organics company, New Jersey, made in the USA).

Suggested methods for Cloud point extraction

For making cloud point extraction, it requires 10 ml aliquot solution containing 0.5–5µg mL^{-1} of Co(II), 0.2–7µg mL^{-1} of Cu(II). Then, a solution containing 15C5 dissolved in Triton X-114 was added to the aliquoted solution at a suitable pH. The phase separation occurs when heated the solution in the water bath at 60 ^{0}C for 15 min, So accelerating phase separation by using centrifuging the solution at 5000 rpm for 10 min. Then cooling, the surfactant-rich phase changed to viscous, and the aqueous phase was easily removed using a syringe pipette. The surfactant-rich phase was made up to 1.0 mL by adding ethanol and Trans to a quartz cell to the determination of the absorbance at 290,252 Nanometer.

Application of foods samples:

Heating spinach sample (40) gram for three hours in silica crucible on heater and the charred substances was moved to oven for heating 24 hours at 650◦C. then cooled, after that treated by nitric acid (10) mL and H_2O_2 (3) mL at concentration (30) and return to the oven for two hours at 650 ◦C, and shouldn't any organic compound. Treatment of final residue by nitric acid (3) mL and convert by evaporated to the fumes. Final solid was kept in distal water, then keep at pH (4) made up to 25mL. Black tea one gram, green tea one gram and tomato sauce one and a half gram were digested with the mixture of 8 mL concentrated nitric acid, H_2O_2 (2) ml at a concentration (30%) in microwave and dilution it by deionized water (50) mL. Also, the blank digest too submitted for the same way. The CPE methods were used to the final solutions. The analyte ions levels were determined by the procedure provided in section 2.3.

The Results and the Discussion

Absorption spectra and Characteristics of the method:

The absorption spectra of Co (II)-15-C-5and Cu (II)-15-C-5 complexes in the surfactant-rich phase after CPE procedure against reagent blank are shown in Fig. 1 the detection wavelengths were chosen to be 290 and 252 nm. The stoichiometry of 15-Crown-5 complexes with Co (II) and Cu (II) was examined by mole ratio method, andthe continuous variation was found to be 1:1.The preconcentration factor results in by dividing aqueous phase volume to the preconcentrated phase volume. Table 1 summarizes the analytical characteristics of the method under the optimum experimental conditions.

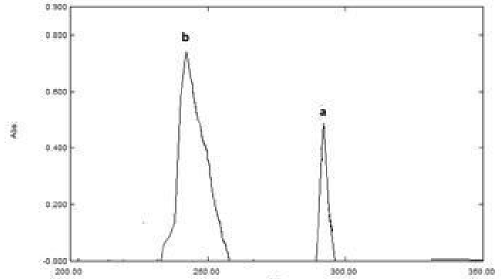
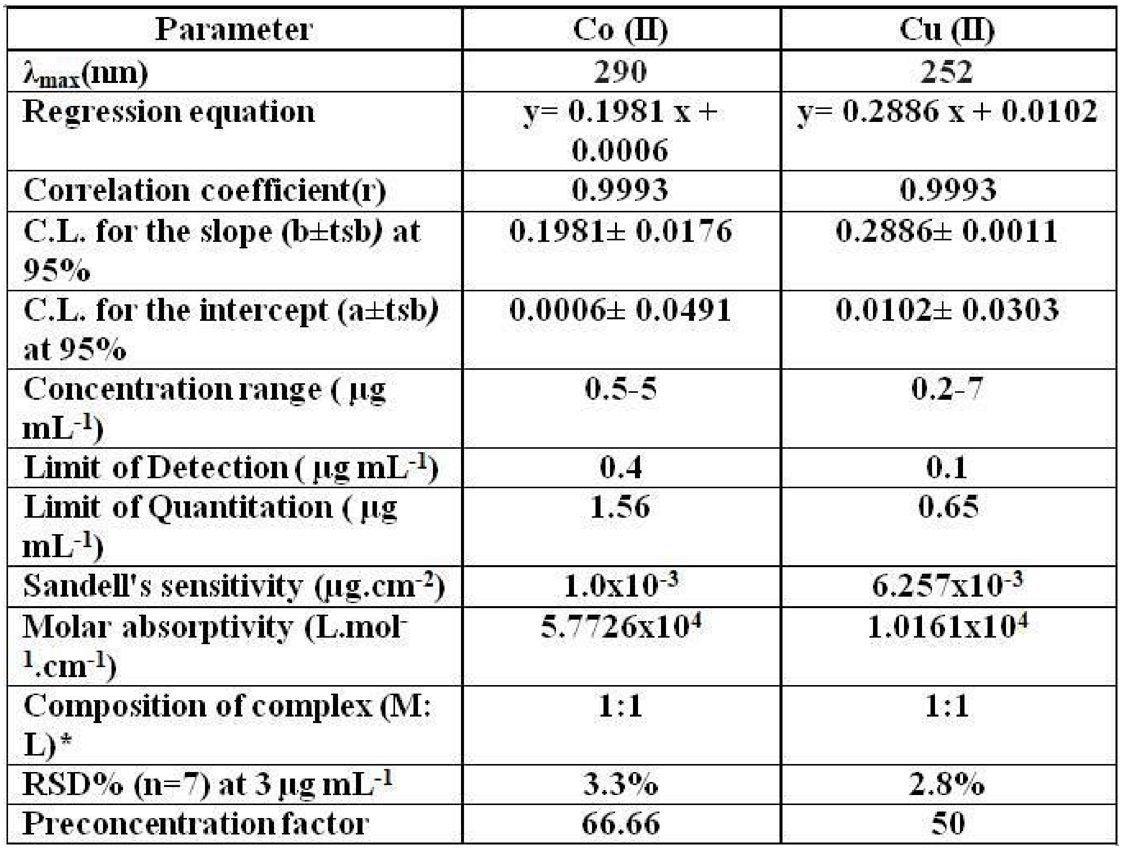


