



Spectrophotometric Study of Fe(III), Cd(II) and Pb(II) Complexes with 5,10,15,20-Tetra(p-Hydroxyphenyl)Porphyrin

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ABSTRACT

In this paper, the reaction of meso-tetra (4-hydroxyphenyl)porphyrin with ferric, Cadmium and Lead ions have been studied in DMF solvent. The porphyrin was found to be a highly sensitive and highly selective reagent for direct Spectrophotometric determination of these ions at μg level. The soret band of the complexes was found at 424 nm ($\epsilon = 1.84 \times 10^5 \text{ L.M}^{-1}\text{.CM}^{-1}$), 440 nm ($\epsilon = 5.2 \times 10^5 \text{ L.M}^{-1}\text{.CM}^{-1}$) and 466 nm ($\epsilon = 5 \times 10^5 \text{ L.M}^{-1}\text{.CM}^{-1}$), which is well separated from that of the reagent at 422 nm ($\epsilon = 3.3 \times 10^5 \text{ L.M}^{-1}\text{.CM}^{-1}$), in the DMF solvent respectively. The complexes formation are slow at room temperature, however, it can be accelerated by heating and completed within 10 min at 100°C . Four determination of standard solutions containing 30 $\mu\text{g}/5\text{ml}$, 20 $\mu\text{g}/5\text{ml}$ and 30 $\mu\text{g}/5\text{ml}$ for Fe(III), Cd(II) and Pd(II), gave a relative standard deviation of 0.495%, 1.29% and 2.039%. Beer's law is obeyed in the range of 0.01- 1.0, 0.01-0.5 and 0.01-0.84 $\mu\text{g}/5\text{ml}$, sandell's index were 0.00395, 0.000212, 0.000416 for the absorbance of 0.001 respectively. The molar ratio of complexes are 1:1, the interferences of cations and anions were studied as well. This method was used to determine these ions in clay samples were taken from west of Iraq region and gave a satisfactory results. **Keywords:** *Mammography, Quality Assurance, Quality Control, Mean Glandular Dose.*

Keywords: *Porphyrin, Ferric, Cadmium and Lead, Spectrophotometry.*

1. INTRODUCTION

The porphyrin ligands have the general structure show in figure 1, they are derivatives of porphyrine (the compound in which all the R groups are hydrogen atoms), which has a cyclic structure of four pyrrole molecules linked together through the four methine bridge (=CH-) [1]. The porphyrins are a class of naturally occurring macro cyclic compounds, which play a very important role in the metabolism of living organisms. These have been extensively studied due to their biological importance as well as analytical applications [2]. The porphyrin nucleus is a tetradenate ligand in which the space available for a coordinated metal has a maximum diameter of approximately 3.7 Å [3]. Many workers have been used the porphyrins as the highly sensitive chromogenic reagents for spectrophotometric determination of several metal ions based on the use of the soret band at 400 -500 nm [4-9]. Almost all metals form complexes 1:1, although Na, K, Li complexes are 2:1 in which the metal atoms are incorporated slightly below and above the porphyrin monocycle plane. When divalent metal ions (e.g. Co(II), Ni(II), Cu(II)) are chelated, the resulting tetra coordinate chelate has no residual charge. Some metalloporphyrins Fe(II), Co(II), Mn(II) are able to form distorted octahedral with two extra Ligand molecule [2]. Workers were used tetra (4-bromophenyl)porphyrin (TBPP) as a chelating reagent with Lead, Cadmium and mercury ions in 0.05 mol.L⁻¹ of PH10.0 pyrrolidine-phosphoric acid buffer solution containing 10% THF as mobile phase. They found the linearity ranges are 0.01-120

