Ministry of Higher Education and Scientific Research



Journal of Kufa for Chemical Sciences

A refereed

Research Journal Chemical Sciences Vol.2 No.9 Year 2022 ISSN 2077-2351

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Preconcentration and Spectroscopic estimation of Zn (II) by sensitive Cloud Point Extraction Technique using Imidazole Azo Reagent

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الخلاصة : تم استخدام الكاشف العضوي (CMePAI) في استخلاص ايون الخارصين (II) باستخدام تقنية نقطة الغيمة وتم تحديد ذلك من خلال قياس طيف الاشعة المرئية-فوق البنفسجية Uv-viseble للكاشف والمعقد والاشعة تحت الحمراء ممتعد ذلك من خلال قياس طيف الاشعة المرئية-فوق البنفسجية Uv-viseble للكاشف والمعقد والاشعة تحت الحمراء ممتعد ذلك من خلال قياس طيف الاشعة المرئية-فوق البنفسجية Uv-viseble للكاشف والمعقد والاشعة تحت الحمراء ممتعد ذلك من خلال قياس طيف الامتصاصية العظمى للكاشف Λ max =447 للمعقد حيث كانت الامتصاصية العظمى للكاشف Λ max =447 المعقد حيث كانت المعقد من المعقد وكانت الظروف المثلى المختبرية للحصول على اعظم استخلاص حيث كانت الدالة الحامضية العظمى للمعقد 300 وكانت الظروف المثلى المختبرية للحصول على اعظم استخلاص حيث كانت الدالة الحامضية (IO من ايون 100 من ايون في 100 من 100 من المحلول المائي الذي يحتوي على 10.50 (Trition X-114) وبدرجة حرارة تسخين 300 وزمن تسخين 100 من 100 من المحلول المائي الذي يحتوي على المعال (10.50 من ايون 10.50 من ايون 10.50 من ايون 10.50 من 10.50 من الخرصين في 100 من المحلول المائي الذي يحتوي على المعال (20.50 من 10.50 من ايون 10.50 من 10.50 من 10.50 من الخرصين في 100 من المحلول المائي الذي يحتوي على المحدات الاتية 15.50 من 10.50 من 10.50 من ايون 10.50 من المعقد كان التالي 20.50 من 10.50 من 10.50 من ايون 10.50 من 1

Abstract: The organic reagent is using is [4 –CMePAI], the reagent was spectra methed by using (FT-IR), and (uv-vis) as an identification using Spectrophotometric study for ion pair complex of Zn(II) ion extracted into cloud point extraction, appeared wave length of maximum absorbance was $\lambda = 447$ nm for organic reagent, $\lambda = 470$ nm for extracted Zn (II) ion as ion-pair association, laboratory produced novel azo the study about Determination the optimum extraction and determination conditions were pH = 8 in the presence of 100 µg Zn (II) in 10 mL aqueous solution, 0.5 mL Triton X-114, and heating temperature of 80 c° for 15 minutes, Theromdynamic parameters of CPE for extraction process of the ion -pair association complex in the triton X-114 were also considered ΔH = + 0.2627 kJ mol⁻¹, ΔG - 58.973 kJ mol⁻¹, ΔS = + 167.8 J mol⁻¹ K⁻¹ That referred endothermic reaction, with limit of Detection (LOD=0.3798 ppm) and limit of quantitation (LOQ= 1.266 ppm) ,RSD%=0.362, Molar absorptivity $(E=43590 \text{Lmol}^{-1} \text{.cm}^{-1})$. stoichiometry shows the ion- pair complex extracted was 1:2 [Zn- 4 – CMePAII⁺²:2Cl⁻, in addition to study of electrolyte effect and spectrophotometric determination of Zn(II) in different samples. The calibration curve linear with correlation coefficient [Zn 4 – $CMePAII^{+2}$:2Cl⁻ of r =0.999 .The proposed method applied for the determination of zinc in vegetables pills.

Keywards: Cloud point extraction, Imidazole ,Extraction,Zinc determination, Azo .

1.Introduction

Cloud Point Extraction (CPE) is a process in which organic, inorganic, or biological materials ar e extracted utilizing nonionic surfaces that are employed for separation in the form of a cloud

when heated to a temperature above the critical temperature [1]. They are also known as micelle-extraction technique Initially, in CPE extraction, a micellar (surfactant-rich) phase is added to the sample which homogeneous surfactant solution.

