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RESEARCH ARTICLE

Cloud Point Extraction for the Separation, Preconcentration and Spectrophotometric Determination of Trace Copper (II) In Herbal Plants Samples Using New Synthesized Reagent

Azhar A. Ghali[1*], Ashwoq S. Hussein[2]

1. *Department of Chemistry Pharmaceutical, College of Pharmacy, University of Al-Qadisiyah, Iraq.*
2. *Department of Chemistry, College of Education, University of Al-Qadisiyah, Iraq.*

***Corresponding Author: Azhar A. Ghali**

Abstract

A new Cloud point extraction method was showed determination and preconcentration of copper in plant and herbs. The final products of analysis are complex of Cu (II) with new reagent is 6-(4-bromophenylazo) m-anisidine [6-(4BrPAA)] in Triton X-114. Centrifuge is used after that, then the surfactant-rich phase is diluted by ethanol (1.5) mL after separation. Then measurement of the copper was done by spectrophotometry at 512 nm. The complexing agent concentration, pH, Triton X-114, centrifuge rate, time and temperature are important analytical parameters. The used analytical methods in the study are included limits of detection, molar absorptivity, linear range, quantification and sandell sensitivity, factors of improvement and preconcentration. Linear range was (0.007-1.50) µg mL^{-1} of Cu (II). The quantification limits and detection were (0.0199 and 0.0059) µg mL^{-1} of Cu (II), consequently. The cations and anions influence was examined; it is represent the method which used for evaluation the copper amount in the herbal plants samples.

Keywords: *Copper (II); 6-(4-bromo phenylazo) m-anisidine [6-(4BrPAA)]; Triton X-114; spectrophotometry; Cloud-point extraction.*

Introduction

In recent years the use of herbal plants has been increasing because their suitable prices and people are unaware of their side to their fewer side effects than chemical compounds effects. The medicine by herbs hasn't negative side effects because it natural not treated compounds; these compounds have long-term effects in treatment of many chronic diseases [1]. The Herb consists from metal ions with several ranges of concentrations. Some ions are toxic and some other is not. The toxic metals included (lead, mercury, arsenic and cadmium) while others essential nutrients (chromium, Zn, Fe and Cu), yet become toxic at high concentrations [2-5].

The levels of heavy metal ions contrast depending on the geographical aria, soil determinants, and the plants ability to accumulating some the elements. These elements are absorbed by the root transfer to remain body parts [6, 8].Copper at very low levels is representing very important for body activates. It will be very toxic in high dose. Range between essential dose and toxic dose is narrow, therefore scripting herbal plants should be systematic [9, 10], although the copper is useful for the body, but it is very toxic at high dose [11].Evaluation of the copper level is necessary because it cans oxidation of chains of fatty acid, and it has effect on nutritional value and shelf life [12].

So, for evaluation of trace amount of copper is need accurate and sensitive analytical methods, such as (ICP-AES) and (AAS) [13, 14], furthermore, spectrophotometric techniques [15]. The spectrophotometric technique has great attention because the required instrumentation is available, fastness, simple application, accuracy and precision. But, the spectrophotometric technique has insufficient sensitivity because; it is very low copper levels in different samples the matrix interferences.

For that causes, an preconcentration procedure and efficient separation is need to spectrophotometric detection level is important for reaching to good level. Nowadays, there are used wide of the preconcentration methods which involved many techniques are liquid–liquid extraction [16], liquid phase micro extraction [17], resins chelation [18], electrochemical deposition[19], ion-exchange [20], solid-phase extraction [21, 22], fiber chelation [23].

As well as, the cloud point extraction (CPE) methods is used wildly [24]. CPE method become more popular than liquid-liquid extraction due to its high recovery, high enrichment factor, low organic solvents, and low cost, rapid phase separation and deepened on combination ability with detection. In cloud point extraction, choosing of the complexing factors is vital stage.

Azo stain is used as complexing factor because it's low solubility and ability to produce hydrophobic materials with many types of metals. The low solubility and forming the metallic complexes were applied in CPE. Also, it has high sensitivity and complexing agents were exploited, that is a new type for the cloud point extraction process [25].

Many chelating extract ants, such as oxine [26] DDTC [27] thiamine, [28] (PAR) [29] and dithizone [30] have been used to extract Cu^{2+} in many specimens. In the present study, 6-(4-bromo phenylazo) m-anisidine [6-(4BrPAA)] was formed which used for evaluation of copper level by spectrophotometry according to cloud-point extraction by [6-(4BrPAA)] by using Triton X-114. The suggested way was used to the calculation of copper amount levels in herbs.

The Experimental

The Apparatus

The absorbance were confirmed with spectrophotometer (Shimadzu 1800 double-beam) with (5.0) mm quartz cuvettes. A digital pH meter (Wellhem 7110, Germany) with a combined glass-calomel electrode was used for determination of pH. The centrifuge was used for achievement the separation process. A water bath (OPTIMA WB710, Japan) with a good temperature control was used for cloud point temperature experiments. For characterize the created reagent, FT-IR spectrometric (Shimadzu 8400S, Japan) was used KBr discs (Japan), within the frequency range (4000-400) cm^{-1}.