$\mu\text{g.L}^{-1}$ for each metal ion and the detection limits of lead, cadmium and mercury are 1.0, 0.5 and 1.0 $\mu\text{g.L}^{-1}$ respectively [10]. Others have been used tetra (P-sulfophenyl) porphyrin (TPPS4) as a reagent for

determination of uranium, iron(III), iron(II) and SO_4^{2-} ions in aqueous solution, they found Beer's Law is obeyed in the range of 0.01-120 $\mu\text{g.L}^{-1}$, 0.01-2.0 $\mu\text{g}/10\text{ml}$, 0.01-15.6 $\text{mg}/10\text{ml}$, and 0.01-1.85 $\text{mg}/10\text{ml}$ respectively [11-12]. In this work, the spectrophotometric determination of ferric, cadmium and lead ions was studied with 5,10,15,20- tetra(P-hydroxyphenyl)porphyrin in DMF solvent and the solids complexes for these metals were isolated too.

2. EXPERIMENTAL SECTION

2.1 Apparatus

Spectrophotometer model 6800 Jenway with 1cm silica cells was used throughout this research work hp type computer for spectra recording.

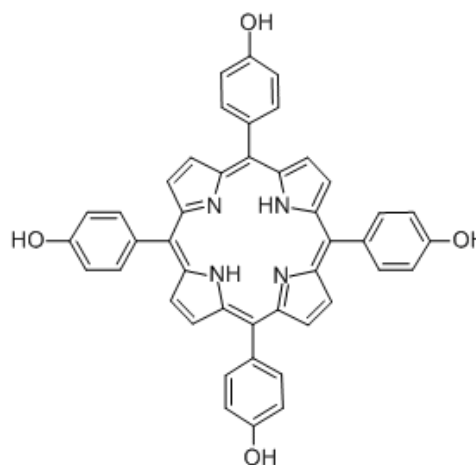


Figure 1. Shows the Structure of Porphyrin
2.2 Materials and Reagents



Most of materials used were of analytical grade and were obtained from fluka.

2.2.1 Tetra (p-hydroxyphenyl) porphyrin.

THPP was prepared by refluxing of 2.45 ml pyrrole with 4.3 gm p-hydroxybenzaldehyde 1:1 mole ratio in propanoic acid media for 1.5 hours[3]. After cooling to the room temperature the solution was filtered and the product washed with a minimum quantity of ethanol and distilled water, a blue crystals of THPP were obtained.

2.2.2 Preparation of solid FeTHPPCl Complex

The complex was prepared by refluxing (0.3gm) of H_2THPP in (30ml) N,N-dimethyl formamide with (0.088gm) of $FeCl_2 \cdot 4H_2O$ for (20)minutes [13,15]. The completeness of the reaction can be checked by measuring the UV-Vis spectrum of the reaction mixture; the four band spectrum of H_2THPP should be absent, being replaced by two band spectrum of the product. When the reaction is complete cooled to room temperature slowly and (300ml) of acidic water was added (1ml 6N HCl), a brown precipitate was collected and dried in oven at (50-70)C for (30)minutes, the product weighted of (0.312) gm(91%).

2.2.3 Preparation of solid PbTHPP Complex

The complex was prepared by refluxing of (0.1) gm THPP with (0.05)gm of $Pb(CH_3COO)_2$ in (30)ml DMF solvent, after (10)minutes of heating (100) C, the color change to deep green, the reaction cool to room temperature, the solid separated by using rotary evaporator (50) C, the unreacted THPP can be removed by dissolving the product in chloroform solvent, the complex was found less solubility than the porphyrin and collected by filtration and washed by acidic water to remove the unreacted salt of lead, dried in oven (50) C for (30)minutes, the product was found (0.122)gm (93.7%).

2.2.4 Preparation of solid CdTHPP Complex

(0.1)gm of THPP was refluxed with (0.035)gm of $Cd(CH_3COO)_2$ in (30)ml DMF for (10)minutes at (80) C, the reaction was stopped when the color change to blue-green solution, after cooling the solid separated by using rotary evaporator (50) C, the produced redissolve in chloroform solvent to remove unreacted THPP which is more soluble than CdTHPP, the collected product by filtration was washed by acidic water, and dried at (50) C in oven (30) minutes, the product was found (0.05)gm (90.5%).

