Determining Traces Metal Ions using Porphyrins as a Reagent

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Abstract

Porphyrins moleculars is a macrocyclic compounds, suitable to be an excellent analytical reagent for spectrum analysis due to its highest molar absorption coefficient, for its complexes with wide range for several metal ions compared with the open chain reagent, so it can be used to determine traces of metal ions which coordinate with it.The multiplity of the bands for porphyrins reagent itself which reach to five bands cover all the spectrum (350-800)nm create inefficient direct molecular spectrum methods, because of overlap between reagent spectrum and formed complex spectrum, for thought, employment of (HPLC) can separate the excess reagent from the formed complex ,and separate the formed complexes from each other, at the same time, because the difference at retention time in the column, and all the formed complexes with porphyrin have a common absorbance band called (Soret band) appear in the range (400-420)nm which allowed to fixing wavelength in the detector on (HPLC), thus enable to record the analytical signal for nano molar concentration for most metal ions which coordinate with porphyrins molecular formed a chelate complexes, these formed complexes are very stable, the dissuasion possibility is less for long storage period, comparing with other reagents, the overlap on spectrum will be minimized.

This research can be a serious procedure to develop analytical high quality method to determine later transition metal ions, using HLPC technique and tetraphenylporphyrin (H_2TPP), we have acheived the following :

1- We studied the chromatographic behavior for the H_2TPP by using (UV-Vis) in several solvents: (DMF, CH_2Cl_2, CCl_4,C_6H_5-CH_3).

2- The possibility to form a chelating complex between H_2TPP and Zn ion has been studied, in addition to all effective factors which include the best formation, we have reach to the optimum conditions.   we have known to the chromatographic behavior of formed complex, and reach to the optimum separation condition between the formed complex and the excess concentration of the reagent .

3- we calculated the steichiometric composition for the formed complex by (Molar ratio and continuous method), calculated the molar absorption coefficient for formed complex, its constant formation, the linear relation between the analytical signal (peak surface) and the Zn concentration was achieved, which in contestable to Lambert-Beer law in the wide range.

4- The proposed method was applied on model samples of Zn indented with its actual contain.

5- we reached to the optimum chromatographic peaks separation for formed complexes(Zn-TPP, Ni-TPP, H_2TPP, VO-TPP), as the following retention time respectively : t_R=4.2 < t_R=6 < t_R=6.8 < t_R=12.4   (min)

6- We can confirmed according to the results which we obtained: (RP-HPLC) to solve spectrums overlap between H_2TPP and formed metal complexes, the possibility to insulate analytical chromatography peaks: sharp, symmetric, and related to the metal ions concentration in a wide range and for nanomol ion concentration, consequently it well allow us to determine traces of metal ions.

Keywords: porphyrins , chelate , complex , RP-HPLC , and traces ion.

1- Introduction

Porphyrins chemistry consider an interest subject when using as reagent in spectrum analysis [1,2,3]. Due to high absorption molecular coefficient. and the effect negative method using porphyrins to determine metal ions by direct method [4] is the slow combination reaction between metal ions and porphyrins ring, and low rendement formed complexes. this require a long period to achieve the equilibrium, as well as, related to porphyrins ring symmetry, and a strong stability. It is difficult to deform the porphyrins ring as a previous step to insert metal ions.

we can surmount all above by [4,5]

1- Heating.

2- Add aromatic base hetrogeneous such as, Imidazole, or Pyridine.

3- Using reduction substances (Ascorbic acid, Hydroxylamine).

4- Using replacement reaction with Cadmium, or Mercury porphyrins .

5- Using Porphyrins has a substituant on pyrrole nitrogen.

6- Insert a function group to be bound with metal ion near porphyrins core.

Different type of porphyrin has been studied [6] in a different temperature, different solvent: (CCl4 , CH2Cl2) , the spectrum showed peaks at (475-690)nm, this peaks does not related to any of react substances. React mechanism Mg2+,Fe2+with porphyrin ring has been studied [7] as well as all effective factors and Imidazole has been used to remove protons porphyrin ring. Porphyrin sepration : meso tetra butyl porphyrin, meso tetra ethers butylporphyrin, and porphyrin complexes, has been studied [8], all sepration factors has been studied: type of

Column, and mobile phase were defined. At [9] all factors separation had been clarified for seven kind of bioporphyrin found in human urine, the separation done in 3.2 min using 0.1 M Ammonium citrate, with fluorescence detector for RP-HPLC.