The ^{1}H-NMR spectrum of the reagent was done by using Bruker (Ultra, Shiel 300 MHZ, SWISS) in d6-DMSO as solvent using tetramethylsilane. The microanalysis of C, H and N of this compound was performed in the Elemental Analysis (Carlo Erba3764, Europ, Shimadzu GSA-4B, Japan).

Chemicals and Reagents

The surfactant Triton X-114 (Acros Organics) was used .Copper solution (1000 mg L^{-1}) was composed by dissolving (0.3816) g of $CuCl_2.6H_2O$, (Merck) with deionized water for (100) mL. Sodium nitrite (BDH), hydrochloric acid (BDH), and ethanol were purchased from (GCC), m-anisidine (Sigma).

Synthesis and Characterization of 6-(4-bromo phenyl azo) m-anisidine

The azo dye was prepared by derivatives of aromatic compounds. P-bromoaniline (0.01) mole was changed to hydrochloric form by adding HCl 1:1 then diluting by deionized water then cooled at -3.0 ˚C. The cooled liquid of $NaNO_2$ (0.01 mole) is mixed with amine salt. Diazonium salt is put stand in ice for fifteen minute and added m-anisidine (0.01) mole with NaOH (10) % then cooled. Product solution is put stand for fifteen minutes with stirring for production azo dye. The product azo is purified and dried, then crystallized in ethanol. Azo dye is tested its melting point constancy (mp 133-135˚C) Yield 86.44%.Fig. 1 the chemical structure of 6-(4BrPAA).

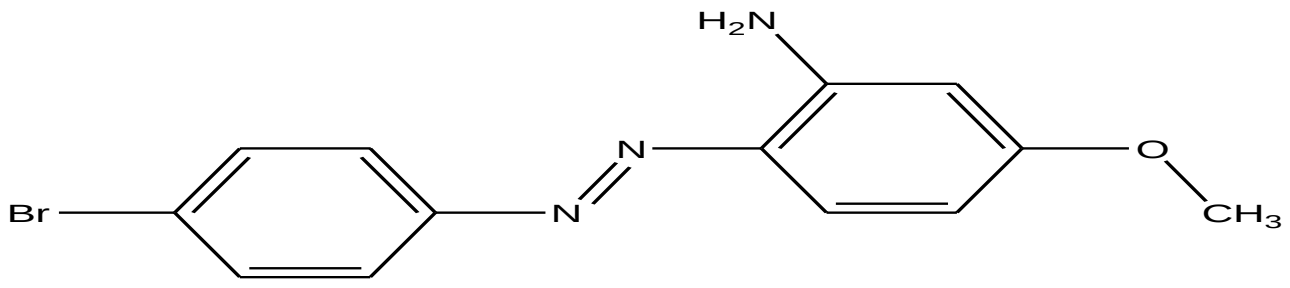

Fig. 1: The chemical structure of 6-(4-bromo phenyl azo) m-anisidine 6-(4BrPAA)

The elemental analysis of the synthesized 6-(4-BrPAA); anal.calcd. for $C_{13}H_{12}N_3OBr$ (306.158 g mol^{-1}) C,50.95;H,3.91; N,13.71; O,5.22; found C,50.08;H,3.83; N,13.23; O,5.02. IR (KBr) vmax/cm^{-1}, 3417 (v, N-H), 2923 (v,Ar-H), 1627(v, C=C), 1550(v, N=N), 1265(v,C-N), 1134 (v,C-O),879,817,709(δ,Ar-H)), 517(δ, C-Br).

The signals lying at downfield side 3.94 ppm are due to the hydrogens of amine group. A multiple signals at 3.23 ppm is due to the protons of CH_3 group. The multi signals at 7. 82-7.63 and 7.58-6.15 ppm are due to the protons of rings 4-bromo phenyl azo and m-anisidine respectively. In water, it is insoluble but it solved in organic solvents such as DMF, ethanol, methanol, DMS and acetone.

General Procedure

The cloud point extraction is done by adding buffer 2.0 mL (pH 8), 0.6 mL of 6-(4BrPAA) (1.0 $x10^{-3}$ M) and Triton X-114 3.0 % and a solution containing Cu (II) ion (0.007-1.5µg mL^{-1}) and then completed with deionized water to 10 mL in a 10 mL measuring flask, were kept for 10 min in the thermostatic bath at 60 °C. The separation was done by centrifuge 6000 RPM ten minutes. Product mixture was keep at 25 ˚C for cooling then transfer to ice to more cooling and for viscosity increasing, The product micellar solution from this technique was diluted by ethanol (1.5) ml then transferred to quartz cell 5 mm to evaluation the absorbance at 512 nm.