Fig. 1: Absorption spectra (a) Co(II)-15-C-5 complex, Co (II) = 2.5 µg mL^{-1}, 15-C-5 = 1 x 10^{-2} M , pH = 4 , 0.4 mL of 2 % (v/v) Triton X-114 (b) Cu(II)-15-C-5 complex, Cu (II) = 2.5 µg mL^{-1}, 15-C-5 = 9 x 10^{-3} M , pH = 4 , 0.5 mL of 2 % (v/v) Triton X-114.

Table (1): showed parameter methods that used for detection values of cobalt and cupper by using CPE.



Parameter	Co (II)	Cu (II)
λ_{max}(nm)	290	252
Regression equation	y= 0.1981 x + 0.0006	y= 0.2886 x + 0.0102
Correlation coefficient(r)	0.9993	0.9993
C.L. for the slope (b±tsb) at 95%	0.1981± 0.0176	0.2886± 0.0011
C.L. for the intercept (a±tsb) at 95%	0.0006± 0.0491	0.0102± 0.0303
Concentration range (µg mL^{-1})	0.5-5	0.2-7
Limit of Detection (µg mL^{-1})	0.4	0.1
Limit of Quantitation (µg mL^{-1})	1.56	0.65
Sandell's sensitivity (µg.cm^{-2})	$1.0x10^{-3}$	$6.257x10^{-3}$
Molar absorptivity (L.mol^{-1}.cm^{-1})	$5.7726x10^{4}$	$1.0161x10^{4}$
Composition of complex (M: L)*	1:1	1:1
RSD% (n=7) at 3 µg mL^{-1}	3.3%	2.8%
Preconcentration factor	66.66	50

Optimizing of CPE parameters:

Effect of pH:

The separation of ions includes primary production sufficient hydrophobic with metal-chelate to be extraction of a little amount of surfactant-rich phase [(38)]. PH test is the main parameters [(39)]. PH effect to the CPE method was applied in (1–5) range. Adjusting of PH values is with HNO_3. Figure (2) showed a pH effect on the percentage of extraction; it included the extraction percentage increasing with nitric acid decreasing. The final results, pH (4) were chosen.

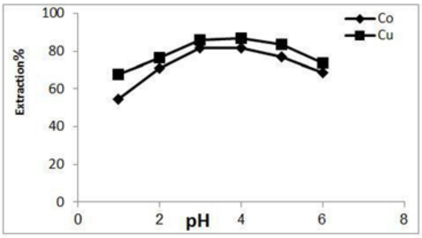


Fig. 2: PH effect on the determination of Cu (II) and Co (II) Conditions: Co (II) = 2.5 µg mL^{-1}, 15-C-5 = 1 x 10^{-2} M , 0.4 mL of 2 % (v/v) Triton X-114 (b) Cu(II)-15-C-5 complex, Cu (II) = 2.5 µg mL^{-1}, 15-C-5 = 9 x 10^{-3} M , 0.5 mL of 2 % (v/v) Triton X-114.