Due to bio-natural origin of porphyrins, it can be used in a wide range in analytical chemistry, there is a kind of porphyrins called petroporphyrins (PPS): A typical chemical fingerprint,can be uses as a biological mark to decide origin and manner formation petroleum, at [10] selective extraction has been used for metalporphyrin which can be founded in petroleum ,the study show the high catalyst on cyclo-dextrinsepoxide reaction. At [11] chromatographic method to isolate petroporphyrins with Methyl sulfonic acid has been used, monitoring extraction and purified using UV-Vis to analysis petroporphyrins has been done by. Laser desorption ionization-time of light mass spectrometry

A theoretical study has been applied [12] using (DFT/B3LYP) to be sure about porphyrin structure and stability , this study depends on (Density Functional Theory), this information available in Gaussian94 program .

2- Result and discussion

We studied the reagent tetraphenylporphyrin (H_2TPP) , figure (1)
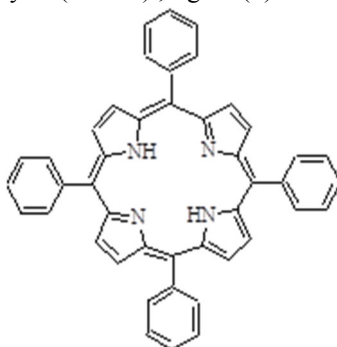

Figure(1) : H_2TPP Molecular structure

Spectrum scanning in several solvent such as (Dimethylformamide (DM F)- Chloroform-Toluene and Dichloromethane) , for several concentrations , as show in figure(2). the reagent acts distinct band at Vis named Soret band at 418 nm, and 4Q bands graduated in its intensities and wavelength from right to left ,
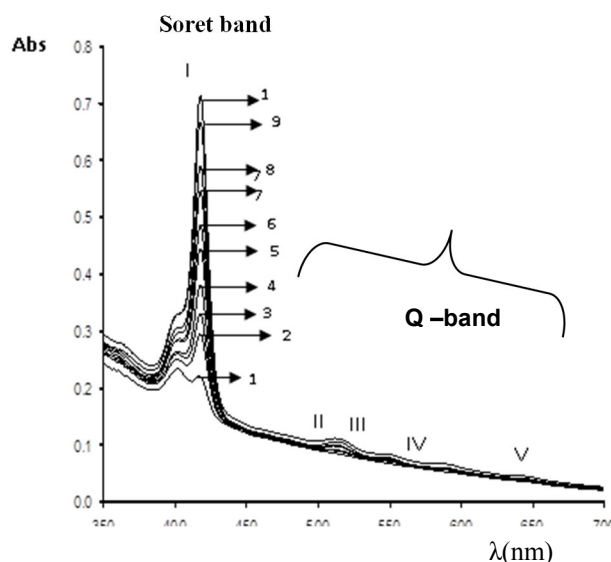
Figure(2) : Spectrum scanning of H_2TPP in DMF
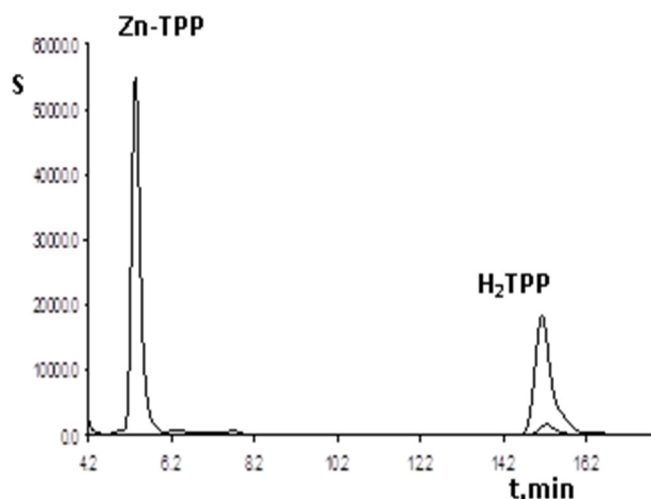$C_{H2TPP}.10^7$,M (1) 1 , (2)2, (3) 3, (4) 4, (5)5, (6) 6, (7)7, (8) 8, (9) 9, (10) 10.