Herbal Sample Preparation

Herbal samples provided from Al-Diwaniyah city markets, Iraq were prepared, drying of solid food by temperature degree (105) °C for one day. Herbal plant sample (1) g was added at 95°C with concentrated HNO_3 (10) mL. The product mixture was mixed with H_2O_2 (3) mL then evaporate the sample for drying then added 1 M HNO_3(9) mL .The product mixture was purified by filter paper, then it is complete to 25 mL with 1 M HNO_3 solution and analyzed for cupper according to the prescribed general procedure for CPE.

Results and Discussion

Absorption Spectra and Calibration Curve

[6-(4BrPAA)] shows maximum absorbance at 425nm ,Cu(II)reacts with [6-(4BrPAA)] in absence (λ_{max}530 nm)with Triton X-114 and the absorbance of solution changed to (512) nm. So, Cu (II)-6-(4-BrPAA)-Triton X-114 complexes could prepare by using CPE technique. The surfactant is separated then absorbance was calculating at (512 nm) as (Fig. 2). So, it is perfect for spectrophotometric and preconcentration evaluation of copper.

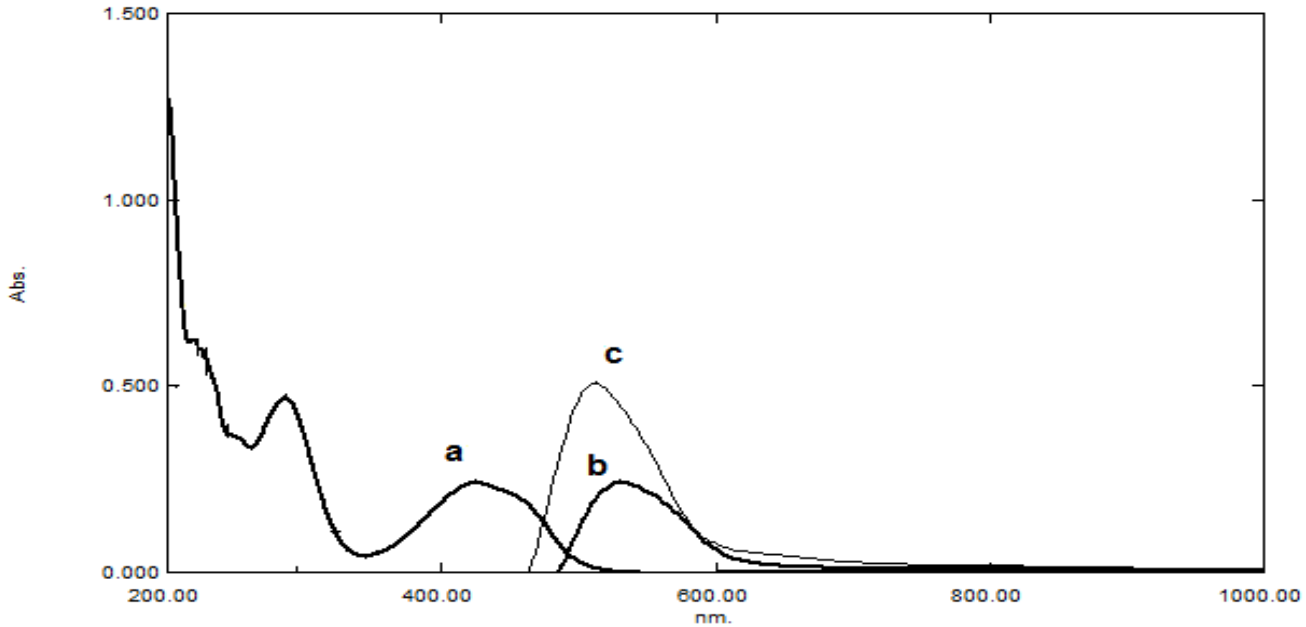

Fig. 2: Absorption spectra (a) Reagent 6-(4-BrPAA) = 6 x 10^{-5} M(b) Cu(II)- 6-(4BrPAA) complex without CPE, Cu(II) = 30 µg mL^{-1} , 0.6 ml of 6-(4-BrPAA) = 1 x 10^{-3} M , Buffer pH= 8(2 mL),(c)Cu(II)- 6-(4BrPAA) complex with CPE , Cu(II) = 0.5 µg mL^{-1} , 0.6 ml of 6-(4-BrPAA) = 1 x 10^{-3} M , Buffer pH= 8(2 mL) , 3%(v/v)Triton X-114

Table 1: Analytical characteristics of the proposed method

Parameter	CPE
λ_{max}(nm)	512
*Regression equation	y= 0.954x + 0.016
Correlation coefficient(r)	0.9993
C.L. for the slope (b±tsb) at 95%	0.954± 0.0011
C.L. for the intercept (a±tsb) at 95%	0.016± 0.0303
Concentration range (µg mL^{-1})	0.007-1.5
Limit of Detection (µg mL^{-1})	0.005
Limit of Quantitation (µg mL^{-1})	0.0199
Sandell's sensitivity (µg.cm^{-2})	0.0027
Molar absorptivity (L.mol^{-1}.cm^{-1})	$2.3152x10^4$
Composition of complex (M: L)* *	2:1
RSD% (n=7) at 0.5 µg mL^{-1}	2.8%
***PF	100
**** EF	23