Effect of 15-Crown-5 concentration:

The effect of 15-Crown-5 on the extraction and determination of Co (II) and Cu (II) complexes were investigated in the range 2.0x 10^{-3} -2.0 x 10^{-4} mol L^{-1}, the results present in Fig. 3. The extraction will result in high concentrated of 15-Crown-5 and remained almost constant. That explains that micelles are filled by the chelating agent. At higher concentration, extraction efficiency was decreased. That due to the free 15-Crown-5 competes with the complexes in extraction to surfactant-rich phase results in low extraction[(40,41)]. Therefore, a concentration of 1.0×10^{-2} and 9.0×10^{-3}mol L^{-1} of 15-Crown-5 was selected as the optimum concentration Co (II) and Cu (II).

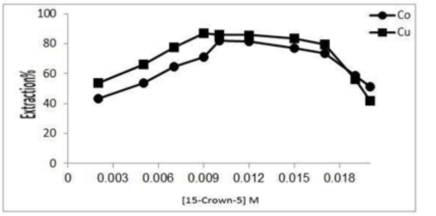


Fig. 3: 15-C-5 effect on determine of Co (II) and Cu (II) Conditions: Co (II) = 2.5 µg mL^{-1} , pH = 4 , 0.4 mL of 2 % (v/v) Triton X-114 , Cu(II)-15-C-5 complex, Cu (II) = 2.5 µg mL^{-1}, pH = 4 , 0.5 mL of 2 % (v/v) Triton X-114.

Triton X-114 Effect:

One of a critical factor that in the CPE is the concentration of surfactant, Triton X-114 is non-ionic surfactant wide using in CPE due to its achieves a good cloud point extraction that means increase the extraction efficiency by reducing the phase volume ratio, results in improvement of concentration factor. Where Triton X-114 present in markets at high purity, with low point temperature, low cost and toxicity and the surfactant-rich phase (high density)$^{(42,43)}$. The preconcentration efficiency depends on the Triton X-114 level (0.001-0.015) as range M, as shown in Fig. 3. At lower concentrations of the surfactant, The highest extraction efficiency for cobalt and copper ions was obtained with 0.007 and 0.009 M Triton X-114. The extraction decreases with increasing of the surfactant amounts. That may be belonging to increasing in viscosity and volume of the micellar phase leading to poor sensitivity$^{(44)}$. An amount of 0.4 and Triton X-114 (0.5 Ml) were selected for subsequent experiments.

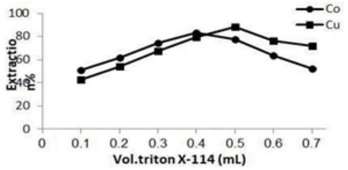


Fig. 4: Effect of Triton X-114 concentration on the determination of Co (II) and Cu (II) Conditions: Co (II) = 2.5 μg mL^{-1}, 15-C-5 = 1 x 10^{-2} M , pH = 4 , Cu(II)-15-C-5 complex, Cu (II) = 2.5 μg mL^{-1}, 15-C-5 = 9 x 10^{-3} M , pH = 4 .

Effect of time and temperature of Equilibration Incubation:

Determination of incubation is done by temperature and time. As well as, the extraction process depends on temperature. Figure (5) showed the influence time and temp of the incubation of Cobalt and cupper. The cloud point temperature of Triton X-114 is (23-25) °C in (0.1–5) weight percentage, heating more than ten °C is important for getting good separation $^{(45)}$. When temperature or incubation time is an increase, it will increase Co (II) and Cu (II) extracted amount in the surfactant-rich phase with quantitative separation after fifteen minutes in 60 °C (water bath). The prolonged times is necessary to apply it at high temperatures for satisfactory mange extraction$^{(46)}$.

Wide ranges are used in our study (30–70) **°C** as temperature degree and (5–30) minutes as a time. Time (15) minutes and temperature (45) °C were optimum conditions for extraction.

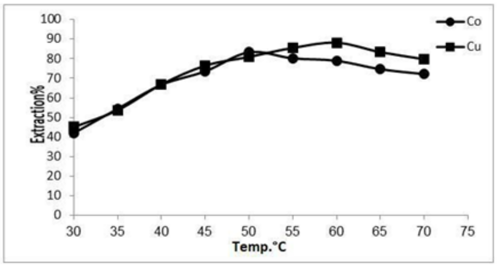


Fig. 4: Effect of Triton X-114 concentration on the determination of Co (II) and Cu (II) Conditions: Co (II) = 2.5 μg mL^{-1}, 15-C-5 = 1 x 10^{-2} M , pH = 4 , 0.4 mL of 2 % (v/v) Triton X-114 , Cu(II)-15-C-5 complex, Cu (II) = 2.5 μg mL^{-1}, 15-C-5 = 9 x 10^{-3} M , pH = 4 , 0.5 mL of 2 % (v/v) Triton X-114.

