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Spectrophotometric Determination of Trace Amounts of Nickel ion By Using Tetra(4-hydroxyphenyl) Porphyrin (THPP) and Tetra(4-bromo phenyl)Porphyrin (TBPP)

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ABSTRACT

In this work , the reaction of THPP and TBPP with nickel ion was studied Spectrophotometrically and kinetics as well as the thermodecomposition of NiTHPP complex with increasing the heating temperature as function of time was determined. The porphyrins were found to be a highly sensitive and selective reagents for direct Spectrophotometric determination of nickel ion at 0.031 µg/5ml for THPP and at 0.236 µg/10 ml level. The soret band of NiTHPP complex lies at 420 nm (€ = 2 x 10^5 L.M^{-1}. cm^{-1}), and at 414nm (€ =5.7 x 10^4 L.M^{-1}. cm^{-1}) for NiTBPP complex in DMF solvent. The complexes can be formed within 10 minutes by heating on hot plate (80 C°). Four determination of standard solutions containing 0.946 µg/5ml Ni(ll) ion with THPP and 0.685 µg/10ml Ni(ll) ion with TBPP gave relative standard deviation RSD 0.074% and 0.065% respectively. Beer's Law is obeyed in the range of 0.01-2.55 µg/5ml and 0.01-2.34 µg/10ml , sandell's index were 0.00367 and 0.001 for the absorbance of 0.001 respectively. The mole ratio of complexes are 1:1, the interference of cations was studied as well. These ligands were used to determine nickel ion in phosphate crude stones sample and gave a satisfactory results.

Introduction:

The porphyrins are a class of naturally occurring macrocyclic compounds, which play a very important role in the metabolism of living organisms. These have been exten- sively studied due to their biological import- ance as well as analytical applications[1]. The porphyrin molecule contains four pyrro- le rings linked via methine bridges and the porphyrin nucleus is a tetradentated ligand in which the space available for a coordinated metal has a maximum diameter of approximately 3.7A°[2]. The porphyrins are a highly sensitive chromogentic reagents for Spectrophotometric determination of several metal ions based on the of so-called soret band at 400-500nm[3-8]. Porphyrin metal play an important role in biological activiti-es for instance iron complex in the haem-oproteins, used to transport (haemoglobin), or to store oxygen (myoglobin)[9].

Also are found in cytochrome in the hydroxylation of a wide range of substrates (cytochrome P-450)[10], or in electron transport, enzymes (cytochrome c,b). Vitamins B_{12} (contain cobalt macrocylices) are catalytic intrmedia-tes and hydrogen transfer catalysts[11]. THPP and TBPP were applied previously as a complexing reagents of many metal ions such as Hg(ll), Pb(ll), Cd(ll) and Zn(ll) ions [1,5,12,13], and many workers have been used $TPPS_4$ and TBPP to determine trace amounts of many transition metals such as Cu, Ni, Pb, Zn, Fe and Mn[14-20]. They found the linearity ranges are 0.01-120µg.l^{-1} for Pb, Cd and Hg ions and the detection limits are 1.0, 0.5 and 1.0 µg.l^{-1} respectively for TBPP, ligand[21], and 0.01-120 µg.l^{-1} , 0.01-2.0 µg/10ml, 0.01-15.6 mg/10ml and0.01-1.85mg/10ml for U, Fe(lll), Fe(ll) and $S_2O_4^{-2}$ respectively for $TPPS_4$ porphyrin[22,23]. In this work, the spectrophotometric determination of nickel ion was studied with THPP and TBPP in DMF solvent and the solid nickel complexes were prepared and isolated in pure from.

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Experimental Part:

Tetra (p-hydroxyphenyl) porphyrin and tatra(p-Bromo phenyl)porphyrin.