*A=a+bC, C mean Cu concentration in µg mL^{-1}, **Job's and mole ratio methods used, **PF is monitoring of ratio of aqueous phase volume to surface-rich phase, *** EF is determination ratio of slope of curves that gotten with or without CPE

The calibration curve showed that the system obeys Beer's law in the concentration range of 0.007-1.5 µg mL^{-1} Cu. Equation of linear regression was A = 0.954C + 0.016 (r = 0.9996). Calculation of molar absorptivity was done by $0.23152x10^5$ L mol^{-1} cm^{-1} at (512) nanometer, the sandell sensitivity was (0.0027) ng cm^{-2}. The standard deviation was (1.25) %.Many studies showed the relationship between the proposed method and the preconcentration procedures [31, 48] as Table 2. The proposed method is rapid, simple and cheap compared with other preconcentration method wider linear and lower detection are used for the determination of small amount of Cu. The method showed how procedures lead to analyzing of mixtures by spectrophotometer.

Table 2: Comparison of the proposed method with reported methods for the pre-concentration and CPE of Cu (II)

Sample	Micellar system	Technique	Reagent	Detection limit(ng mL^{-1})	PF	Ref.
Water	Triton X-114	FAAS	Alizarin Red S	1.07	21	31
Water	Triton X-114	FAAS	Me-BDBD	1.5	14	32
Environmental and	Triton X-114	FAAS	PDBDM (chrysoidine)	0.6	15	33
Liver	Triton X-114	ST	Dithizone	4.6	10	34
Water and saturated saline	Triton X-114	ST	HEPTS	0.1	5	35
Food and water	Triton X-100	ST	Isoleucine	5	22	36
Water and food	Triton X-100	ST	Diethyldithiocarbamate	0.4	18	37
Water and parenteral solutions	Triton X-114	SF	Thiamine	0.29	10	38
waters	Triton X-114	FAAS	Me-BTABr	1.08	17	39
Water	Triton X-114	FAAS	NDTT	0.22	22.4	40
River water and sea waterr	Triton X-114	FAAS	Cupron	0.04	88	41
Environmental Waters	Triton X-114	FAAS	PTU	1.6	30	42
Water, blood, vegetables	Triton X-114	FAAS	DFID (thiophenytoin)	1.5	39	43
Waters	Triton X-114	FAAS	N,N0-bis(2-hydroxyacetophenone)-	0.06	20	44

			1,2-propanediimine			
Waters	Triton X-100	FAAS	Sulfathiazolylazo resorsin	0.64	25	45
Water and hair	Triton X-114	FI-FAAS	N-phenyl benzohydroxamic acid	1	45	46
Rice flour and water	Triton X-114	FI-FAAS	MPMP	0.15	81	47
Tea, milk and water	Triton X-114	FAAS	DDTC	1.1	11	48
herbal plants	Triton X-114	ST	6-(4BrPAA)	5	100	This work

HEPTS: 4-ethyl-1-(pyridin-2-yl) thiosemicarbazide; 4-BPDC: (4-bencylpiperidine-ditiocarbamate; Me-BTABr: 2-[20-(6-methyl-benzothiazolylazo)]-4-bromophenol; NDTT: 6- (2-naphthyl)-2,3-dihydro-as-triazine-3-thione; Me-BDBD: 6-[20-(60-methyl-benzothiazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid; Alizarin Red S: 1,2-dihydroxyanthraquinone-3-sulfonic acid sodium salt; PDBDM: 4-(Phenyl diazenyl) benzene-1,3-diamine; PTU: 4-hydroxy-2-mercapto-6-propylpyrimidine; PAN: 1-(2-pyridylazo)-2- naphthol; MPMP: 2-[(2-mercaptophenylimino)-methyl]phenol; DDTC: sodium diethyldithiocarbamate; OP-10: Polyoxyethylated phenol; OP = 7: polyoxyethylated alkylphenol; Cupron: 1,5-diphenyl-benzoin; DFID (thiophenytoin): 5,5-diphenylimidazolidine-2-thione-,4-one; Triton X-114: octylphenoxypolyethoxyethanol; FAAS: flame atomic absorption spectrometry, ST: spectrophotometry; SF: spectrofluorimetry; CE: capillary electrophoresis; SRP surfactant-rich phase; PF preconcentration factor.

Ph Effect

The extraction of ions by using CPE technique includes production the metal-chelate with enough hydrophobic to be prepared with the surfactant. Degrees of acidity (pH) have great effect on metal-chelate production and extraction, (Fig. 3) reveals pH influence on the absorbance the materials at (512 nm). The extraction became maximum was done at pH (8). So, pH (8) was choosing for the study.