And to make this peaks very clear we increase the H_2TPPconcentration , the result show in figure (3), we summarize the result obtained for the study in all solvents in Table (1) . And to prevent any interferences between the reagent (H_2TPP) peaks, and complex (Zn-TPP) peak , we used High performance liquid chromatography (HPLC) method ,figure (4) show the peaks for (H_2TPP, Zn-TPP). The complex formed as follow we used $ZnCl_2$ as a source for Zinc ions,we prepared a stock solution $C_{Zn} = 1 \times 10^{-2}$ M, In distilled DMF . In a flask we put $C_{Zn} = 6 \times 10^{-6}$ M ,
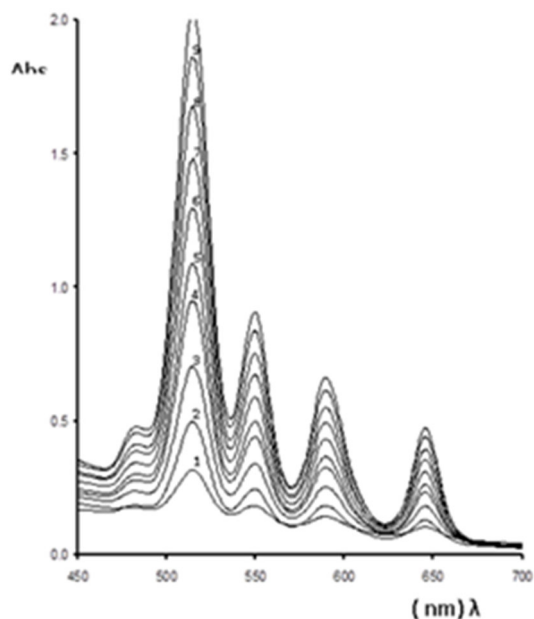
Figure(3) : Spectrum scanning of H_2TPP in DMF
CH_2TPP10^5,M : 1(1);2(2);3(3);4(4);5(5);6(6);7(7);8(8);9(9);10(10)

Table (1) : Result of spectrum behavior for H_2TPP in(CCl_4, C_6H_5-CH_3,CH_2Cl_2 , DMF)

λ(nm) Solvent		**418**	**515**	**550**	**590**	**645**
C Cl₄	Linearity	10^{-7}-10^{-6}	10^{-6}-10^{-4}	10^{-6}-10^{-4}	10^{-6}-5.10^{-4}	10^{-6}-5.10^{-4}
	ε	5.39×10^5	2.00×10^4	8.20×10^3	6.00×10^3	4.20×10^3
C₆H₅.CH₃	Linearity	10^{-6}-10^{-5}	10^{-5}- 10^{-4}	10^{-5}-10^{-4}	10^{-5}-10^{-4}	10^{-5}-10^{-4}
	ε	8.70×10^4	1.68×10^4	6.90×10^3	4.90×10^3	3.20×10^3
CH₂Cl₂	Linearity	1.10^{-7}-5.10^{-7}	10^{-6}-10^{-4}	10^{-6}-10^{-4}	10^{-6}-10^{-4}	10^{-5}-5.10^{-4}
	ε	6.70×10^5	2.00×10^4	9.00×10^3	5.60×10^3	4.48×10^3
DMF	Linearity	10^{-7}-10^{-6}	10^{-6}-10^{-4}	10^{-6}-10^{-4}	10^{-6}-10^{-4}	10^{-6}-10^{-4}
	ε	3.70×10^5	1.50×10^4	6.60×10^3	4.50×10^3	3.70×10^3

Figure(4): Chromatographic peaks : H_2TPP ; Zn-TPP
;mobile phase: Methanol , ф=1.5 ml/min ; λ_{max} =420 nm
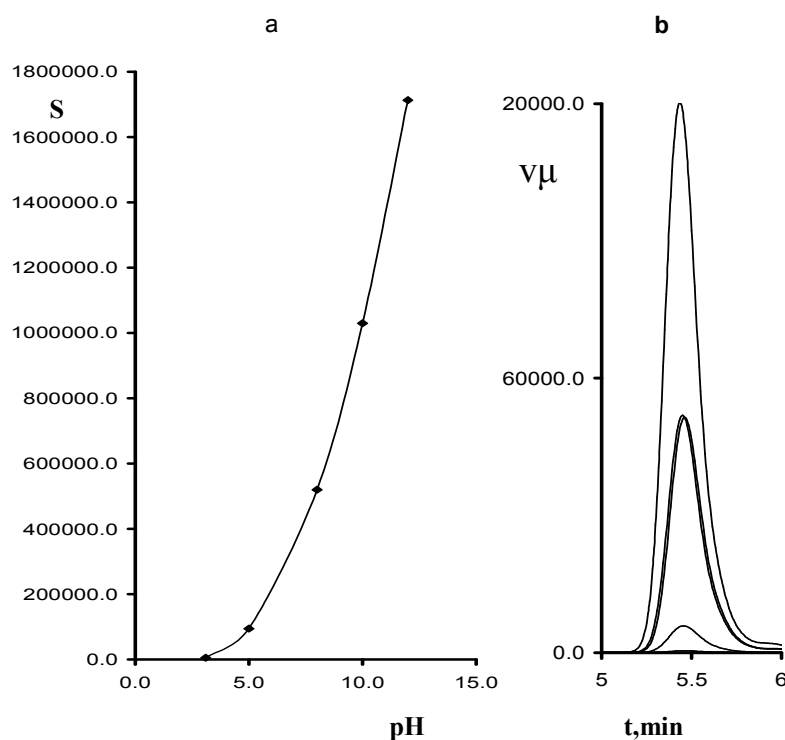C_{H2TPP} = (6×10^{-6}, C_{Zn}= 6×10^{-6}).M