THPP and TBPP were prepared by refluxing of 2.45 ml pyrrole with 4.3 gm p-hydroxybenzaldehyde and 2.88 ml pyrrole with 7.77 gm p-Bromo benzaldehyde, 1:1 mole ratio respectively in 250 ml propionic acid media for 1.5 hours[24]. After cooling to the room temperature the solutions were filtered and the product washed with a minimum quantity of ethanol and distilled water, a blue crystals of THPP and TBPP were obtained. Chemical analysis of formula ($C_{44}H_{30}N_4O_4.CH_3CH_2OH$) for THPP (C.H.N.O) is Calc (Exp ±) C : 76.16 (76.2 ± 0.1) , H:4.96 (4.94±0.2) ,N: 7.72 (7.69 ±0.2) and O: 11.04 (11.0 ± 0.02) and for TBPP formula($C_{44}H_{26}N_4Br_4$) (C.H.N.O) is Calc (Exp ±) C:56.79(56.81 ± 0.22) , H: 2.79(2.77± 0.15) and N:6.02 (5.99 ± 0.19) .Figure 1.0 shows the structure of porphryins.

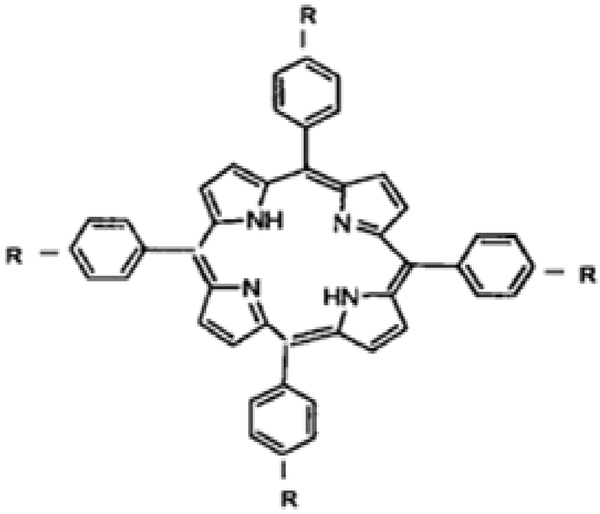

Figure 1.0 The structure of porphyrins in this study.

Preparation of solid NiTHPP and NiTBPP complexes.

The complexes were prepared by dissolving 0.1gm THPP and 0.25gm TBPP in N,N-dimethyl formamide (30ml) respectively and the solutions heated on hot plate (80C°),with 0.024gm and 1.0gm from $NiCl_2.2H_2O$ salt were added and the mixture allowed to react for (10)minutes. The completeness of the reaction can be checked by measuring the UV-Vis spectrum of the reaction mixture; the five band spectrum of THPP and TBPP porphyrins should absent, being replaced by the two band spectrum of the product. When the reaction is complete cool to room temperature slowly and then add 300 ml of acidic water (1ml HCl 6N), then the reaction mixture is again cooled to 2C°for 30minutes, red-brown precipitates were obtained, filtered off, washed with water and dried in oven 50-70C° for 30 minutes, the product was 0.103gm (95.37%) of NiTHPP and 0.222gm(83.8%) of NiTBPP. Chemical analysis of formula ($C_{44}H_{28}N_4O_4Ni$) for NiTHPP(C.H.N.O) isCalc (Exp±) C:71.84(71.9 ±0.2), H 3.81(3.79±0.1),N:7.62(7.65 ±0.2) ,O:8.37 (8.4±0.15) and Ni:7.89(7.90±0.11),for NiTBPP formula ($C_{44}H_{28}N_4Br_4Ni$) (C.H.N.O) is Calc (Exp ±) C: 53.53 (53.7 ± 0.23), H:2.43 (2.47±0.25) ,N:5.67(5.77±0.26) and Ni: 5.95(6.0±0.35)

Preparation of standard solutions.

Standard solution of(1.473x10^{-3}M) THPP and (4.3x10^{-4}M) TBPP.

These solution were prepared by dissolving (0.05)gm of THPP in(50)ml DMF and (0.01)gm of TBPPin (25)ml DMF solvent.

Standard solution of NiTHPP and NiTBPP complexes

These complexes were prepared by disso- lving (0.01)gm of NiTHPP and (0.01)gm of NiTBPP in (25)ml of DMF to give concen- trations of (5.44x10^{-4}M) and (4X10^{-4}M) respectively.

Standard solution of Ni(ll) ion.

The solution was prepared by dissolving 0.125gm of $NiCl_2.H_2O$ in (25)ml DMF to gave concentration of 0.03M.

Composition of complexes.

