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Research Article

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Combined-Cloud Point Extraction and Spectrophotometric Detection of Copper (II) by Using a New Synthesized Ligand

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ABSTRACT

A Cloud point extraction procedure was presented for preconcentration of Cu (II) after complexation by new azo reagent 4-(Nitro phenylazo imidazole) (NPAI) are quantitatively extracted in Triton-x-114 following separation, prior to its analysis by UV-Vis Spectrometry. The experimental conditions such as pH, concentration of Triton-x-114, temperature, time of heating, stoichiometry for complex extracted were studied .Under the optimum established conditions, the detection limit of 0.045μg mL^{-1} of Cu (II) and concentration range of 0.1-5 μg mL^{-1}, the molar absorption $2.85x10^4$ $L.mol^{-1}.cm^{-1}$. The precision for seven replicate measurements of 5μg mL^{-1}Cu (II) was of 0.30%. The method was applied to the determination of copper in amalgam dental material sample by CPE technique and comparing the result with atomic spectroscopy.

Keywords: 4-(Nitro phenylazo imidazole) (NPAI),Copper, Cloud point extraction, Spectrophotometry

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INTRODUCTION

Cupper is heavy metal, when the diet do not have the recommended daily requirement of cupper it will cause many of disorders such as bone malformations, irregular pregnancies ,reduced heart beats, paleness …etc.[1]. Thus, the determination of trace amount of Cu (II) in different samples it's important for life and pollution. Several methods for the determination of copper are used, such as electro thermal atomic absorption spectroscopy (ETAAS)[2], differential pulse adsorption stripping voltammetry [3]. , ion selective electrodes [4], Flame atomic absorption spectrometry (FAAS)[5], and reverse phase in HPLC [6]. A cloud point extraction procedure was presented for the preconcentration of copper, Nickel , Zinc and Iron ions in various samples, after complexation by 2-(6-(1H-phenyl[d] imidazole-2-yl)-1H benzo[d]imidazole[7]. Cloud point extraction depends primarily on the basis of the existence of two phases are separated from each other between the process of balance in the distribution between phases , and draw analytical material in one of these phases . In the technology CPE and at a temperature suitable we will have two phases do not mix separated from each other. The process is a layer Cloud and nature of the points gathered micelles surface depends mainly on the basis of a set of Conditions and the main conditions that contribute to the composition of this layer, so the control of the circumstances Optimum minute separation process contributes to an ideal and a good separation [8-11].

This paper is concerned with the cloud point extraction of copper(II) from aqueous solution by associated with 4-(Nitro phenyl azoimidazole) as extractant and Triton X-114 as a nonionic surfactant.

EXPERIMENTAL SECTION

Apparatus

Double beam (UV-Vis) Spectrophotometer , Shimadzu (UV. 1650) made in Japan, and IR Spectrophotometric used LegeunicamspΛ-2001 Infrared spectrophotometers, pH meter, as well as used electrostatic Water Bath, (Hamburg - 90) , made in England for maintain temperature.

Materials and Solution

All chemicals imported from trust worthy commercial company and used as received without more purification stock solution of Copper(II) 1000μg mL^{-1} was prepared by dissolved 0.3803g of **$CuCl_2.6H_2O$ (**Merck company**)** in 100ml distilled water by used volumetric flask . Other working solutions prepared by dilution with distilled water in suitable volumetric flask, as well as all other solution need in this search prepared at the same procedure.

General procedure for CPE (optimum conditions)

For cloud point extraction, 0.4 mL of 20%(v/v) Triton X-114 , 0.5 mL of (NPAI)5×10^{-3}, in a 10 mL flask were added and a proper concentration of copper was (0.1-5μg mL^{-1}) added to it, and diluted to 10 mL with distilled water. The tubes were kept for 15 min in the thermostatic bath at 70℃. Subsequently, separation of the phases was placed by centrifugation for 15 min at 3500 rpm. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by tilting the tube. The surfactant-rich phase in the tube was made up to 1 mL by adding ethanol. The absorbance of the complex was measured at λ_{max}511 nm against the corresponding reagent blank prepared under identical conditions but without copper.