2.3 Preparation of Standard Solutions

2.3.1 Standard Solution of (1.473x10⁻⁶ M)THPP

The solution was prepared by dissolving (0.05)gm of THPP

in(50)ml DMF.

2.3.2 Standard solution of FeTHPPCl, PbTHPP and CdTHPP complexes

These complexes solutions were prepared by dissolving (0.1)gm from each one in (25)ml of DMF to give concentrations of (5.2x10⁻⁴M), (4.53x10⁻⁴M) and (5.05x10⁻⁴M) respectively.

2.3.3 Standard solution of Fe⁺²,Pb⁺² and Cd⁺² ions

They were prepared by dissolving (0.05)gm of $FeCl_2 \cdot 4H_2O$, (0.01)gm of $Pd(CH_3COO)_2$ and (0.01)gm $Cd(CH_3COO)_2$ in(25)ml DMF, to give concentrations of (10⁻²M), (1.23x10⁻³M) and (1.74x10⁻³M) respectively.

2.4 Composition of Complexes

Determination of composition of the forming complexes were conducted using mole ratio method for Fe(III) ion. Metal Fe(II) was added to (1x10⁻⁵M) porphyrin solution in the concentration range (1x10⁻⁶-4x10⁻⁵M). After (20)minutes of reaction on the hot plate, the absorbance at wave length of (424nm) was measured, but the method were used for determination of Pb(II) and Cd(II) is a continuous variable method, seven volumetric flasks containing (0-10)ml of (10⁻⁵M) Pd(II) or Cd(II) ions and (10-0)ml of (10⁻⁵M)THPP were mixed together, to give the total volume of (10)ml, than heated for (10)minutes to complete the reaction, the absorbance at wave length of (440nm) and (466nm) were measured against blank reagent respectively.

2.5 Construction of calibration curve for ions

Ten of (5)ml volumetric flasks containing a liguos of standard FeTHPPCl, PbTHPP and CdTHPP ions solutions in the range of (0.145-3.06)µg/5ml Fe(III), (4.71-848) ng/5ml Pb(II) and (8.41-509) ng/5ml Cd(II), the volume of solutions was completed to the mark by using DMF solvent, and the absorbance was measured at λ_{max} for each ion against blank reagent.

2.6 Determination of Fe(III), Cd(II) and Pb(II) ions in Phosphate Crude Stones

(2) grams of phosphate crude stones was dissolved in (3)ml of concentrated nitric acid, than 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 (5x10⁻⁶M), four samples were used to determine the elements. All samples were heated on the

hot plate for (20)min, after cooling these samples to the room temperature, the absorbance were measured at the soret band of each elements in this study against blank reagent. The calculations were made and recorded.

3. RESULTS & DISCUSSION

3.1 Spectrophotometric study of porphyrin and metals porphyrin

Solution of ($5.1 \times 10^{-6} \text{M}$) THPP in DMF solvent is purple and exhibit six absorption maxima one is soret band at 422nm ($\epsilon = 3.33 \times 10^5 \text{ L.M}^{-1} \text{ CM}^{-1}$), 400nm as shoulder ($\epsilon = 6.26 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$), 520nm ($\epsilon = 1.47 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$), 556 ($\epsilon = 1.312 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$), 594 ($\epsilon = 5.2 \times 10^3 \text{ L.M}^{-1} \text{ CM}^{-1}$) and 652 ($\epsilon = 7.07 \times 10^3 \text{ L.M}^{-1} \text{ CM}^{-1}$). FeTHPPCl complex spectra shows soret band at 424 nm ($\epsilon = 1.84 \times 10^5 \text{ L.M}^{-1} \text{ CM}^{-1}$) and at 646nm ($\epsilon = 1.58 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$) in DMF solvent. Where PbTHPP complex spectra was at 466nm λ_{max} ($\epsilon = 5 \times 10^5 \text{ L.M}^{-1} \text{ CM}^{-1}$), at 616nm ($\epsilon = 2 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$) and 666nm ($\epsilon = 4 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$), but CdTHPP complex spectrum was at 440nm λ_{max} with ($\epsilon = 5.28 \times 10^5 \text{ L.M}^{-1} \text{ CM}^{-1}$), 576nm ($\epsilon = 2.9 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$) and 620nm ($\epsilon = 3.78 \times 10^4 \text{ L.M}^{-1} \text{ CM}^{-1}$), all spectra were measured in DMF solvent. Figure 2.0 shows these spectra together.