Determination of composition of the form- ing complexes were conducted using mole ratio method . Metal Ni(ll) was added to (1x10^{-5}M) porphyrin solution in the concen- tration range (1x10^{-6}-3x10^{-5}M) . After (10) minutes of reaction on the hot plate, the absorbance at wave length of (420nm) for THPP and (414nm) for TBPP porphyrins was measured against blank reagent.

Construction of calibration curve for ions.

Ten of (5)ml volumetric flasks containing a liguos of standard NiTHPP and NiTBPP solutions in the range of 0.0319-2.872 µg/5ml Ni(ll) and 0.234-2.347 µg/10ml Ni(ll) respectively, the volume of solutions was completed to the mark by using DMF solvent, and the absorbance was measured at 420 nm and 414 nm respectively against blank reagent.

Determination of Ni(ll) ion in phosphate crude stones.

(2) grams of phosphate crude stones was dissolved in (3)ml of concentrated nitric acid, then heated for (10)min, with stirring until most of vapors of nitric oxides are not seen. Solution was diluted with (50)ml of distil water and filtered. The solution concentrated on the hot plate for (30) min. The solid obtained by drying in the oven for (30)min. . (100)mg from solid sample was dissolved in (50)ml DMF solvent. (200) micro liter from solution sample was added to (10)ml of THPP or TBPP (5X10^{-6}M), four samples were used to determine the nickel ion. All samples were heated on the hot plate for (10)minutes (80 C°), after cooling these samples to the room temperature, the absorbance was measured at the soret band of 420 nm for THPP and 414 nm for TBPP against blank reagent.

Results and Discussion

Spectrophotometric study of porphyrin and metals porphyrin

Solutions of THPP and TBPP in DMF solvent is purple and exhibit six absorption maxima one is soret band at 422nm (€=3.33 x10^{5} L. M^{-1}. cm^{-1}) , 400 nm as shoulder (€=6.26x10^{4} L.M^{-1}.cm^{-1}), 520 nm (€= 1.47x10^{4} L.M^{-1}. cm^{-1}), 556(€= 1.312x10^{4} L.M^{-1}. cm^{-1}),594 (€ =5.2 x10^{3}L.M^{-1}.cm^{-1})and 652(€=7.07x10^{3} L.M^{-1}.cm^{-1}). This for THPP, and for TBPP one is soret band at 416nm(€=2.2x10^{5}L.M^{-1}.cm^{-1}), 512nm(€= 1.1x10^{4} L.M^{-1}.cm^{-1}), 548 nm (€ =5.6 x10^{3}L.M^{-1}.cm^{-1}), 590nm (€ =3.8 x10^{3}L.M^{-1}.cm^{-1}), 646nm(€ =3.5 x10^{3}L.M^{-1}.cm^{-1}), 400nm as a shoulder (€=6.1x10^{4} L.M^{-1}.cm^{-1}). NiTHPP complex spectra shows soret band at420nm(€=2.x10^{5}L.M^{-1}.cm^{-1}), and at 530 nm(€=1.66x10^{4} L.M^{-1}.cm^{-1}), where NiTBPP complex spectra shows soret band at 414nm (€=5.7 x10^{4} L.M^{-1}.cm^{-1}) and at 526 nm (€ = 5.6 x10^{3} L . M^{-1} . cm^{-1}) , all spectra were measured in DMF solvent. Figure 2.0 shows these spectra together.

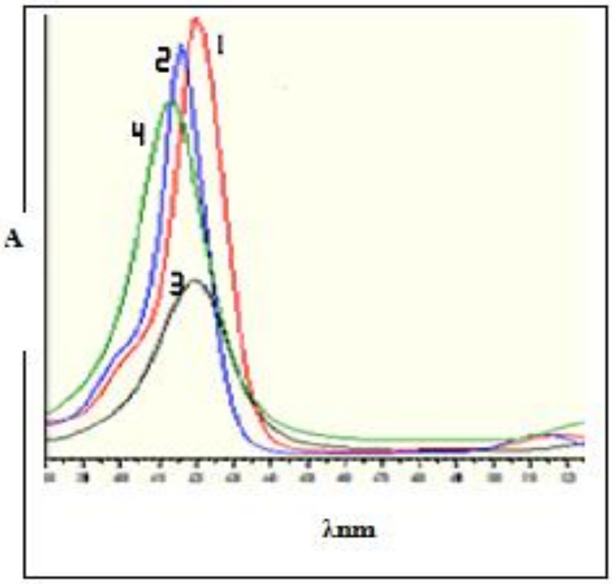

Figure 2.0 Shows the spectra (1)THPP, (2)TBPP, (3)NiTHPP, (4)NiTBPP in DMF solvent at 25 C°.