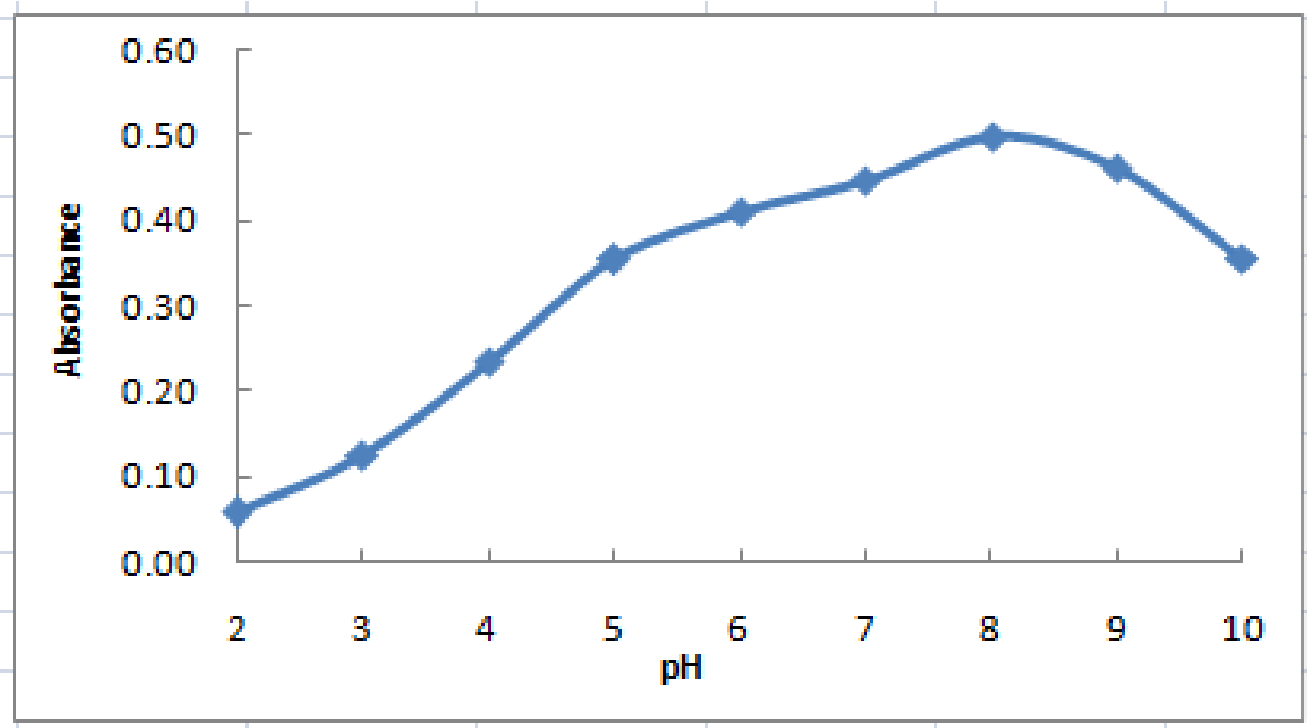

Fig. 3: Effect of pH on the absorbance of the Cu(II)- 6-(4BrPAA) complex, Conditions: Cu(II) = 0.5 µg mL^{-1}, 0.6 mL of 6-(4BrPAA) = 1 x 10^{-3} M , 3 %(v/v)Triton X-114, temperature:60°C

Effect6-(4BrPAA) Concentration

The effect of agent on the analytical responses is investigated.6-(4BrPAA) level factor have effect on the extraction level and determination of Cu (II) was found in (0.1–1.0mL) from 1.0x10^{-3} M of the reagent. The sensitivity of the test increased with increasing 6-(4BrPAA) level more than (0.6) mL and stay constant in high level, so, 6-(4-BrPAA) (0.6) ml was used in study as (Fig. 4).