A non-polar core is developed due to its hydrocarbon tails towards the centre by a micelle [1] The surface of the micelles is such that the polar hydrophilic part is directed directly towards the aqueous side and the non-polar hydrophobic part is directed towards the lipid layer and the micelles gather in the form of balls and the number of surface micelles is called the degree or number of the aggregation [2].

In 1882, Radziszewski synthesized imidazole by reacting benzyl with benzaldehyde and an excess of ammonia in an acidic medium[3]

In analytical chemistry for the extraction process, among the most frequent chemical reagents - their complexes in organic solvents. Azole dyes, often known as azo dyes, are chemicals with groups or atoms in their molecules. It has electron pairs that allow it to form effective bonds with the ions of metallic elements (function group) 60 % of all dyes are made up of bonding. Coordination to produce coordination complexes has been discovered earlier. Pigment compounds are the building blocks of color (70) %.

The chemist Peter Kress associated the system SP2 with hybrid (N=N) in 1858, and the reason for its name is due to the presence of the azo group Aromatic. Because of their excellent stability and speed of interaction with ions, azo compounds are classified as spectroscopic reagents. Aromatic azo derivatives are more prevalent and used than azo derivatives, owing to their great sensitivity and selectivity. The azo compoundis an example of an aliphatic compound since it is characterized by stability and high stability due to the resonance that occurs in these derivatives[4]

Imidazole is one of the substances that prevents copper from corroding in the presence of sulfuric acid, nitric acid, hydrochloric acid, sodium chloride, sodium hydroxide, and a variety of other chemicals and environmental factors. [5]

Heterogeneous catalysts, such as zinc-supported imidazoles, have been used in a variety of applications due to their non-toxic, low-cost, and reusability.[6]

Imidazoles in vitro and in the organism's body High blood pressure, anti-neuropathic, antiviral, anti-tuberculosis [7,8] anti-inflammatory, anti-bacterial, anti-obesity, anti-parasitic, and anti-cancer medications all include imidazole. As well as other medications for a variety of ailments.[8,9]

Zinc is the second most important element in the human body, as more than 300 enzymes and more than 2000 transcriptional factors need zinc in their work, as it has three functional factors: cataylytic, co-acive, and structural[10].

Zinc is an essential element in the human organism. It is involved in the formation of enzymes such as carboxypeptidase A, which stimulates esterification and hydrolysis of peptides. It also has an important role in the metabolism of proteins, carbohydrates and fats. Zinc is also important in the synthesis of DNA and RNA. Zinc deficiency causes problems such as loss of appetite, stunted growth, and lethargy. Mental illness, skin infections, and immune problems . The increase or decrease in the concentration of zinc has effects, so we find that determining or detecting a small amount of it in foods or drinks consumed by humans is important and this requires techniques such as spectrophotometry.[10,11] In developing countries, zinc deficiency is considered an important problem in children, as it has significant effects on several factors,

including growth retardation and hypogonadism, Therefore, the amount of zinc in the plasma is an important indicator for measuring its rate in the human body [10-13].

2.Experimental

2.1. Apparatus

spectrophotometric studies and absorbance measurement, used double beam spectrophotometer (A Harvard Bio science company Cambridge UK), While absorbance measurements in the optimization study and detection of metals were done with Single beam (UV-Vis) Spectrophotometer, TRIUP International Corp - TRUV. 74, S (Italy), FTIR-8400S, Shimadzu (Japan)), pH-meter, Listed, Laboratory Equipment, E163694 CE ,Germany. so for heating used water bath with regulator (Hamburg 90) England and electrical balance company limited, Dool, CE, HR200, Japan.

2.2. Reagents and materials :

Stock Solution Zn(II) ion in concentration 1mg/10mL prepared by dissolved 0.0208 g of ZnCl₂.2H₂O in 10ml distilled water in volumetric flack presence 0.5 ml of conc. Hydrochloric acid HCl and(0.5 mL) from TritonX-114.

3.Synthesized of 2-[4-(Carboxymethylphenyl)azo]-4,5-diphenyl Imidazole (4 –CMePAI).

The reagent was made by combining the diazonium salt with the imidazole derivative in an .alkaline alcoholic solution, as described in the equation[14].