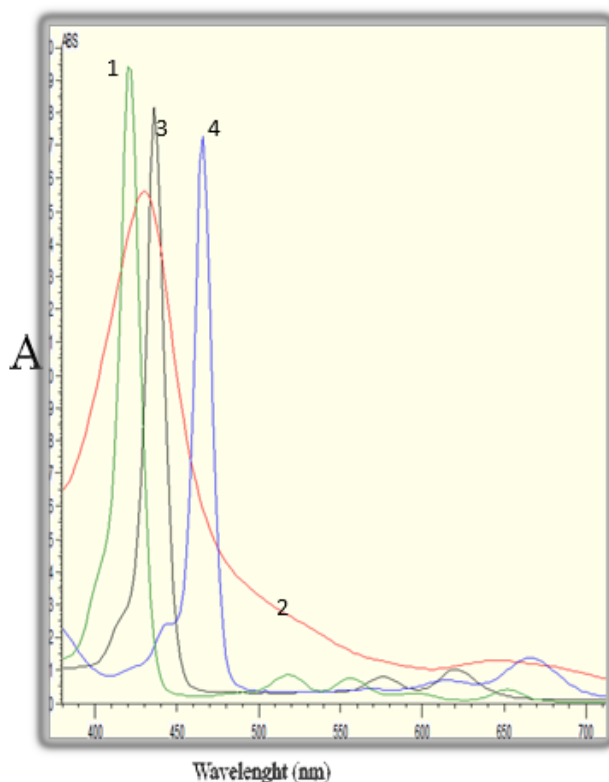


Figure 2. shows the spectra (1)THPP, (2) FeTHPPCl, (3) CdTHPP, (4) PbTHPP, in DMF solvent at 25 C.

Composition of Complexes

By using the mole ratio method to calculate the composition of Fe(III) ion at λ_{max} 424nm, and the continuous variation method for Pb(II) and Cd(II) ions at λ 466nm and λ 440nm to the THPP respectively, the ratio was found 1:1 for all complexes, see the figures 3 and 4.