It has been found when the NiTHPP complex solution heated on the hot plate temperature above 80C°. (100 C°), the complex was found unstable and decomposed completely to the starting materials, this decomposition is time dependent as shown in figure3.0 and 4.0.

Composition of complexes.

By using the mole ratio method to calculate the composition of Ni(ll) ion with THPP and TBPP at 420 nm and 414 nm respectively, the ratio was found for both porphyrins 1:1.

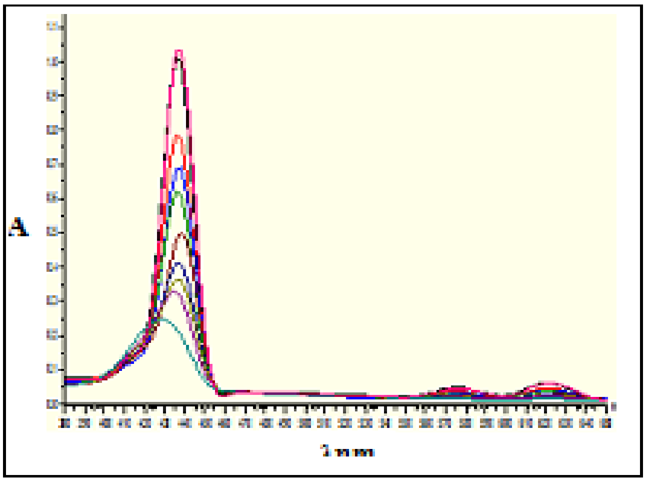

Figure 3.0 Shows the changing in spectrum of NiTHPP complex at λ420nm with increasing heating temperature as a function of time.

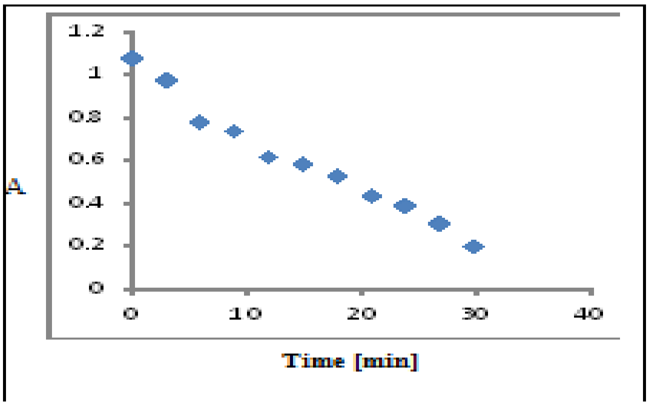

Figure 4.0 Shows the decreasing in absorbance at λ420nm with increasing heating time for NiTHPP complex

Calibration curve for Ni (ll) ion with THPP, TBPP and the interferences.

Table.1: shows the analytical and regression parameters.Figure.5.0 shows the calibration curve for Ni(ll) ion with THPP porphyrin. Under the condition employed, the calibrat- ion graphs were liner up to 2.51/5ml, for THPP and 2.36 µg/10ml, for TBPP and the sandell's index for the 0.001 absorbance was 0.00367 and 0.001 for THPP and TBPP respectively, thus the sensitivity is superior to that obtained previously for porphyrin[25-27,22,23]. Application of THPP and TBPP porphyrions allowed the determination of small amount of Ni(ll) ion in solid materials of phosphate stones. The precision of four replicate measurements at 0.946 µg/5ml and 0.685 µg/10ml Ni concentration level with THPP and TBPP respectively was in the range (0.074-0.065%) RSD and the average recovery percentage % of 102.14 and 102 respectively. The effect of foreign ions was investigated for determination of this ion by using both porphyrins color reagent, it was found in present of the cations such as Zn(ll), Cu(ll), and Cd(ll) make increasing in the amount of nickel recovery due to the interference with both THPP and TBPP around 2%, but in the present Pb(ll) ion cause decreasing in the amount of Ni(ll) recovery by factor of 1.0% due to the same reason, and these results are similar to those reported by other workers see table 2.0.