Diazonium salt

4,5-diphenyl-1H-imidazole

4-CMePAI

4. Results and discussion4.1. Spectrophotometric study

Absorption spectrum of prepared [4-CMePAI] reagent and ion pair Association complex Zn(II): 2(4-CMePAI)]. The UV-visible spectrum of the synthesized reagent that dissolved in Triton X - 114 (0.5 of 0.1 w/v) were composed of absorption peak show in Fig.1,2.

The formation ion pair –association complex between Zn(II) and 4-CMePAI] in basic medium of pH=8 ,critical micelle concentration (CMC) of TritonX-114 was 0.5 mL, heating time 80°C critical concentration of [4-CMePAI] $1x10^{-4}$ M under conditions of CPL product is also achieved via an emergence of a new absorption maximum at Λ_{max} =447 nm while absorption maximum at

 Λ_{max} =500 nm for complex of Zn⁺² –[4-CMePAI] due to the (π - π *) transitions of the aromatic rings, while the second absorption peak appeared at wavelength λ =530 nm that belongs to the (n- π *) transitions.

As for the FT-IR signals, the spectrum showed several bands: (A band at 3421.72 v^{-1} belongs to the (N-H) group, a band at 1680 v^{-1} belongs to the (C=O) group, and a band at 1597.06 v^{-1} belongs to the (C=N) group, and a band at 1575.84 v^{-1} belongs to a group (N=N) show in Fig.3



Fig. 1.UV-visible spectrum

of [4-CMePAI]

Fig. 2. UV-visible spectrum of [Zn⁺²;4-CMePAI]



Fig. 3. FT-IR spectrum of [Zn⁺²- 4-CMePAI]

5.2. practical part

10 ml aqueous solution containing 100µg Zn(II) with $3x10^{-4}$ M of 4-CMePAI at pH=8 and in presence 0.5mL of TritonX – 114, heated this solution for suitable temperature(80 °C) and

time(15 min.) until formation cloud point layer, then separated this layer and dissolved in 5ml ethanol and measured the absorbance of alcoholic solution against blank prepared at the same manner in absence Zn^{2+} ion at wave length of maximum absorbance for ion pair association complex extracted to CPL (, λ_{max}) 500 nm, on well on the aqueous phase treated according to Dithizone spectrophotometric method [14] and return to calibration care to determine the remainder quantity of Zn(II) ion in aqueous solution at extracted the subtraction this quantity from the original quantity of Zn(II)ion which is already in the aqueous solution to determine the transfer quantity of Zn²⁺ ion to the CPL in order to formation an association complex afterward calculated distribution ratio[15,16,17,18]

$$D = \frac{\left[Zn^{+2} \right]_{org}}{\left[Zn^{+2} \right]_{aqu}}$$

5.3.Optimal conditions for reaction

5.3.1. Effect of pH

In the CPE extraction process, pH has a role in the efficiency of metal ion extraction show in Fig. 5 out from aqueous solutions with a volume of (10mL) containing (100µg) of the Zn(II) and within the range of pH=7-11, and in the presence of (0.5mL) of 1% TritonX-100, with the presence of the organic reagent (4- CMePAI) its concentration is (3×10-4M) and these solutions are heated in a water bath at a suitable temperature until the formation of the cloud point layer (CPL) and for a time (20 minutes), this layer is separated from the aqueous solution and dissolved in (5mL) of ethanol, and the absorbance is measured to her which is a critical factor between the metal and the ligand, giving an appropriate environment for bonding by the sites that join and create complexes. The optimum pH for the extraction of zinc ions Zn(II) is As for the high and low pH, the complex dissociates and the equilibrium constant decreases, but the optimum pH, which is 8, is higher than that, Zn(OH)₂ is formed and the metal is not extracted then its absorption was measured at the wavelength of the greatest absorption, λ_{max} =500 nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 °C) [19].



Fig. 5. Effect of pH on extraction of Zn(II).