Synthesis and characterization of Reagent

The synthesis of (4- nitro phenyl azo imidazole) by adding (1.38g) of nitro aniline in a mixture consisting of 3 ml of hydrochloric acid and 20 ml of distilled water and cooling the mixture to a degree (-5℃) in a ice bath is then added to the mix 15 ml of sodium nitrite solution of (10%) during the period half hour with constant stirring and then leaves the solution for twenty minutes, where consists diazoniumsalt. Diazonium solution is added with constant stirring to a solution of the component (0.68g) of imidazole dissolved in 100l ml of ethanol, and 10 ml of sodium hydroxide and 10 ml of sodium carbonate and then the mixture cools below zero degrees Celsius(Color changes to orange) and after the completion of the added half-hour run of the solution and wash with water and then crystallized returned ethanol and dried over CaCl2 to give a red color crystals of compound as shown in Fig.1.Yield 65%; mp130℃; anal.calcd.for $C_9H_7N_2O_5$ (217.18 g mol-1) C.H.N.S, C49.77,; H3.25,; N32.25,; S 0,; found C49.03,;H4.03,; N31.82,; S 0,; .

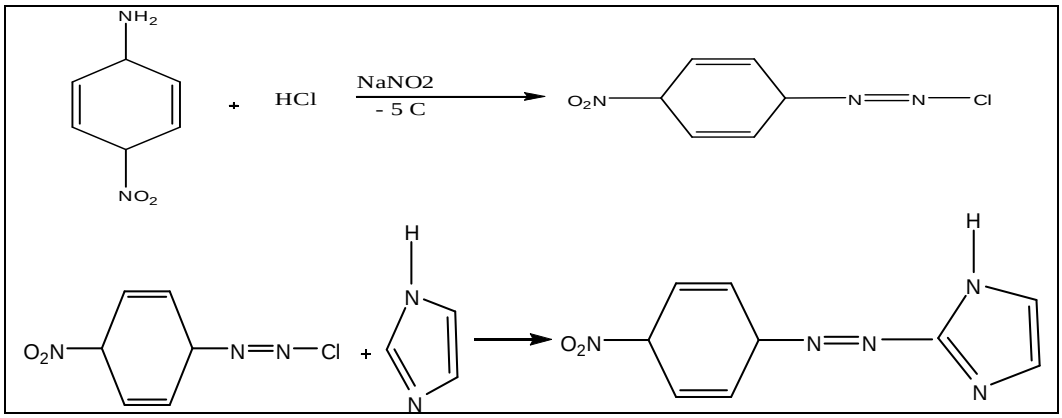

Figure (1): Synthesis route of reagent4-(Nitro phenyl azo imidazole)