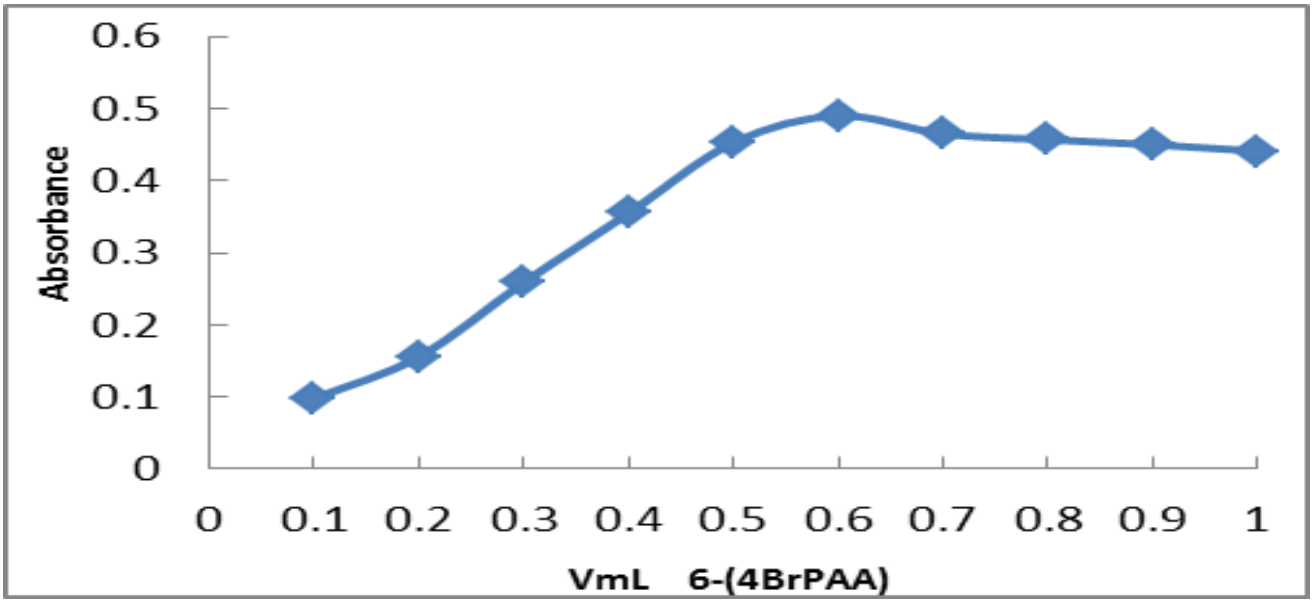

Fig. 4: Effect of 6-(4-BrPAA) concentration=1 x 10^{-3} M on the absorbance of the Cu (II)–6-(4BrPAA) complex. Conditions: Cu(II) = 0.5 µg mL^{-1} , Buffer pH= 8(2 mL) , 3 %(v/v)Triton X-114, temperature:60°C

Triton X-114 Effect

The surfactant level is used in CPE for optimum level of TritonX-114; surfactant level is increase in the absorbance was done in (0.1-0.6) mL from 20 %(v/v) Triton X-114. (Fig. 5) reveals absorbance levels of the liquid and it's related with TritonX-114 level. When the surfactant is increase, the absorbance will increased, Therefore, the Triton X-114 used (3.0) %concentration reports. The surfactant is very viscous; therefore the ethanol was added after CPE to make it easy transferring in spectrophotometric cell, while ethanol (1.0) mL is chosen to have an appropriate amount of sample concentration to be good amount for measuring the absorbance.

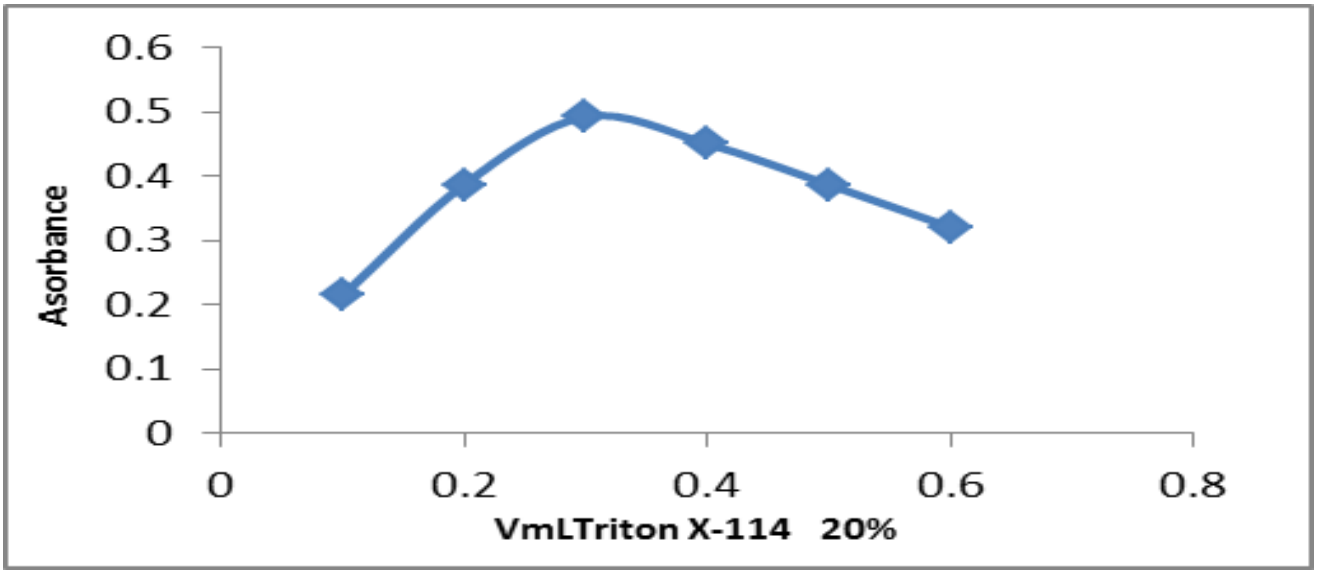

Fig.5: Effect of Triton X-114 concentration on the absorbance of the Cu (II)-6-(4BrPAA) complex. Conditions: Cu (II) = 0.5 µg mL^{-1}, 0.6 mL of 6-(4BrPAA) = 1 x 10^{-3} M, Buffer pH= 8(2 mL), temperature: 60°C

Effects of Time and Temperature

It was desirable to employ lowest temperature and shortest time .Efficiency depended of extraction was time (5-30) minutes and temperature **(**30-90) °C. The result reveals the temperature of 60 °C and the time of ten minutes were enough for extraction. The time of ten minutes was selected is the best. The high temperatures are not good in the analytical technique due to the high temperature decreases concentration of the critical micelle of non-ionic surfactants [49]. The experiment was optimized in heating**(**60**) °C** for ten minutes and centrifuging by (6000) rpm for ten minutes then cooled by ice results in high recovery of copper. Furthermore, the surfactants have hydrophobic effect in high

temperatures, because a change dehydration of the oxygen. That produces increasing in the number of micelles [50].