5.3.2.Effect of TritonX-114 volume

We prepare a series aqueous solutions of (10mL) were prepared containing a concentration of (100µg) of the Zn(II), and at the pH_{ex} = 8, using a concentration of (3×10-4M) of the organic reagent, (4-CMePAI) respectively. With the presence of different volumes of TritonX-114 within the range (0.3-1 mL) to study the effect of surface volume on the efficiency of zinc ion extraction, then these solutions are heated in an electric water bath at an appropriate temperature and time (20 minutes) until the cloud point layer (CPL), then The cloud point layer is separated from the aqueous solution and dissolved in (5mL) of ethanol until the CPL completed then its absorption was measured at the wavelength of the greatest absorption, , λ_{max} =500 nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 °C) [15,19,20].



Fig. 7. The effect of TritonX-114 the on the formation bonding complex and extraction of the ionic

3.2.3.Type of surfactant:

Zinc ion extractions were carried out from its aqueous solutions with a volume of 10mL containing to determine the effect of the surface type on the extraction process, and the efficiency of extraction according to the CPE cloud point extraction technique. 100µg/10 mL of Zn(II)and at pH(8) and the optimum surface volume (0.5 mL) using The surfaces (Tween 60, Tween 20, Tween 80, TritonX-100, TritonX-114) separately and after heating these solutions in the water bath at the optimum temperature (80 °C) and the optimum time (15) minutes to form a cloud point layer CPL separating the CPL layer from the aqueous solution The CPL layer was dissolved in 5 mL ethanol, then its absorption was measured at the wavelength of the greatest absorption, , $\lambda_{max} = 500$ nm. They need a higher temperature (80 °C)[16,18,21]



Fig. 8. Effect of surfactant type on extraction efficiency

5.3.5.Effect of ligand (4-CMePAI)

A series aqueous solutions 10 ml in volume contain increasing quantities $(1 \times 10^{-6} - 4 \times 10^{-4})$ M of 4-CMePAI at pH=8 with 0.5 ml Triton X-114 and 100 µg of Zn(II)heated there solutions at suitable temperature and time until formation cloud point layer CPL complated the procedure as in the general method the result then its absorption was measured at the wavelength of the greatest absorption, , λ_{max} =500 nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 °C) (10,11,19,21).



Fig. 10. The effect of [4-CMePAI] on the formation complex.

5.3.6.Effect of temperature

The 10 mL series aqueous solutions contain containing 100 µg of Zn(II) at pH = 8 with 0.5 mL Triton X-114 and $3x10^{-4}$ 4-CMePAI heating solutions at temperature gradients until the cloud point layer CPL is completed and the optimum temperature is observed at which the best separation procedure occurs and as then its absorption was measured at the wavelength of the greatest absorption, λ_{max} =500 nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 °C) The result is illustrated in the figure (11) [15,16,22-24].



Fig. 11 The effect of temperature on the values of distribution ratios D

The extraction constant is then calculated using the equation below[16]

Kext. = $\frac{D}{[Zn^{+2}] \quad [4-CMePAI]}$



Fig. 12. The effect of the on the temperature formation values of distribution ratios D and extraction of the ionic bonding complex

We get the slope after sketching the graphic relationship between log 1/T and log K_{ext} and using it to perform the rest of the thermodynamic calculations.

slope = $\frac{-\bigtriangleup Hex}{2.303 R}$ $\frac{\bigtriangleup \log K_{ex}}{\bigtriangleup_{1/T}}$ = $\frac{-\bigtriangleup_{Hex}}{2.303 R}$

 $\Delta G_{ex} = nRTln K_{ext.}$

 $\Delta G_{ex} = \Delta H_{ex} - T\Delta Sex$

Table (1) The thermodynamic values for the extraction of complex ion (Zn^{2+}) according to (CPE) technique[20]

ΔS_{ex}	ΔG_{ex}	ΔH_{ex}
+ 167.8 J mol ⁻¹ K ⁻¹	- 58.973 kJ mol ⁻¹	+ 0.2627 kJ mol ⁻¹

3.2.7.Effect of time Heating

To clarify, by preparing aqueous solutions with a volume of (10mL) containing a concentration of (100 μ g) (1.5210⁻⁴M) of the zinc ion (Zn²⁺) and at pH_{ex} =8, and using a concentration (3 x10⁻⁴M) of the organic reagent (4-CMePAI), and in the presence of (0.5mL) of TritonX-114, these solutions are heated in an electric water bath at the optimum temperature (80°C) then at various intervals between 5 and 30 minutes, until a layer forms.