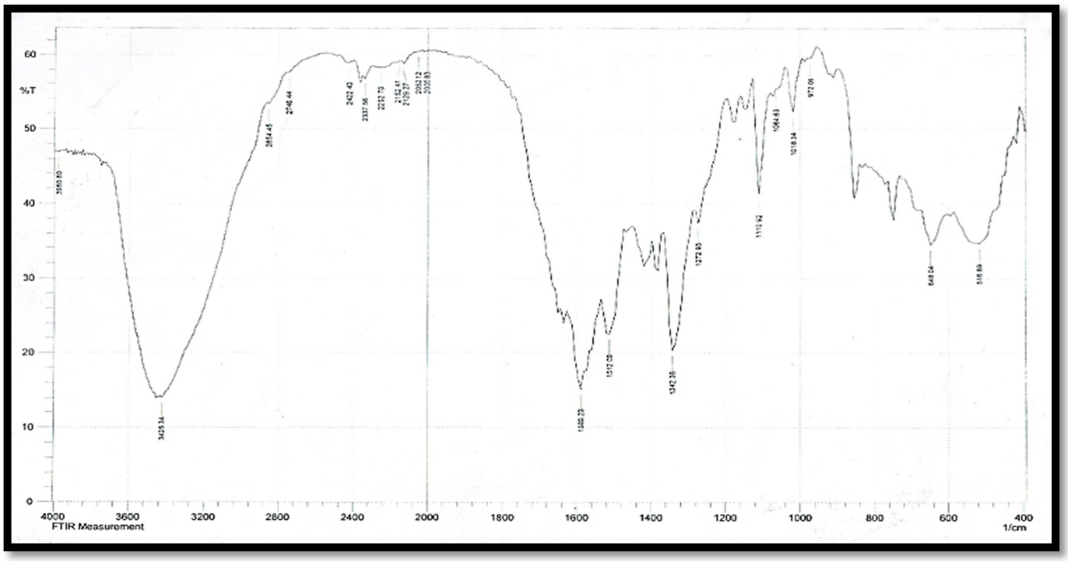

Figure (2): IR – spectrum for NPAI(Reagent)

Fig. (2) Shows the IR spectrum for the reagent NPAI. This spectrum shows bands at 2854, 2746(ν, Ar-H), 3425(ν, N-H), 1589 (ν, C=N), 1342(ν, N=N), 1512 (C=C), 1272(ν, C-N), 1110(ν, N-O).

RESULTS AND DISCUSSION

Absorption spectra

Extracted 5μg mL^{-1} Cu^{+2} ion in 10mlaqueous solution contain 0.2ml of $5x10^{-3}$ M NBIA and 0.2ml 20%TritonX -114 heating this solution at 50℃ for 15 minute in electrostatic water bath until formation CPL which is separated and dissolved in 1ml ethanol, then taken UV-Vis spectrum for alcoholic solution against blank prepared at the same manner without Cu^{+2} ion the spectrum appear λmax =511nm as maximum absorbance wave length for complex extracted as in Fig3.