Analytical application of method for determination of Ni(ll) ions in phosphate stones.

The proposed method was applied to the determination of this Ni(ll) ion in four sam- ples, the results are given in table 3.0 and comparative data obtained by AAS method are also presented . It was found that results not far away from our proposed method.

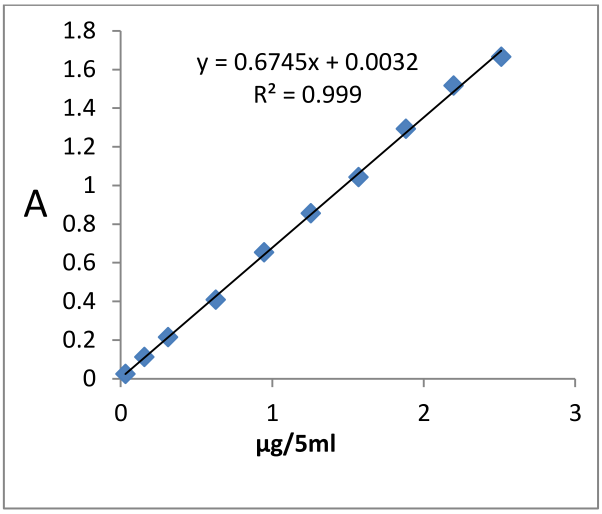

Figure 5. Shows the calibration curve for Ni(ll) ion with THPP ligand.

Table 1. Shows the analytical and regression parameters. Y^*=ax+b, Where x is the concentration of ions.

Parameters	Ni(ll)with THPP	Ni(ll)with TBPP
Beer's law limits	0.01- 2.55 (µg/5ml)	0.01-2.34 (µg/10ml)
Molar absorptivity (L.mol^{-1}.cm^{-1})	2 x10^5	5.66 10^4
Sandell's sensitivity (µg.cm^{-2})	0.00395	0.001
Average recovery(%)	102.14	102
Correlation coefficient	0.999	0.993
Regression equation. y	-----	------
Slope. a	0.6745	0.096
Intercept. b	+0.0032	+0.001
RSD(%)	0.074	0.065

Table 2.0 Spectrophotometric determination of metal ion with porphyrin reagent.

Metal ion	Reagent	Condition	Spectra λ_{max}, nm (x10^5)€ LM^{-1}cm^{-}	Range of determination	Interference	Ref.
Cd(ll)	T_4BPP	pH 10 by HPLC	436	0.01-120µgl^{-1}	-----	[2]

Fe(lll)	TPPS$_4$	pH 5 (NH$_2$OH,100C°, 10min)	394, 3.88	0.01-200 μgl^{-1}	- ---	[23]
Cu(ll)	p-NO$_2$Bz-TPPS	pH 5 (90C° ,7 min)	413 , 4.2	1 30μgl^{-1}	Co(ll),Pd,Fe(lll)	[28]
Cd(ll)	T(1-MPy)P	pH 9.8+Pb(ll)+L-tryptophan	448, 1.7	0.3-23 μgl^{-1}	Zn,Hg(ll)	[29]
Pd(ll)	TPPS$_4$	pH 4 +ascorbic acid(100C°,7 min)	411, 2.2	---	Cu,Hg(ll)	[30-33]
Fe(lll)	THPP	DMF(100 C°,20min)	424, 1.84	0.01-1.0 μg/5ml	Cu(ll),Ni(ll),Pb(ll) Cd(ll)	[34]
Cd(ll)	THPP	DMF(80C°,10 min)	440, 5.28	0.01-0.5 μg/5ml	Mn(ll),Fe(ll), Zn(ll) Ni(ll),Pb(ll), Cu(ll)	[34]
Pb(ll)	THPP	DMF(100C°,10min)	466, 5.0	0.01-0.84 μg/5ml	Mn(ll),Fe(ll),Zn(ll) Ni(ll),Cd(ll), Cu(ll)	[34]
Ni(ll)	THPP	DMF(80C°, 10min)	420 , 2.0	0.01-2.51 μg/5ml	Zn(ll),Cu(ll),Mn(ll), Fe(lll),Pb(ll)andCd(ll)	This work
Ni(ll)	TBPP	DMF(80C° ,10min)	414 , 0.56	0.01-2.6 μg/10ml	Zn(ll),Cu(ll),Mn(ll), Fe(lll),Pb(ll)andCd(ll)	This work