The reaction proceed under reflex. We determined the ideal condition to form the complex (Zn-TPP) such as [PH, wave length, heating time, the reagent concentration, the molar ratio C_{Zn}:C_{TPP} and it was (1:1). we confirmed it by two methods (Continuous variation, saturation curve)], the results obtained show as figures (5-

10). Table (2) show the ideal condition found .

Table (2) condition found to form ZZn-TPP complex

Study effect		Result obtained
pH		Increase PH from3.1 to 12 well increase the surfer peak 315.6 times
wave length		λ_{max} =420 nm
heating time		1 hour , T= 150 ^{o}C
H$_2$TPP concentration		C_{H2TPP} = (1-10) 10^{-6}; M
Molar ratio	Continuous variation	0.961 = 1
	saturation curve	0.978 = 1
Stability		24 hours

We calculated the absorption molecular coefficient (ξ), and constan formation (βk) for the formed complex (Zn-TPP) by two methods (Schwarzenbach, Saturation curve). The result by this methods was : $\xi = 1.10^5$ l.mole^{-1}.cm^{-1} (β_k) =3.10^7

Figure(5): The relation between (S) peak surface for the complex Zn-TPP and PH (a), corresponding chromatograms(b), C_{H2TPP} = (6 × 10^{-6}; C_{Zn}= 1×10^{-6}).M ;mobile phase: Methanol, ϕ=1 ml/min, λ_{max} =420 nm   .
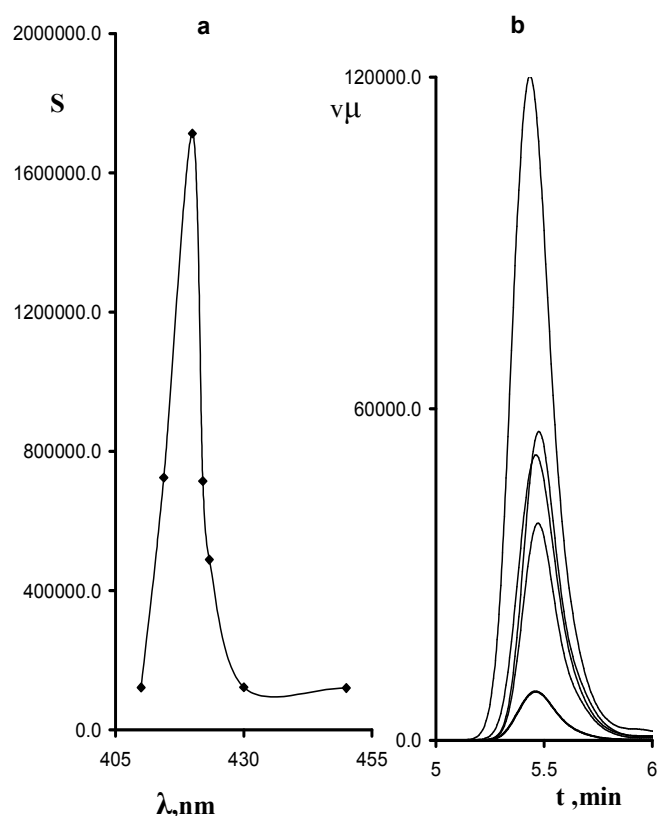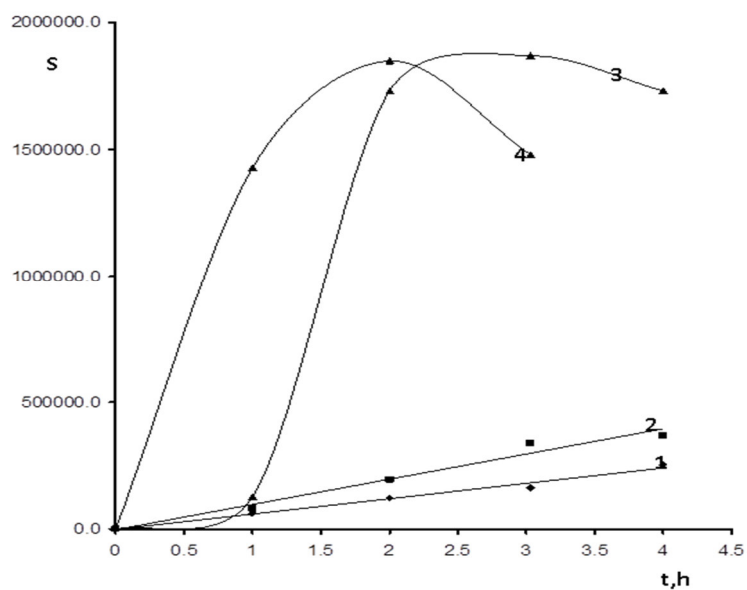
Figure(6): The relation between (S) peak surface for the complex Zn-TPP and wavelength (a), corresponding chromatograms(b)