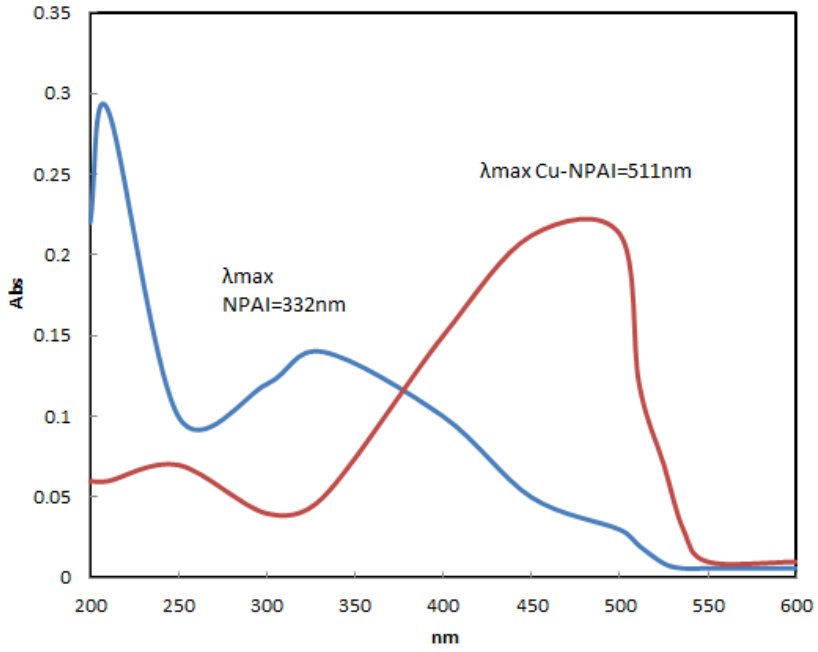

Figure (3) UV-Vis absorption spectrum for NBIA and Cu-NPAI complex

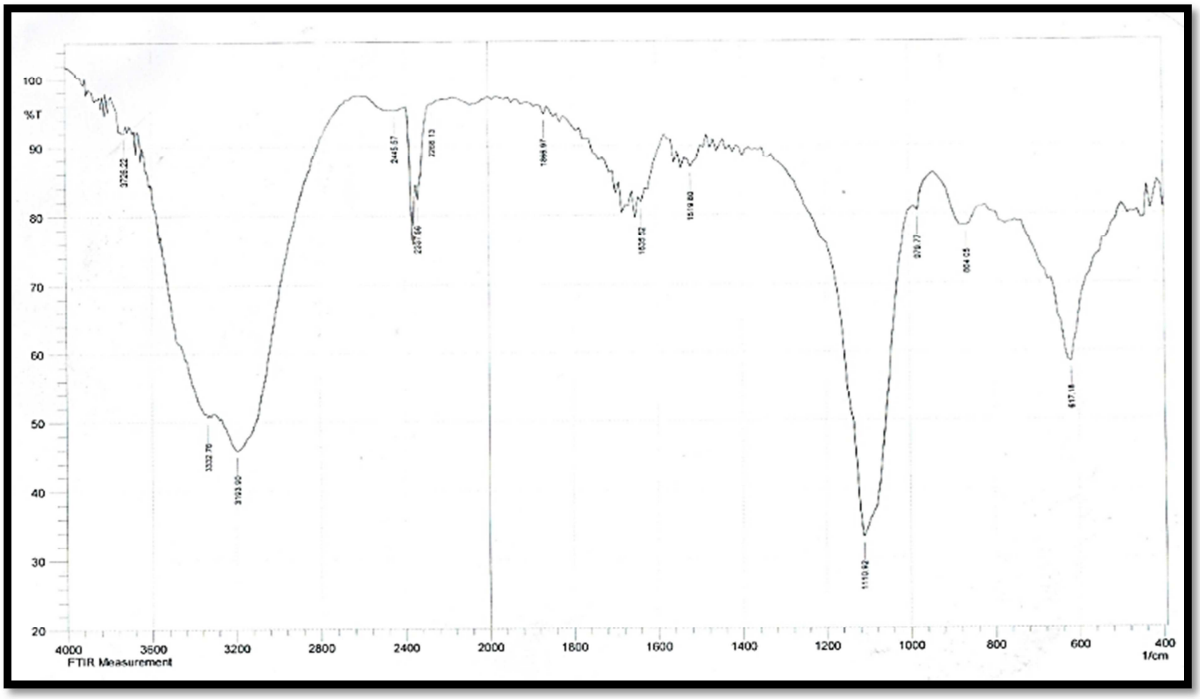

Figure (4) IR – spectrum for Cu-NPAI

The ν(C=N) of imidazole ring[12]appear at 1589cm^{-1} in the spectrum of the reagent .This band shifts to lower frequency at 1519 cm^{-1} with a little change in shape and shows new band at 617 cm^{-1}. These differences suggest a linkage of copper ion with reagent.

Effect of NPAI concentration

Extracted 5 µg mL^{-1} Cu^{+2}ion from 10ml aqueous solution contain different quantity of 5x10^{-3}M NPAI, according to procedure detailed in principal method , the results as in fig(5) .

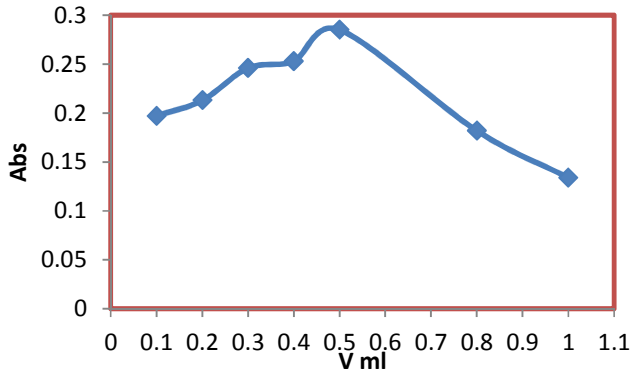

Figure (5): Effect of NPAI concentration

This result show the optimum concentration of NPAI of 2.5 x 10 $^{-4}$ M (0.5 ml of 5x10^{-3}M).