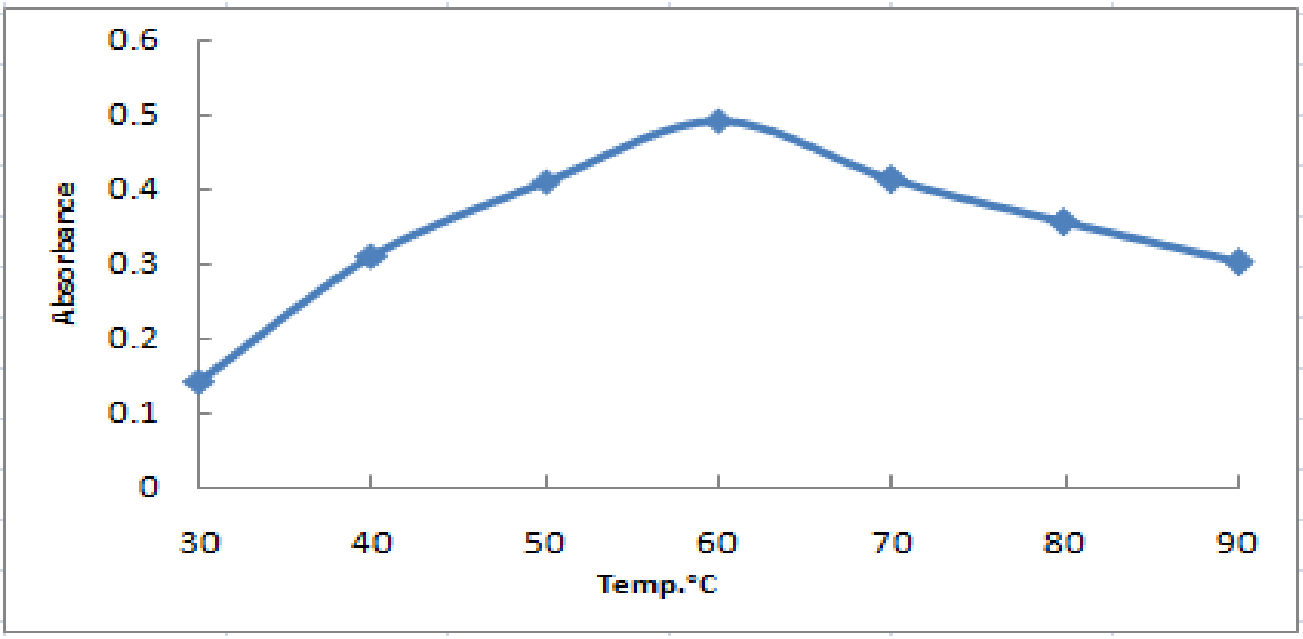

Fig. 6: Effect of Temperature on the absorbance of the Cu (II) - 6-(4-BrPAA) complex. Conditions: Cu (II) = 0.5 µg mL^{-1}, 0.6 mL of 6-(4-BrPAA) = 1 x 10^{-3} M, Buffer pH= 8(2 mL), 3 %(v/v) Triton X-114

Stoichiometric Ratio

The complex was confirmed in prefect conditions as mentioned previous by continuous variation and molar ratio. Molar ratio of 6-(4-BrPAA) to Cu was given by 6-(4-BrPAA) level, revealed inflection at molar ratio was (2.0), mean there are two molecules of 6-(4-BrPAA). Furthermore, the Job method demonstrate a ratio of 6-(4-BrPAA) to Cu (II) was (2.0). The finals results founded the stoichiometric ratio was (2:1) [6-(4BrPAA): Cu].