The cloud point (CPL) separated the layer from the aqueous solution and dissolves in ethanol (5mL). then its absorption was measured at the wavelength of the greatest absorption, , $\lambda_{max} = 500$ nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 °C) [16,18,22-26].





ratios and extraction of the ionic bonding complex.

5.3.4.Effect of Zn(II) concentration

A series aqueous solutions 10 ml in volume containing increasing concentration quantities of 20-120 µg of Zn(II)at pH=8 with presence of 3 X 10⁻⁴ from (4- CMePAI) and 0.5ml Triton X-114 and heated there solutions at suitable temperature(80 °C) and time (15 min.) until formation cloud point layer CPL completed the procedure as in the general method then its absorption was measured at the wavelength of the greatest absorption, $\lambda_{max} = 500$ nm. They need a higher temperature, and this may lead to a disturbance in the equilibrium state because it is the optimum temperature (80 C) [8.9,15,16,21].



Fig. 16. The effect Zn(II)concentration

and extraction of the ionic bonding complex

3.2.8.Effects of Foreign Ions

When extracting the Zn(II)using the cloud point technique (CPE), the presence of some positive ions in the aqueous solution had an effect on the extraction efficiency, which can be seen in the absorption values and distribution ratios D, and by observing the values of D for positive ions when extracting Zn(II)using the cloud point technique (CPE) has an effect on the extraction efficiency, as Ni⁺² bon when it is ionized. In terms of the Cd²⁺ ions in the solution As a result, the process of separating Zn(II)slows down, implying that it has a competitive impact in building a complex between the reagent and Zn(II)lowering the value of D and the separation ratio % E percent As for the rest of the ions They range in effect [15,17-19,21,22,26].

$$Ni^{+2} <\!\!Fe^{+3}\!\!< Co^{+2} < Cu^{+2}\!\!< Cd^{+2}$$



Fig. 17. Effect of Interferences ions on extraction efficiency

4-Methods for determining the extracted complex's probable makeup:

4-1- Mole-Ratio Method:

This method required the preparation of aqueous solutions with a volume of (10mL) containing a fixed concentration of (100µg) (1.52×10-4M) of the Zn(II)and at the pH_{ex} = 8, using increasing concentrations within the range (4×10-4 - 1×10-6M) of the organic reagent ((4-CMePAI) and in the presence of a volume (0.5mL) of TritonX-1, these solutions are heated in a bath Hydroelectricity at the optimum temperature and optimum time for each detector, where the cloud point layer is formed after this layer is separated from the aqueous solution and dissolved in (5mL) of ethanol. Without the presence Zn(II)Calibration curve for determination of Zinc ion (II) in point cloud layer [27].



Fig. 18. The relationship between the absorption values of the Zn-4CMePAI complex and the molar ratios between the organic reagent and the zinc ion.

4-2- Continuous changes method (Job method):

To validate the potential structures of the isolated complexes, a continuous changes procedure was used, which included creating solutions with $(1*10^{-4})$ M of organic reagents. 4-CMePAI, zinc ion (II)) to make a total solution of a volume (10ml) of the mixture by mixing increasing volumes of the aqueous zinc ion solution (9-1) mL with decreasing quantities of the organic reagent solution (9-1) mL and when the function. The cloud point layer is separated from the aqueous solution and dissolved in 5 mL of ethyl alcohol, and its absorption was measured at500 nm with the detector 4 -CMePAI versus Planck's solution without zinc ions for each reagent.



Fig. 19. The relationship between the ratio of the volume of the reagent to the total volume

According to these two methods, it is found that the ratio between the concentration of the reagent: the concentration of the zinc ion (II) is 2:1.[4]





5- Calibration curve

In order to determine the calibration curve of the extracted complex, zinc ion (II) extraction processes were carried out, according to CPE cloud point extraction technique, from 10 mL

aqueous solutions containing increasing concentrations of Zn(II) (2-10) μ g concentrations. Optimum for each of the organic reagent (3×10⁻⁴M) and acid HCl (1M) and an optimum volume of TritonX-114 1%)) 0.5 mL Heat the solutions in a water bath at the optimum temperature 80 °C and the optimum time (15min.) to form a point cloud layer Then the cloud point layer CPL separated from the aqueous solution and dissolved in Calibration curve for Spectroscopic determination of zinc (II) by Cloud Point Extraction (CPE) (5mL) of ethanol and its absorption is measured at the wavelength of maximum absorption λ max =500 nm against Planck's solution prepared in the same way, but in the absence of zinc ions, and then we draw a graphic relationship between the values of absorption (Abs) versus the concentration of Zn(II)we get a straight line relationship, then Calculate the value of the slope of the straight line Slope as in the Fig. 21[28].