Effect of Surfactant Volume Extracted 5 µg mL^{-1}Cu^{+2}ion in 10ml aqueous solutions in different volume of 20% TritonX-114 according to procedure detailed in the principal method the results was as in fig(6) .

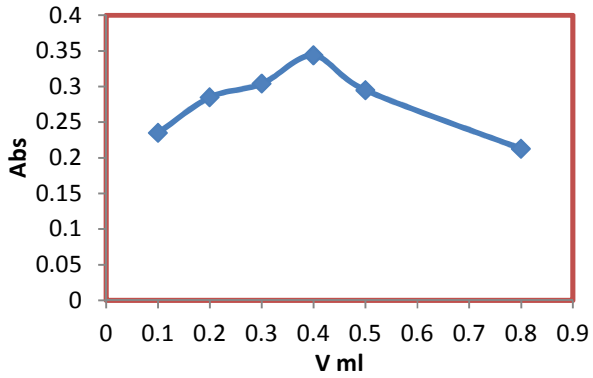

Figure (6): effect of surfactant volume

The results show 0.4ml of20%TritonX-114 was the suitable to formation cloud point layer which is mean giving best kinetic and thermodynamic equilibrium to aggregation micelles to from CPL with higher density and smaller volume to be best layer for transfer ion pair association complex and giving higher extraction efficiency , any volume less than 0.4 ml not permit to reached equilibrium of formation CPL , and decline extraction efficiency volume of surfactant more than optimum value effect to increase diffusion of micelles and decrease aggregation of micelles as well as decrease extraction efficiency .

Effect of pH

In series solution of pH (2-12),Extracted 5 µg $mL^{-1}Cu^{+2}$ion in 10ml aqueous solutions according to procedure detailed in the principal method the results was as in fig(7) .

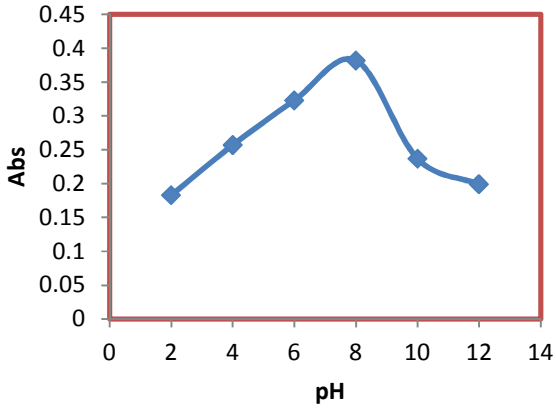

Figure (7): effect of PH

The extraction yield reaches the highest amount at pH =8 for Cu (II). At lower pH values, the formation of complexes is not quantitative, and at higher pH values, the extraction starts to decrease. Therefore, a pH of 8 was selected to perform further Extractions.

Temperature Effect

Extracted 5 µg mL^{-1} Cu^{+2}ion in 10ml aqueous there solution in electrostatic water bath for different temperature and for 10 minutes at each temperature and complete the procedure as detailed in principal method , the results was as in fig(8) .

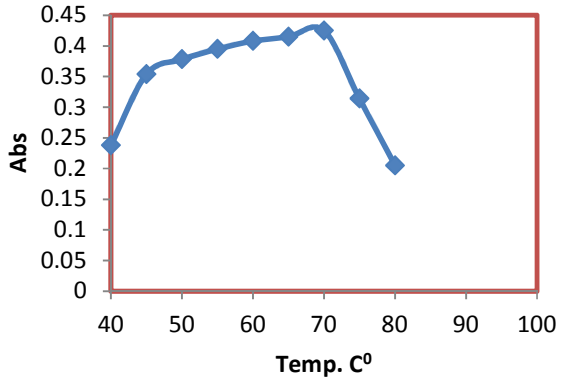

Figure (8): effect of temperature

The results show 70℃was the optimum temperature for formation CPL appear higher extraction efficiency.