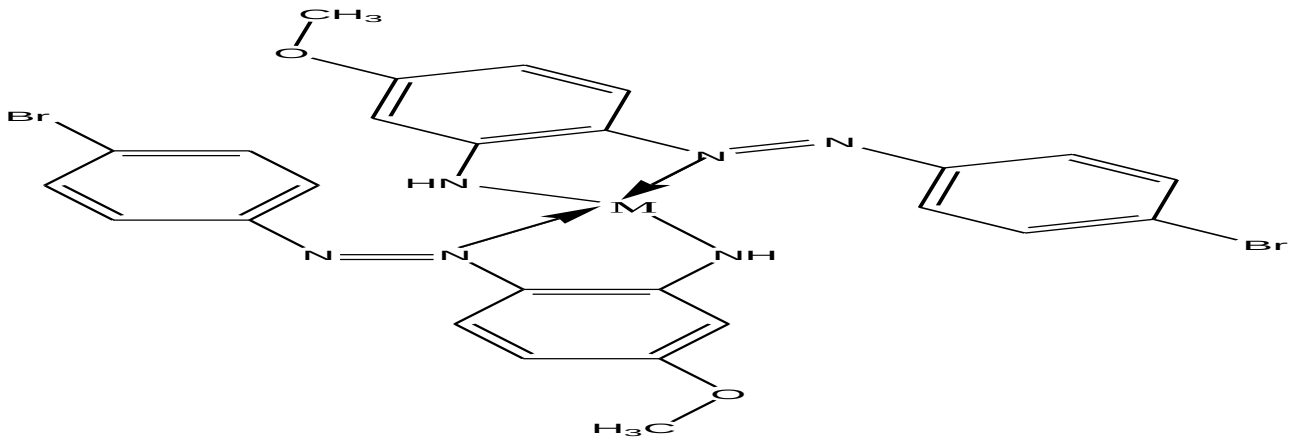

Fig. 7: The chemical strure octuf (6-(4-BrPAA)) $_2$M, where M = Cu^{2+}

Interference

There are interfering between cations and anions with determination of copper ions were examined as Table 3.The solutions consist from Cu (0.5)µg mL^{-1} with interfering ions (l:1) were prepared depended on recommended procedure and the proposed procedure. Tolerance limit is amount of ions that cause ± 5% error in the copper determination. These results are summarized inTable3. At the given level, no significant interference was observed. The result reveals no their interferes between the ions with the suggested method.

Table 3: Tolerance ratio of diverse ions on the determination of 0.5 µg mL^{-1} Cu(II) .

Ion added	Tolerance ratio
Fe^{2+}, Hg^{2+}, Cd^{2+}	230
Mn^{2+}, Zn^{2+},	250
Mo(V), Sb(III)	150

Fe^{3+}, Co^{2+} , Ag^{+}	125
K^{+}, Li^{+}, Na^{+}	550
Ba^{2+}, Ca^{2+}, Mg^{2+}	480
$SO4^{2-}$, $PO4^{3-}$	75
$NO3^{-}$, $NO2^{2-}$	50

Analytical Applications

In herbal plants samples, Copper was determinate in order to confirmt applicability of the proposed method. The presented method was examined by independent analysis and spiking experiments. Three replicates determinations for herbal plants samples were performed. The analytical results are demonstrated in Table (4). AAS techniques were applied as a reference as Table 4. The obtained results of copper were always more than (95.6) %. The results were accuracy and reliability. Less time, more stability and high accuracy shows advantage of the proposed method with the other method.

Table .4: Cu (II) in herbal plants samples (Mean± SD, n=3)

Sample	added(µg g^{-1})	Amount found[a](µg g^{-1})		Recovery(%)
		Proposed	AAS	Proposed method
Laurel	0.0	3.44±0.21	3.37±0.21	-
	2.5	5.89±0.15	5.85±0.15	98.00±1.57
	5.0	8.40±0.11	8.34±0.11	99.20±2.16
Rosemary	0.0	9.23±0.01	9.31±0.01	-
	2.5	11.82±0.13	11.77±0.13	103.60±1.24
	5.0	14.20±0.10	14.24±0.10	99.40±1.16
Basil	0.0	19.17±0.45	19.30±0.45	-
	2.5	21.62±0.10	21.88±0.21	98.00±0.51
	5.0	24.28±0.51	24.18±0.13	102.20±1.24
Mullein	0.0	33.35 ± 0.9	33.43 ± 0.19	-
	2.5	35.82±0.1	36.02±0.15	98.80±0.55
	5.0	38.31±0.1	38.19±0.71	99.20±1.35
Hibiscus	0.0	64.03±1.37	63.83±1.81	-
	2.5	66.26±2.21	66.47±2.57	97.60±1.55
	5.0	68.85±2.01	68.64±2.73	96.40±0.51
Trigonella	0.0	14.11±1.09	14.41±2.09	-
	2.5	16.84±2.81	16.84±2.57	97.20±1.71
	5.0	19.33±1.51	19.05±2.81	98.40±1.36
Spinacia	0.0	16.25±1.90	16.33±1.84	-
	2.5	18.64±1.71	18.79±2.61	95.60±1.02
	5.0	21.04±0.95	20.94±1.21	95.80±1.42

Conclusions

The newly synthesized 6-(4-bromo phenylazo) m-anisidine [6-(4BrBAA)] has proved that it copper is selective reagent as compared to other spectrophotometric techniques. It is easy applicable for evaluation of copper level in herbs which provided us with strong and supported results. The method is done based on the cloud point extraction of the complex of copper with [6-(4BrPAA)], which it used for evaluation of copper. The suggested methods needs cheap instrumentation and good selectivity, offers safety, precision and high accuracy could apply in calculation of copper concentration in the samples. The surfactant used with copper, and as well as, extraction of toxic solvent was avoided .It characterized by rapid, simple and cheap.

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