Fig. 21. calibration curve of the determine Zinc (II).

Table 2. Values related to the extraction of the Zn(II) from its aqueous solution using the organic reagent 4-CMePAI using cloud point technique CPE.

Parameter	Value
λmax (nm)	500 nm
Regression equation with CPE procedure	Y=0.0119x+0.0201
Correlation coefficient(r)	0.9992
Concentration range (µg/10mL)	(10-100)
Limit of minimum detection LOD (ppm)	0.3798
Limit of Quantitation LOQ (ppm)	1.266
sensitivity	0.0119

RSD%	0.362
Composition of complex (M: L)	1:2
Molar absorptivity (L.mol ⁻¹ .cm ⁻¹)	43590
Pre concentration factor	24.5
Enrichment factor	20

6-Applications of CPE technology in the determination of the zinc (II) ion by 4-CMePAI organic reagent

The Zinc (II) ions were estimated in some models, as the calibration curve was used to estimate the concentration of the analyte in the selected samples, which appear on a statistical basis. and reliability.



Referances:

1. Arya, S. S., Admajith M. Kaimal, Moksha Chib, Sachin K. Sonawane, and Pau Loke Show. 2019. "Novel, Energy Efficient and Green Cloud Point Extraction: Technology and Applications in Food Processing." Journal of Food Science and Technology 56 (2): 524–34. https://doi.org/10.1007/s13197-018-3546-7.

2. Melnyk, A., J. Namieśnik, and L. Wolska. 2015. "Theory and Recent Applications of Coacervate-Based Extraction Techniques." TrAC - Trends in Analytical Chemistry 71: 282–92. https://doi.org/10.1016/j.trac.2015.03.013.

3 Indalkar, K., Malge, S. S., Mali, A. S., & Chaturbhuj, G. U. (2021). Expeditious and Highly Efficient One-Pot Synthesis of Functionalized Imidazoles Catalyzed by Sulfated Polyborate. *Organic Preparations and Procedures International*, *53*(4), 387-396.

4. . A. F. Hussein, H. F. Hashem(2013)(A new study for the liquid-liquid extraction of cobalt(II) ion using one of the compounds4-MPADPI) the new azo) Karbala University Scientific Journal - Volume 11 - Issue 4, pp16-32 (2013)/.

5. Kumar, D., Jain, V., & Rai, B. (2020). Imidazole derivatives as corrosion inhibitors for copper: a DFT and reactive force field study. *Corrosion Science*, *171*, 108724..

6 Kerru, Nagaraju, et al. "Recent advances in heterogeneous catalysts for the synthesis of imidazole derivatives." Synthetic Communications 49.19: 2437-2459(2019)...

7. Fan, Yi-Lei, et al. "Recent advances of imidazole-containing derivatives as anti-tubercular agents." European journal of medicinal chemistry 150 (2018): 347-365..

8. Zheng, Xunan, Zhengning Ma, and Dawei Zhang. "Synthesis of imidazole-based medicinal molecules utilizing the van leusen imidazole synthesis." Pharmaceuticals 13.3 (2020): 37 .

9. Hossain, Mossaraf, and Ashis Kumar Nanda. "A review on heterocyclic: synthesis and their application in medicinal chemistry of imidazole moiety." *Science* 6.5 (2018): 83-94..

10 Chasapis, Christos T., et al. "Recent aspects of the effects of zinc on human health." *Archives of toxicology* 94.5 (2020): 1443-1460.

11. Gürkan, Ramazan, and Nail Altunay. "A reliable determination of zinc levels in beverages with and without alcohol by flame atomic absorption spectrometry after cloud point extraction." *Analytical Methods* 5.7 (2013): 1755-1763.

12 Reis, Bruna Zavarize, et al. "Zinc nutritional status influences ZnT1 and ZIP4 gene expression in children with a high risk of zinc deficiency." *Journal of Trace Elements in Medicine and Biology* 61 (2020): 126537...