$C_{H2TPP} = (6 \times 10^{-6}, C_{Zn}= 1 \times 10^{-6}).M$
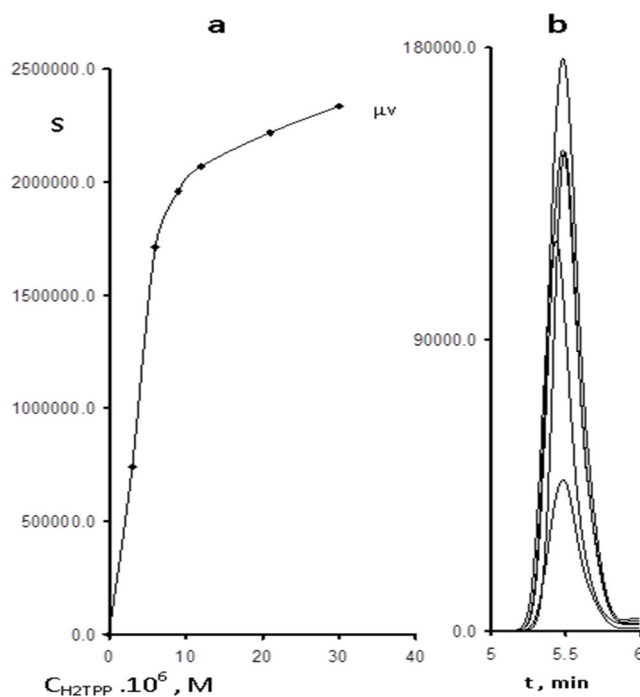
;mobile phase: Methanol , ϕ=1 ml/min

     We achieved The linear relation between the analytical signal (peak surface) and the Zn concentration according to Lambert-Beer law in the wide range of

$(1-10).10^{-8}$ M.Figure(11) The proposed method was applied on model samples of Zn and it was indented with its actual contain . The value of RSD did not excess 7.02%, Table(3)

Table(3): Determination Zinc in Model Samples C_{H2TPP} ,M =1.10^{-6}, (n=5, α=0.95) mobile phase: Methanol , ϕ=1 ml/min

Taken x.10^8,M	Found $(\overline{X} \pm \Delta X)10^8\,M$	RSD%	recovery%
3.00	3.20 $\mp$ 0.24	7.02	107.3
5.00	5.10 $\mp$ 0.24	3.26	102.0
8.00	7.01 $\mp$ 0.18	2.18	88.56

Figure(7): The relation between (S) peak surface for the complex Zn-TPP and time heating, $C_{H2TPP} = (6 \times 10^{-6}, C_{Zn}= 1\times10^{-6})$.M
mobile phase: Methanol, ϕ=1.5 ml/min, λ_{max}= 420 nm
T (^{o}c) : 60(1);90(2);120(3);150(4).