Effect of Heating Time:

According to principal method extracted5 µg mL^{-1} Cu^{+2}ion from 10ml aqueous solution at optimum conditions except heating for different time results was as in fig (9).

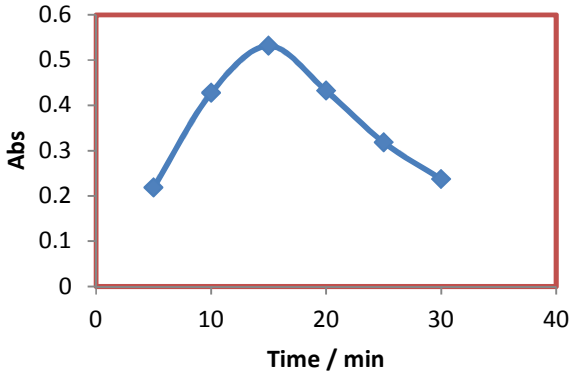

Figure (9): effect of heating time

The results show 15minutes was the optimum heating time giving higher absorbance, because the quantity of heat at this temperature was the favorable to formation CPL with higher density and smaller volume. Any time less than optimum not allow aggregation micelles, but the time more than optimum value giving increasing in diffusion of micelles.

Stoichiometry

To know the probable structure of complex extracted were evaluated by both of the continuous variation and the mol ratio methods(fig.10 , fig.11).Both methods were showed that the molar ratio of Cu-NPAI complex is 1:2, (metal : ligand) .

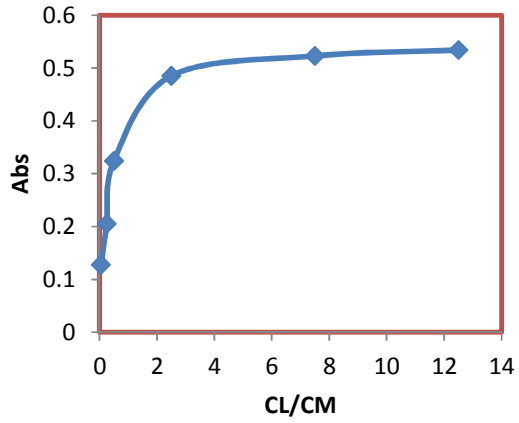

Figure (10): Mole ratio method

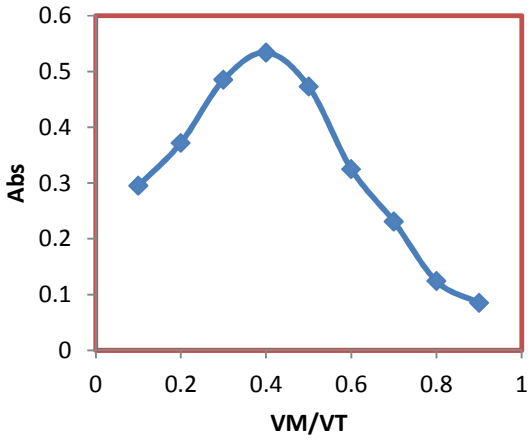

Figure (11): Continuous variation method

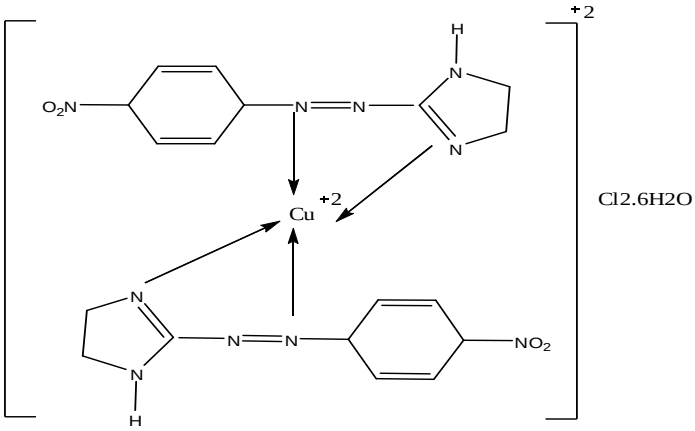

Figure (12):the suggested chemical structure of Cu –NPAI complex

Analytical characteristics

The calibration curve was made giving straight-line with a good correlation coefficient (0.9987) , and the analytical prameters get from the calibration curve are put in table(1).