13. Rahmati, Mohammadbagher, et al. "The prevalence of zinc deficiency in 6-month to 12-year old children in Bandar Abbas in 2013." *Electronic physician* 9.8 (2017): 5088..

14 Ibtehaj Raheem Ali (2005) (Studies in Solvent Extraction of Cu & Ag by use of Ligands 2-[(4- Carboxy methyl azo)]-4,5- Diphenyl Imidazole and 2-[(3- Methyl Benzen azo)]-4,5-Diphenyl Imidazole) A thesis Submitted To the Council of the College of Education For Girls / Kufa University In Partial Fulfilment of the requirements for The Master Degree in Chemistry. 15 Wannas, Fatima A., E. A. Azooz, and S. K. Jawad(2019) "Liquid ion exchange with spectrophotometric method for separation and determination W (VI)." *Journal of Advanced Ressearch And Dynamic Control System*, 11(7),260-269.

16. Wannas, F. A., & Jawad, S. K. (2018). Extraction and determination of Nickel (II) via cloud point method. *Inter. Journal of Engineering Technology*, 7(4), 725-731.

17.Alghurabi, F. A. W., & Jwad, S. K. (2019). Separation, preconcentration, extraction and spectrophotometric determination of Mn (VII) from Acidic Aqueous medium. *Al-Qadisiyah Journal of Pure Science*, 24(1), 31-36.

18 Azooz, E. A., Moslim, J. R., Hameed, S. M., Jawad, S. K., & Al-Mulla, E. A. J. (2021). Aspirin in Food Samples for Separation and Micro Determination of Copper (II) Using Cloud Point Extraction/Solvation Method. *Nano Biomed. Eng*, *13*(1), 62-71..

19. Han, Q., Huo, Y., Yang, L., Yang, X., He, Y., & Wu, J. (2018). Determination of trace nickel in water samples by graphite furnace atomic absorption spectrometry after mixed micellemediated cloud point extraction. *Molecules*, 23(10), 2597..

20. Xu, H., Zhang, W., Zhang, X., Wang, J., & Wang, J. (2013). Simultaneous preconcentration of cobalt, nickel and copper in water samples by cloud point extraction method and their determination by flame atomic absorption spectrometry. *Procedia Environmental Sciences*, *18*, 258-263.

21. Moslim, J. R., & Jawad, S. M. H. S. K. (2021). Cloud Point Extraction with Liquid Ion Exchange For Separation And Determination Of Zinc (Ii). *NVEO-NATURAL VOLATILES & ESSENTIAL OILS Journal*/*NVEO*, 6503-6516..

22 Ghaedi, M., Shokrollahi, A., Niknam, K., Niknam, E., & Soylak, M. (2009). Development of efficient method for preconcentration and determination of copper, nickel, zinc and iron ions in environmental samples by combination of cloud point extraction and flame atomic absorption spectrometry. *Central European Journal of Chemistry*, 7(1), 148-154.

23.Llaver, M., & Wuilloud, R. G. (2020). Studying the effect of an ionic liquid on cloud point extraction technique for highly efficient preconcentration and speciation analysis of tellurium in water, soil and sediment samples. *Talanta*, *212*, 120802.

24. Wannas, Fatima A., S. K. Jawad(2019). " Cloud Point Extraction Combined with Onium Technique for Separation and Determination Nickel (II) and Ascorbic Acid)." *Jour of Adv Research in Dynamical & Control Systems* 11(2), 182-191

25. Thongsaw, A., Sananmuang, R., Udnan, Y., Ross, G. M., & Chaiyasith, W. C. (2019). Dualcloud point extraction for speciation of mercury in water and fish samples by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *160*, 105685.

26. Kori, S. (2021). Cloud point extraction coupled with back extraction: a green methodology in analytical chemistry. *Forensic sciences research*, 6(1), 19-33.

27. Dhahir, S. A., & Mohammed, N. J. (2019, July). Cloud point extraction of Cefixime drug by direct (UV-Vis) spectrophotometer and indirect (Flame Atomic Absorption) technique. In *Journal of Physics: Conference Series* (Vol. 1234, No. 1, p. 012093). IOP Publishing.

28. Marczenko, Z., & Balcerzak, M. (2000). Separation, preconcentration and spectrophotometry in inorganic analysis. Elsevier.