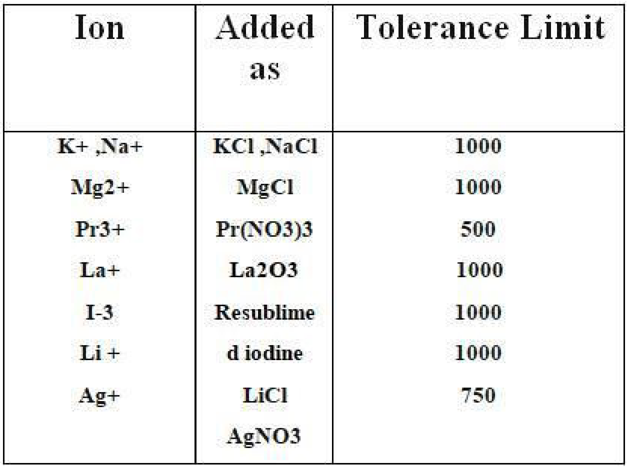
The effect of centrifuge conditions:

Centrifugation was accomplished for separating the aqueous and surfactant-rich phase in the suggested procedure. (5000) recycled per minute and ten minutes are best phase separation$^{(47,48)}$.

Effect of foreign ions:

The interferences are studied in the preconcentration stage, 15-crown-5 react cations or analytes may react with species and the extraction efficiency become low. The solution (10) ml consist of (3) **μ**gmL^{-1} Co (II) and Cu(II) as Table (2).

Table (2): Effects of the matrix ions on the recoveries of the examined metal ions (*N*=3)



Ion	Added as	Tolerance Limit
K+ ,Na+	KCl ,NaCl	1000
Mg2+	MgCl	1000
Pr3+	Pr(NO3)3	500
La+	La2O3	1000
I-3	Resublime	1000
Li +	d iodine	1000
Ag+	LiCl	750
	AgNO3	

Applications and Accuracy:

The suggested procedure was used to determination of the Co(II) and Cu(II) according to Section 2.4 in Spinach, Tomato Sauce, Green tea and Black tea provided from local markets. The results are shown in Tables 1. The values measured by at ranged (96-101) %, the results indicate that confirm the accuracy of the procedure.

Table (3): Contents of analyte ions in the food sample. (N = 3).

Spinach	**0**	**8.61**	**2.3**	**98.8**
Co				
Cu	2.5	11.08	1.9	
	0	14.52	3.1	96
	2.5	16.92	2.1	
Tomato	0	0.82	3.4	100.4
Sauce				
Co	2.5	3.33	2.6	
Cu	0	1.50	4.1	97.6
	2.5	3.94	2.5	
Black tea	0	1.93	3.3	101.2
Co				
Cu	2.5	4.46	2.4	
	0	2.41	3.1	99.2
	2.5	4.89	2.2	
Green tea	0	1.30	2.1	97.2
Co	2.5	3.73	1.0	
Cu	0	7.99	1.8	96.4
	2.5	10.40	0.89	

A comparison between previously studies and the suggested method of pre-concentration and Cu(II) and Co(II) determination as (Table 4) which indicates the method R.S.D. and lower detection limit and the methods are the procedure for detection small Co(II) and Cu(II) in food by use spectrophotometer.

Table 4: Comparison between merit methods with previous studies

Sample	reagent	surfacta nt	LOD(ng (mL^{-1}		PF		detection	.Ref
			Co	Cu	Co	Cu		
water and food samples	PTSC-1	Triton X-114	1	0.67	25	25	FAAS	49
Environmen tal samples	MPKO	Triton X-114	0.19	0.16	67	65	FAAS	50
tap water, snow water,	PAN	Triton X-114	0.12 g/l	0.26	25	25	Capillary electroph oresis	51

Conclusion

Extraction of ions of cobalt and copper is done with 15-crown-5 in non-ionic surfactant Triton X-114 phase. Extraction of complete elements was done by 15-crown-5 because of the hydrophobic production. The molar ratio is determined. Simplicity, Ecological safety, metrological characteristics, the sensitivity and convenience of are procedures used for extraction of the organic compounds. The results found these methods could use it for preconcentration and separation of cobalt and copper ions.

Financial Disclosure: There is no financial disclosure.

Conflict of Interest: None to declare.

Ethical Clearance: All experimental protocols were approved under the Department of Chemistry, College of Education, University of AL-Qadisiyah, Diwaniyah, Iraq and all experiments were carried out in accordance with approved guidelines.

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