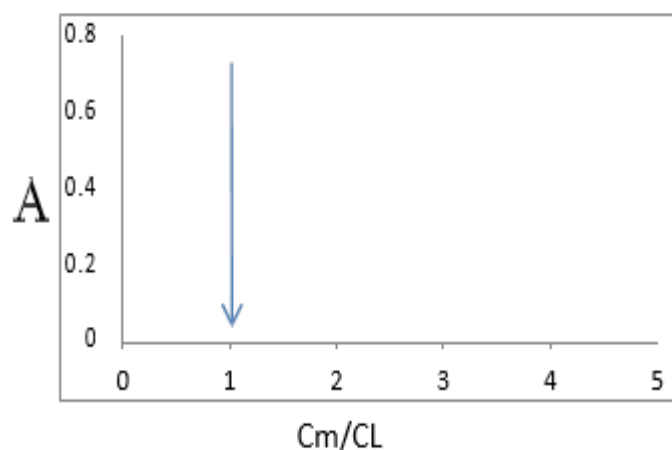


Figure 3: The mole ratio method for Fe(II)ion with THPP ligand

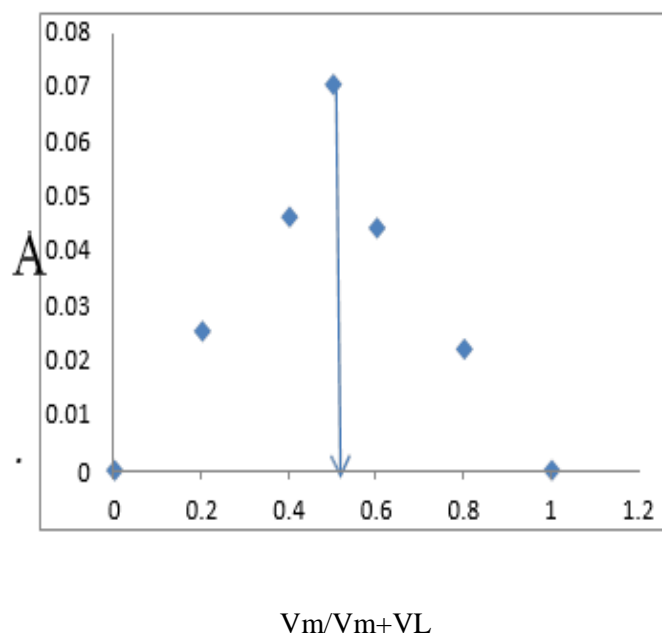


Figure 4: The continuous variation method for Cd(II)ion with THPP porphyrin in DMF

3.3 Calibration curve for Fe(III), Pb(II) and Cd(II) ions and the interferences

Table.1: shows the analytical and regression

parameters. Figure 5 shows the calibration curve for Cd ion with THPP ligand. Under the condition employed, the calibration graphs were linear up to (1.0, 0.5 and 0.84 $\mu\text{g}/5\text{ml}$) and the sandell's sensitivity for the (0.001) absorbance was (0.00395, 0.000212 and 0.000416) for Fe(III), Pb(II) and Cd(II) respectively, thus the sensitivity is superior to that obtained previously for porphyrin [16-18,11,12]. Application of THPP allowed the determination of small amount of Fe, Pb and Cd in solid materials of phosphate stones. The precision of four replicate measurements at 0.874, 0.282 and 0.113 $\mu\text{g}/5\text{ml}$ for Fe, Pb and Cd concentration level was in the range (0.442-2.039%) RSD and the average recovery percentage of 98.50, 99.82 and 99.02 respectively. The effect of foreign ions was investigated for determination of these ions by using THPP color reagent, see table 2 and 3.

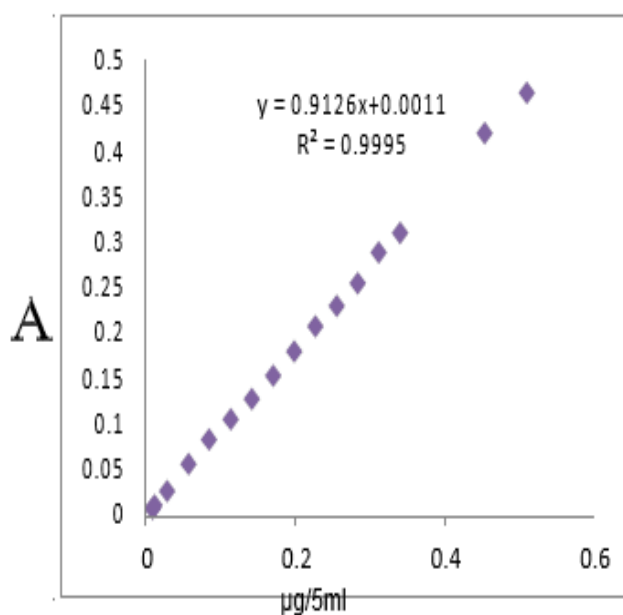


Figure 5. Shows the calibration curve for Cd(II) ion with THPP ligand.