Figure(8): Effect of excess concentration (H$_2$TPP) on the complex formation
(Zn-TPP)(a), corresponding chromatograms(b), $C_{Zn}= 1\times10^{-6}$.M
,mobile phase: Methanol , ϕ=1.5 ml/min, λ_{max}= 420 nm
T (^{o} c) : 150 ; t (min)=90 .
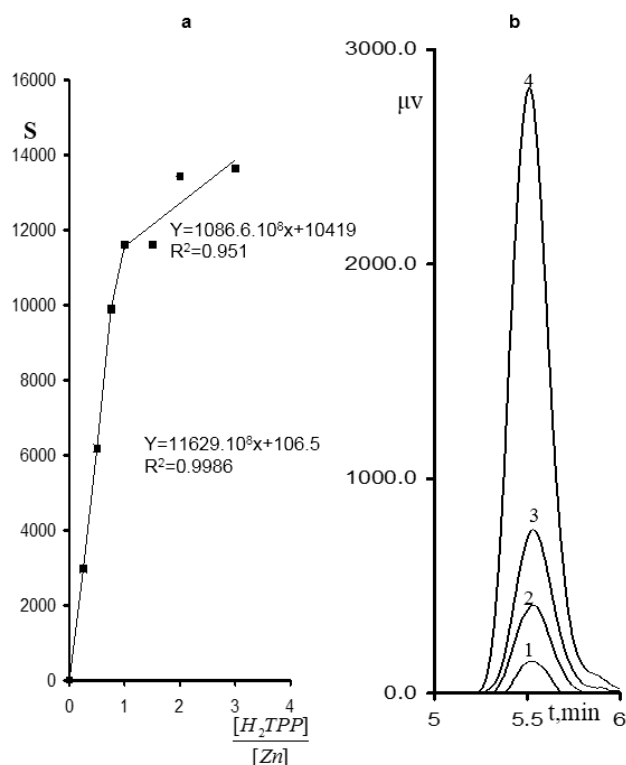
Figure (9): (a) Change of surface for chromatographic peak relate to formed complex
Zn-TPP with Molar ratio, (b) the Sample of chromatographic relate to the formed complex
$C_{H2TPP} .10^8$,M: 1.5(1);3.0(2);6.0(3);9.0(4);18(5).
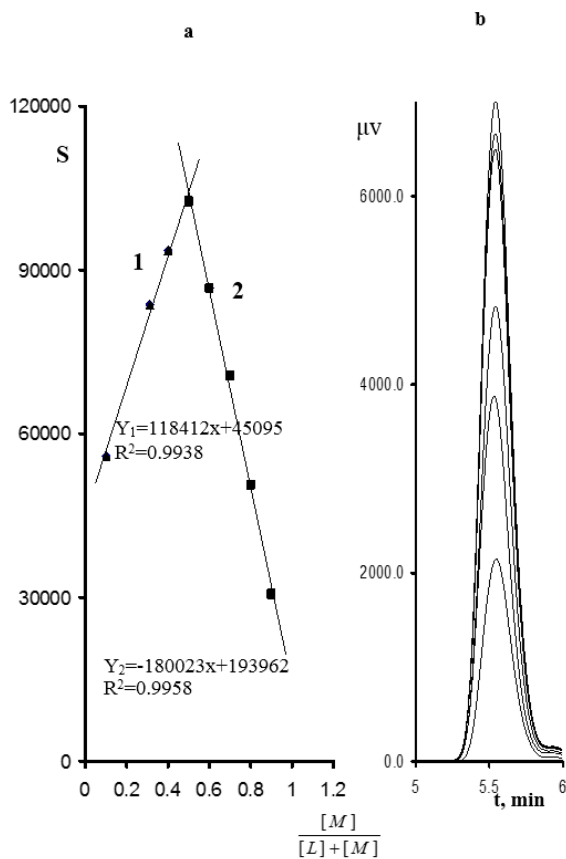, λ_{max}= 420 nm, C_{Zn}= 8×10^{-8}.M

Figure (10): (a) Change of surface for chromatographic peak relate to formed complex
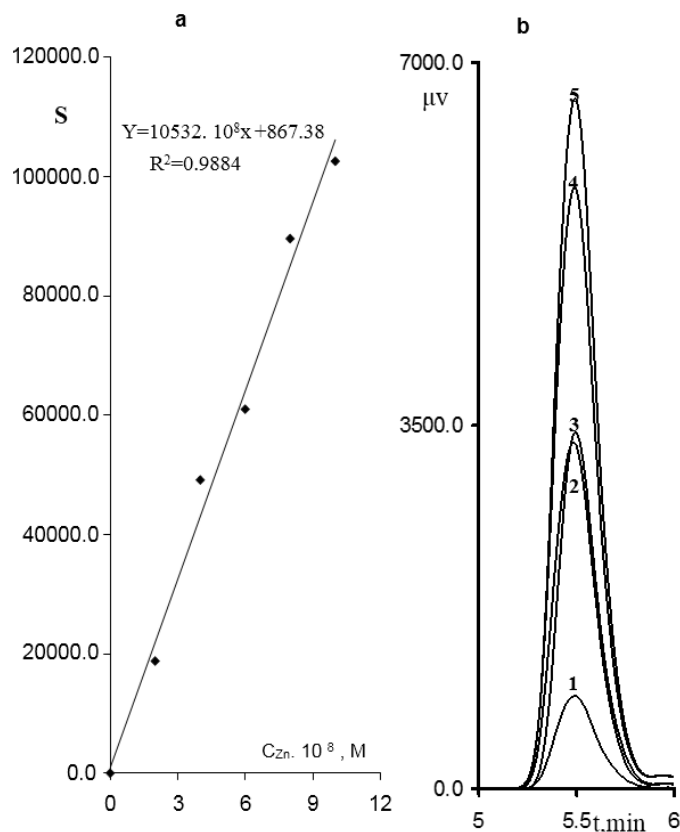Zn-TPP with saturation curve, (b)the Sample of chromatographic relate to the formed complex