Table (1): Analytical characteristics of the proposed procedure

Analytical Parameter	Value
Correlation coefficient(r)	0.9987
Slope	0.106
Intercept	0.0239
Regression equation	y = 0.106x + 0.0239
Molar absorptivity	$2.85x10^4$L.mol^{-1}.cm^{-1}
Sandall Sensitivity	0.0022 µg/cm^{-2}
Linear dynamic range	0.1-5µg mL^{-1}
Standard Deviation	0.0016
Relative Standard Deviation %	0.3%
Detection Limit(D.L)	0.045µg mL^{-1}
Percent Relative error	-1.0%
Percent Recovery	99%
Composition of complex (M: L)	1:2
Preconcentration factor	33.3
Enrichment factor	75.7

Previous studies

This table shows the previous studies:

Table (2) Previous studies using cloud point extraction prior copper detection in different Matrices

Sample	Technique	Detection limit	Surfactant	Reagent	R.S.D	Reference
Water and diet	CPE	0.67μgL^{-1}	Triton x-114	1-PISC	--	13
Liver cow	CPE	4.6ngml^{-1}	Triton x-114	Dithizone	--	14
water	CPE	0.27ngL^{-1}	Triton x-114	TAN	--	15
Orange juice	CPE	1.4ngL^{-1}	Triton x-114	BIYPYBI	--	16
water	CPE	0.06ngL^{-1}	Triton x-114	N,N-bis(HAP)-1,2PD	--	17
Drugs	CPE	4.6ngL^{-1}	Triton x-114	BDB	2.15%	18
Natural water	Flow injection	0.05ppm	--	--	0.78%	19
Dental fillings	CPE	0.045ppm	Triton x-114	NPAI	0.3%	This work

Interference Study

The effect of the ions (Ag^{+1},Hg^{+2}, $Sn^{+2}$and Zn^{+2})which form complexes with the reagent (NPAI) during its reaction with Copper 5 μg mL^{-1} was studied. The selectivity of various masking agents is examined for eliminating the effect of the interfering four ions. These are Oxalic acid, ascorbic acid, and potassium thiocynate and ammonium acetate. The results are shown in table (3).

Table (3): Interference effect

Cu (II) /μg mL^{-1}	Foreign ion 50 μg mL^{-1}	Masking agent(1.0)ml ،[0.01]M	Error%
5	Ag^{+1}	Oxalic acid	0.003
5	Hg^{+2}	Ascorbic acid	0.002-
5	Sn^{+2}	Potassium thiocyanate	0.004-
5	Zn^{+2}	Ammonium acetate	0.004

Application

It was conducted for the application of the analytical method used (CPE) to determination the copper Cu (II) in dental filling using optimal conditions to determination the copper element according to technical(CPE) and compared to the results in the atomic absorption spectrometer results were too close together in the following table :

Dental filling	Atomic absorption method	Cloud point extraction method
15.4%	15%	14.5%

CONCLUSION

The cloud point extraction technique CPE is one of the methods of extraction or separation indirect and longer surface Surfactant is the second phase you get separation or extraction of the items to be separated. The cloud point extraction CPE based on a set of optimal conditions that govern efficiently extraction to add some additional factors that alter the efficiency of the extraction process technology. Proven practical experiments to extract copper(II) from aqueous solutions using organic reagent NPAI according CPE technical possibility to use this technique in the determination of this element under study in various samples have been given a high accuracy results in determination.

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