Table 1. Shows the Analytical and Regression Parameters

Parameters	Fe(III) ion	Cd(II) ion	Pb(II) ion
Beer's law limits($\mu\text{g}/5\text{ml}$)	0.01- 1	0.01-0.5	0.01-0.84
Molar absorptivity($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	1.84×10^5	5.2×10^5	5×10^5
Sandell's sensitivity	0.00395	0.000212	0.000416
Average recovery(%)	98.5	99.823	99.02
Correlation coefficient	0.9989	0.9995	0.999
Regression equation. y	-----	-----	-----
Slope. a	0.6462	0.9126	0.4753
Intercept. b	+0.01	+0.0001	+0.0011
RSD(%)	0.442	2.039	1.29

$$Y^* = ax + b, \text{ Where } x \text{ is the concentration of ions}$$

3.4 Analytical application of method for determination of Fe(III), Cd(II) and Pb(II) ions in phosphate stones

The proposed method was applied to the determination of these ions in four samples. The results are given in table 4, and comparative data obtained by AAS method are also presented. It was found that most of results are not far away from that recorded by our method when the interference of foreign ions has been taken in our calculations. The recovery percentage was found affected in the present of heavy metals ions such as Pb(II), Cd(II) and caused increasing in the amount of Fe(III), the average recovery % is 129.3 and cations such as Cu(II), Zn(II), Mn(II), Ni(II) and Fe(III) caused decreasing in the amount of Cd(II) and Pb(II) recovery, due to the interference of those ions, and the average recovery % is 46.8, 6.5 for Pb(II) and Cd(II) respectively. If we supposed that the results from AAS is the right one, the average recovery % to our result is 103, 65 and 68 for Fe(III), Cd(II) and Pb(II) ions respectively.

Table.2 shows the effect of foreign ions on determination of Fe(III), Pb(II) and Cd(II) ions



Compound	λ 424nm	$\mu\text{g}/5\text{ml}$ interferences	Average Recovery%	RSD%	Fe^{+3} $\mu\text{g}/5\text{ml}$
Fe^{+3} + THPP	1.0499	----	100	----	1.5976
Fe^{+3} + THPP + Zn^{+2}	1.08915	1.5	103.74	0.53	1.6574
Fe^{+3} + THPP + Ni^{+2}	1.52645	1.5	142.38	0.77	2.32275
Fe^{+3} + THPP + Cu^{+2}	1.6148	1.5	153.66	1.91	2.455
Fe^{+3} + THPP + Mn^{+2}	1.0652	1.5	101.43	0.091	1.6205
Fe^{+3} + THPP + Cd^{+2}	1.2659	1.5	121.27	0.219	1.9375
Fe^{+3} + THPP + Pb^{+2}	1.6125	1.5	153.55	0.375	2.4532
Compound	λ 466nm	$\mu\text{g}/5\text{ml}$ interferences	Average Recovery%	RSD%	Pb^{+2} $\mu\text{g}/5\text{ml}$
Pb^{+2} + THPP	0.2657	-----	100	----	0.5526
Pb^{+2} + THPP + Zn^{+2}	0.0194	1.5	7.31	0.032	0.0404
Pb^{+2} + THPP + Ni^{+2}	0.0265	1.5	9.98	0.653	0.05515
Pb^{+2} + THPP + Cu^{+2}	0.01652	1.5	6.21	0.99	0.03435
Pb^{+2} + THPP + Mn^{+2}	0.00935	1.5	3.5	2.98	0.0194
Pb^{+2} + THPP + Cd^{+2}	0.02357	1.5	8.86	1.308	0.0489
Pb^{+2} + THPP + Fe^{+2}	0.00925	1.5	3.5	0.46	0.0193
Compound	λ 440nm	$\mu\text{g}/5\text{ml}$ interferences	Average Recovery%	RSD%	Cd^{+2} $\mu\text{g}/5\text{ml}$
Cd^{+2} + THPP +	0.1161	-----	100	----	0.1231
Cd^{+2} + THPP + Zn^{+2}	0.04415	1.5	37.99	3.24	0.0467
Cd^{+2} + THPP + Ni^{+2}	0.05175	1.5	43.62	0.767	0.0537
Cd^{+2} + THPP + Cu^{+2}	0.0471	1.5	39.39	3.62	0.0485
Cd^{+2} + THPP + Mn^{+2}	0.0525	1.5	45.26	0.098	0.05572
Cd^{+2} + THPP + Pb^{+2}	0.09002	1.5	77.35	0.223	0.09522
Cd^{+2} + THPP + Fe^{+2}	0.04372	1.5	37.6	0.66	0.046325