Figure (11):The linear range between complex formed Zn-TPP and Zinc
concentration , mobile phase: Methanol , φ=1.5 ml/min, λ max= 420 nm,
C_{H2TPP},M= 1× 10^{-6} , C_{Zn}.10^{8},M:2(1); 4(2);6(3);8(4);10(5).

In our study we formed (VO-TPP, Ni-TPP, Zn-TPP), Methanol as a mobile phase did not separate all formed complexes ,from the excess reagent so we changed to

(Ethyl acetate- Acetonitrile) (75:25) , it was suitable for separation, figure (12) shows the corresponding chromatogram.
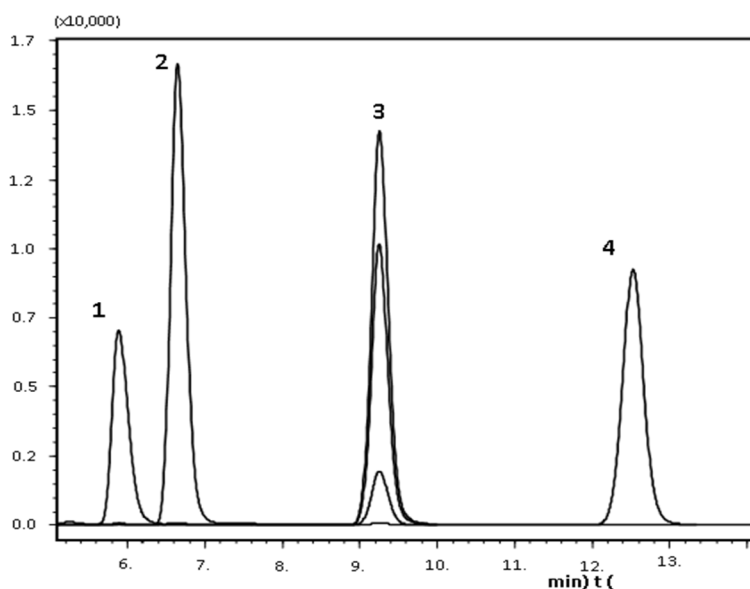
Figure(12): The Chromatographic peaks related to :
Zn-TPP (1), VO-TPP(2), H_2TPP(3), Ni-TPP(4)
C_{Zn}=4×10^{-8} ,C_{VO}=4×10^{-7},C_{H2TPP}=1×10^{-6},C_{Ni}=8×10^{-7} , (M)
The mobile phase is (ACN:EtAC)   (75;25)
λ max =420 nm , φ=1 ml/min

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We restudied The linear relation between the analytical signal (peak surface) and the Zn concentration, and Could reduce the linearity to the rang of $C_{Zn}= (2-10).10^{-8}M$, with mew mobile phase, Figure (13) show the achieved new linearity. It is clear from the figure that the coordination coefficient is $R^2=0.9987$ and it is rare to find this in the low concentration using another reagent, so it is easy now to determined Zinc concentration as 0.13 µg / L ; this is the analytical target we was looking for. We made sure that the formed complex (Zn-TPP) was stable for 24 hours. Again we applied on model samples of Zn and it was indented with its actual contain . The value of RSD did not excess 0.*76%, Table(4)*

Table(4): Determination Zinc in Model Samples

C_{H2TPP} ,M =1.10^{-7}, (n=5, α=0.95) , The mobile phase is (ACN:EtAC) (75;25) , λ max =420 nm , ɸ=1 ml/min

Taken 10^9,Mx	Found $(\overline{X} \pm \Delta X)10^9 M$	RSD%	recovery%
3.00	2.99 ∓ 0.02	0.76	99.5
5.00	5.05 ∓ 0.02	0.33	101.1
8.00	7.08 ∓ 0.01	0.63	101.1