Table 3.0 The effect 0f foreign ion on the recovery of Ni ion inpresent (1)μg/10ml of Ni(ll)with TBPP and (1)μg/5ml with THPP porphyrin.

Interference element	Average Recovery % (n=4)	RSD%	Porphyr in Type
Zn(1)μg/10ml	102.2	0.0121	TBPP
Fe(1)μg/10ml	101	0.0123	=
Cu(1)μg/10ml	103.1	0.019	=
Mn(1)μg/10ml	99.2	0.018	=
Pb(1)μg/10ml	99.5	0.0039	=
Cd(1)μg/10ml	98.2	0.009	=
Zn(1)μg/5ml	101	0.011	THPP
Fe(1)μg/5ml	100.5	0.012	=
Cu(1)μg/5ml	102.5	0.017	=
Mn(1)μg/5ml	98.5	0.016	=
Pb(1)μg/5ml	99.0	0.002	=
Cd(1)μg/5ml	99.5	0.005	=

Table 4.0 Determination of Ni ion in phosphate sample.

Proposed Method (PPM) (n=4)	AAS method (PPM)	RSD (%)	porphyrin
0.006%(60 ± 5)	0.005%(50)	0.0027	TBPP
0.0058%(58± 5)	0.005%(50)	0.003	THPP

Conclusions

In this study, THPP and TBPP porphyrins were using for determination of Ni(ll) ion. Proposed method for the determination of this ion is simple, accurate cheap. The statistical analysis shows that the data of the molar absorbance and the range of determ- ination from proposed method for this ion is in good agreement with those of the reported methods. The color reactions doesn't require long time for heating or buffer. The color complexes are stable for long time under 80C° which is sufficient time for the analyst to perform the analysis.

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تقدير طيفي لكميات قليلة من ايون النيكل بواسطة استخدام (٤ – هيدروكسي فنيل) بورفين ورابع (٤– بروموفنيل) بورفين .

جهاد عبد طعيس ستار جبير نسرين على الله جسام

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الخلاصة

في هذا العمل تم دراسة التفاعل بين (4 – هيدروكسي فنيل) بورفين ورابع (4– بروموفنيل) بورفين مع ايون النيكل وكذلك دراسة ثرموديناميكية معقد NiTHPP مع زيادة درجة الحرارة مع الزمن . البورفينات المستخدمة وجدت حساسة وانتخابية لتقدير مباشر لايون النيكل عند 0.031 مايكرو غرام / 5 مل لكاشف THPP ، 0.236 مايكرو غرام / 10 مل لكاشف TBPP ، كانت اعلى امتصاص لمعقد NiTHPP عند 420 nm($2x10^{5}$ (€=L.mol ⁻ .cm ⁻) و 414nm لمعقد NiTBPP ($€ = 5.7x10^{4}$ L . mol⁻ . cm^{-1}) في مذيب DMF . المعقدات تتكون خلال 10 دقايق عند التسخين على سطح ساخن درجة الحرارة 80 C^{0} . رابع محاليل قياسية تم تقديرها تحتوي على 0.946 مايكروغرام / 5 مل ايون النيكل T THPP و 0.685 مايكروغرام / 10 مل ايون النيكل TBPPT اعطت R.S.D % 0.074 و 0.065% على التوالي . قانون بير كان مطاوع في مدى (2.55 – 0.01 مايكروغرام / 5 مل) و 2.34 – 0.01 مايكروغرام / 10مل . ساندل اندكس كان 0.00367 و 0.001 لامتصاص 0.001 على التوالي . النسبة الموالية للمعقدات كانت 1 : 1 ، المتداخلات تم دراستها واستخدمت هذه الكواشف لتقدير النيكل في الصخور الفوسفاتية واعطت نتائج مقنعة .