Table 3. Spectrophotometric determination of metal ion with porphyrin reagent



Metal ion	Reagent	Condition	Absorption Spectra λ_{max} , nm $\epsilon(\times 10^5)$ $LM^{-1}cm^{-1}$	Range of determination	Interference	Ref.
Cd(II)	T4BPP	pH 10 by HPLC	436	0.01-120 $\mu g l^{-1}$	-----	[3]
Fe(III)	TPPS4	pH 5 (NH ₄ OH, 100°C, 10min)	394, 3.88	0.01-200 $\mu g l^{-1}$	----	[12]
Cu(II)	p-NO ₂ Bz-TPPS	pH 5 (90°C, 7 min)	413, 4.2	130 $\mu g l^{-1}$	Co(II), Pd, Fe(III)	[19]
Cd(II)	T(1-MPy)P	pH 9.8+Pb(II)+L-tryptophan	448, 1.7	0.3-23 $\mu g l^{-1}$	Zn, Hg(II)	[20]
Pd(II)	TPPS4	pH 4 +ascorbic acid(100°C, 7min)	411, 2.2	---	Cu, Hg(II)	[21-24]
Fe(III)	THPP	DMF(100°C, 20min)	424, 1.84	0.01-1.0 $\mu g/5ml$	Cu(II), Ni(II), Pb(II) Cd(II)	This work
Cd(II)	THPP	DMF(80°C, 10min)	440.5.28	0.01-0.5 $\mu g/5ml$	Mn(II), Fe(II), Zn(II) Ni(II), Pb(II), Cu(II)	This work
Pb(II)	THPP	DMF(100°C, 10min)	466, 5.0	0.01-0.84 $\mu g/5ml$	Mn(II), Fe(II), Zn(II) Ni(II), Cd(II), Cu(II)	This work

T4BPP=Tetra-(4-bromophenyl)-porphyrin, TPPS4=meso-Tetrakis(-sulfophenyl)porphyrin. p-NO₂BZ-

TPPS=N-4-Nitrobenzyl-tetrakis(4-sulfonatophenyl)porphyrin.

T(1-MPy)P=meso-Tetrakis(1-methylpyridinium-4-yl)porphyrin.

Table 4. Determination of Fe(III), Pb(II) and Cd(II) ions in phosphate crude stones

Elements	Proposed Method(n=4)	(ppm)	RSD(%)	AAS method	(ppm)
Fe ⁺³	0.027% ± 0.0003	(270)	0.76	0.0262%	(262)
Cd ⁺²	0.003% ± 0.00016	(30)	0.09	0.0047%	(47)
Pb ⁺²	0.00041% ± 0.000004	(4.1)	0.49	0.0006%	(6.0)

4. CONCLUSIONS

In this study THPP used for determination of Fe(III), Cd(II) and Pb(II) ions. The proposed spectrophotometric method for the determination of these



ions is simple, accurate and cheap if the interferences should be previously removed by knowing analytical methods. The statistical analysis show that the data of the molar absorbance and the range of determination from proposed method for these ions are in good agreement with those of the reported method. The color reaction doesn't require long time for heating or buffer. The color complexes are stable up to many hours, which is sufficient time for the analyst to perform the analysis.

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