Our study which we showed, can confirmetied (RP-HPLC) to solve spectrum overlap between H_2TPP as a reagent and formed metal complexes, the possibility to insulate analytical (chromatography peaks) sharp, symmetric, and related to the metal ions concentration in a wide range for nano mol ion concentration. consequently ,this method suitable to determine traces of metal ions.
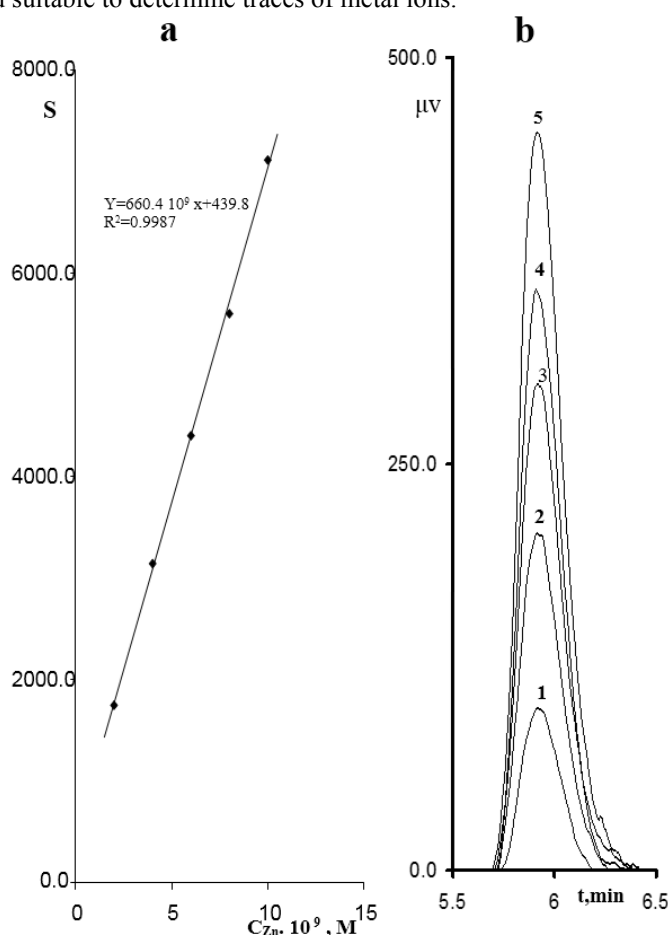

Figure (13): The linear range between comples formed Zn-TPP and Zinc concentration , λ max=420 nm , C_{H2TPP},M= 5×10^{-7} ; ɸ=1 ml/min

The mobile phase is (ACN:EtAC) (75;25)

$C_{Zn}.10^9$,M:2(1);[4(2);6(3);8(4);10(5).

Finally we indicated that the fascinating chromatogram which show the successful separation (Zn-TPP, Vo-TPP, H_2TPP, Ni-TPP) , for a various standard concentrations related to formed complexes, by using mobile phase
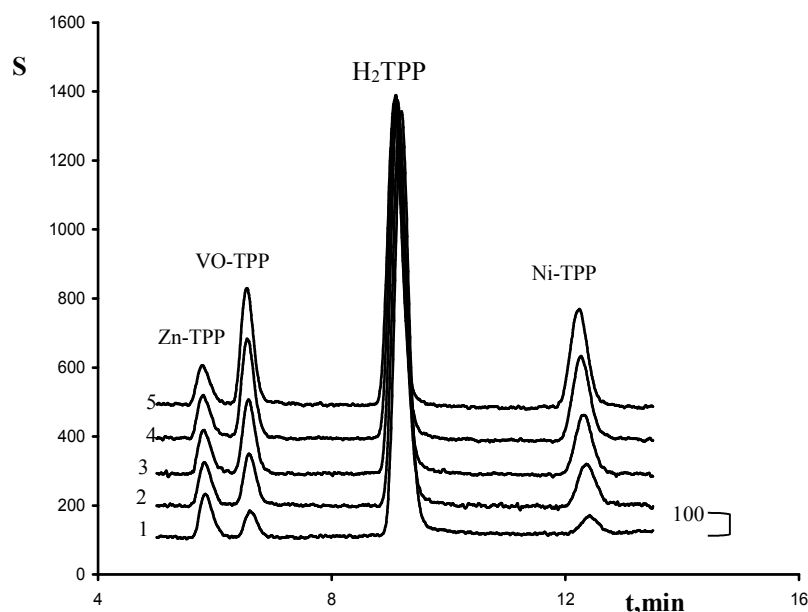
(Ethyl acetate- Acetonitrile) (75:25).

Figure (14):   The Chromatographic peaks related to :
Zn-TPP, VO-TPP, H$_2$TPP, and Ni-TPP.
The mobile phase is (ACN:EtAC)   (75;25)
, λ max =420 nm , ϕ=1 ml/min

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