MODIFIED METHOD FOR THE DETERMINATION OF MERCURY II BY ADOPTING PORPHYRIN COMPLEX

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ABSTRACT

A new method was adopted for the determination of mercury ions in water samples after complexation between mercury and TPP (meso-tetraphenylporphin). Water samples were investigated in the presence of mercury, 3 samples along Shatt Al-Arab River close to discharging point of waste from Basrah paper factory as follows; 1) 5 km north to discharging point, 2) discharging point it self and 3) 5 km from the discharging point towards the south as well as station 4) Karmatt Ali as a control. Mercury was determined spectrophotometricaly after the formation of the complex Hg-TPP at wave length of 440 nm. It was found that mercury concentration was 0.0492 $mg.l^{-1}$ in the discharging point from basrah paper factory to shatt Al-Arab River compared to undetectable in all other sites. The method is reliable with sensitivity of 0.0134 $gm.cm.l^{-1}$, accuracy of 9×10^{-6}, standard deviation of 0.00317 and detection limit of 0.75×10^{-7}.

Key Words: Mercury, HgTPP Complex, Basrah paper factory. Shatt Al- Arab, Spectrophotometry.

INTRODUCTION

Pollutants which could threaten water Environment are Petroleum hydrocarbons, trace metals, pesticides, micro-organisms, heat ….etc [1] . Among trace metals, Cd,Pb and Hg are the most toxic metal which affect the environmental system. Sources of these metals in aquatic environment are originated from natural processes and manmade activities, mostly due to rapidly developed industrialization and urbanization [2] .

Mercury is a persistent and bioacumulative metal in the whole environment [3].It exists both in organic and inorganic forms of various levels and ubiquitous.

The concentration of mercury in water samples from rivers is caused by industries represented by chlorine production and sodium hydroxide in which mercury electrodes are used as well as paper and pulp mill factories in which their waste discharge directly with out any treatment towards the rivers [4].Muzumdar and Shome [5] have determined mercury spectrophotometricaly by using thiosalicylamide as reagent.Sharma and Singh [6] determined mercury spectrophotometricaly by complexation with [1-(2-pyridiylazo)2-naphtol]PAN.Water samples were analyzed spectrophotometrically for mercury following the procedure given by Mudukavi [7]. The procedure depends upon the formation of ternary system between mercury,1,10-phenonthroline and eosin at pH 4.5 in the presence of EDTA and gelatin. In this study we report a modified method for mercury determination using the ligand meso-tetra phenyl porphyrin (TPP) as a complexing agent.

SAMPLING AND ANALYSIS

Four stations were chosen to collect water samples for the determination of mercury, (1) 5 km north to Basrah paper factory (close to Al-Deer city), (2)Discharging point towards Shatt Al-Arab River from Chlorine production unit in Basrah paper factory, (3) 5 km south to Basrah paper factory and (4) Karmatt Ali canal as a control station . This is shown in Fig. 1. Dark glass bottles (5)L were used for the collection of subsurface (30 cm) water sample during Nov. 2007. In the laboratory, 30-40 ml of CCl_4 were added to each water samples and followed by severe shaking for 30 minutes for the extraction of petroleum hydrocarbons, where the organic content was separated for petroleum hydrocarbon's while the aqueous layer was used for the determination of mercury, after drying it on hot plate (at 105°C).The

remaining salts were allowed to react with porphyrin according to the following procedure.

Freshly distilled pyrrole (2.8 ml,0.8 mole) and (4 ml,0.8 mole) of reagent grade benzaldehyde were added to (150 ml) of refluxing reagent grade propionic acid. After refluxing for (30 min), the solution was cooled to room-temperature and filtered, then the filter cake was washed thoroughly with methanol and later with hot water , The resulting purple crystals were dried in air and finally dried in vacuom to remove the absorbed acid and to yield (1.25 gm,20% yield) of TPP [8] according to the following equation:

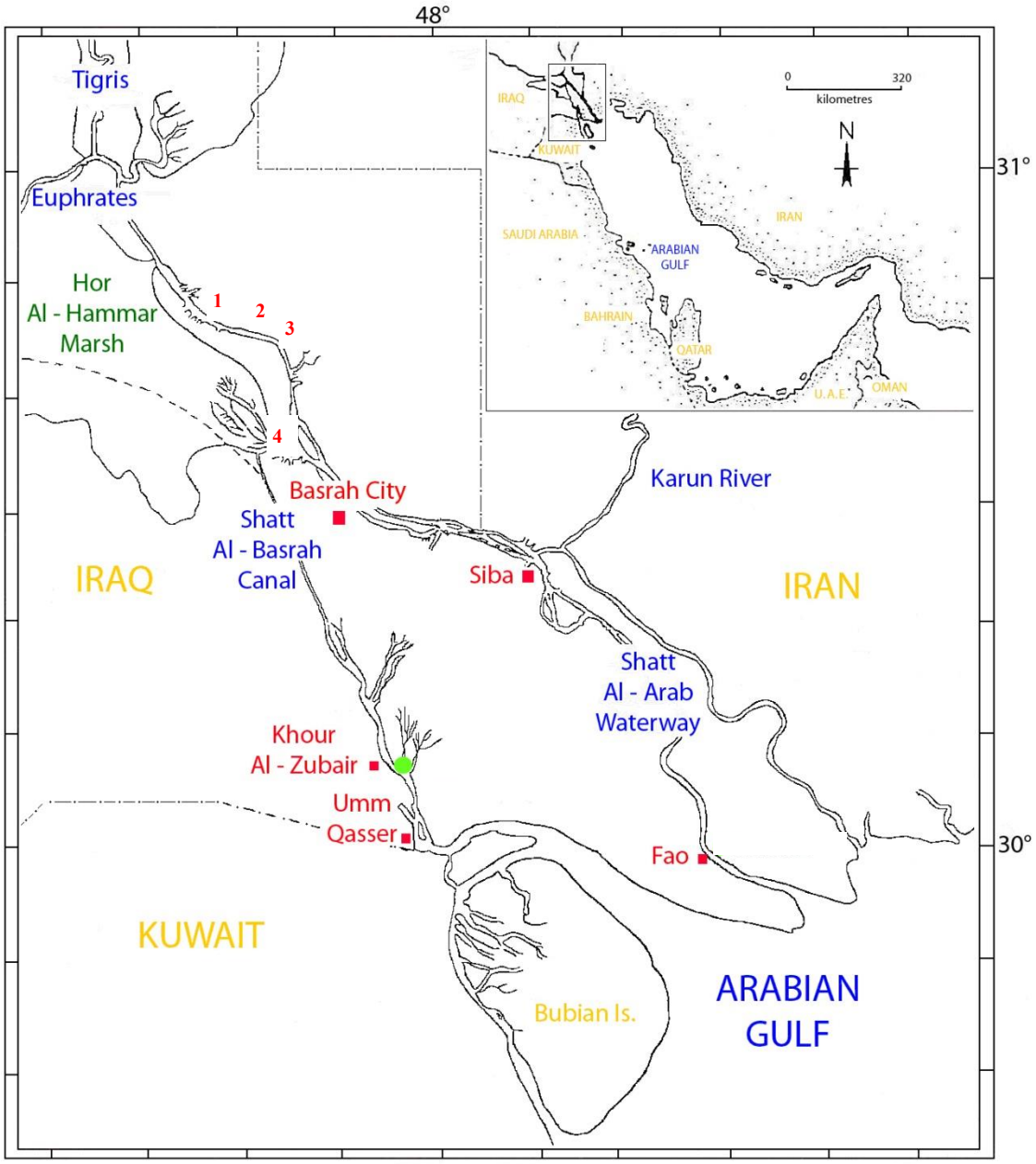

Fig. 1. Location map of Shatt Al-Arab River showing the sampling stations (1-3) and the control station (4)

$$4\,C_4H_4N\ (\text{Pyrrole}) + C_6H_5CHO\ (\text{Benzaldehyde}) \xrightarrow[\text{reflux}]{CH_3CH_2COOH} C_{44}H_{30}N_4\ (\text{TPP}) \quad \ldots\ldots\ldots(1)$$

TPP = meso-tetraphenylporphin.The result of C H N analysis is shown in Table (1).

Table (1). C H N Analysis of TPP

Sample		C%	H%	N%
TPP	Theoretical	85.26	4.92	9.12
$C_{44}H_{30}N_4$	Found	85.97	4.99	8.91

The complex was prepared according to the method of Adler et al [9]. Reagent grade N.N`-dimethylformamide (100 ml) is brought to reflux in a 250 ml flask on a stirring hot plate. TPP (1)gm is added,1 min is allowed for the formation of complete solution, then a stoichiometric amount of mercuric chloride $HgCl_2$ (0.3) gm is added too. The reaction is allowed to proceed for (60) min. For Hg^{2+} complex the followed procedure was used. The reaction vessel is removed from the hot plate and cooled in an ice-water bath for (15) min.100 ml of chilled distilled water is added and the resulting product, partially crystalline precipitate, is filtered by a Buckner funnel until the filtrate will be clear. The filtered material is washed with water and then dried in air. The yield was (0.9) gm of the complex (98%), according to the following equation:

$$C_{44}H_{30}N_4\ (\text{TPP}) + Hg^{2+} \xrightarrow[\text{reflux}]{\text{DMF}} C_{44}H_{28}N_4Hg\ (\text{HgTPP}) \quad \ldots\ldots\ldots(2)$$

After that, a stock solution from the synthesized complexes, resulting from the reaction 1 was prepared. Then the absorbance of this solution was scanned at (440) nm and compared with the calibration curve of Hg^{2+} ions. All spectral measurements were taken by UV/VIS spectrophotometer and supplied by Philips Company model PU 8670 Vis/NIR spectrophotometer by using benzene as a solvent for porphyrins. The visible spectra for TPP and HgTPP were scanned along the wavelength, 400-700 nm. The optimum conditions for best absorbance measurements with lower error was done at wavelength of 440 nm as shown in fig.(2). Then sample solutions of HgTPP were prepared and the absorbance for each solution was measured at 440 nm, then the Calibration Curve for Hg^{+2} ion was plotted as shown in fig.(3).

RESULTS AND DISCUSSION

To insure a complete reaction between pyrrole and benzaldehyde, the component have been distilled before the beginning of reaction to produce TPP with maximum yield. Then the reaction was proceeded between TPP and product from dried samples. Fig. (2) show the visible spectra of TPP and HgTPP in benzene as solvent because of good solvation of the complex in this solvent.

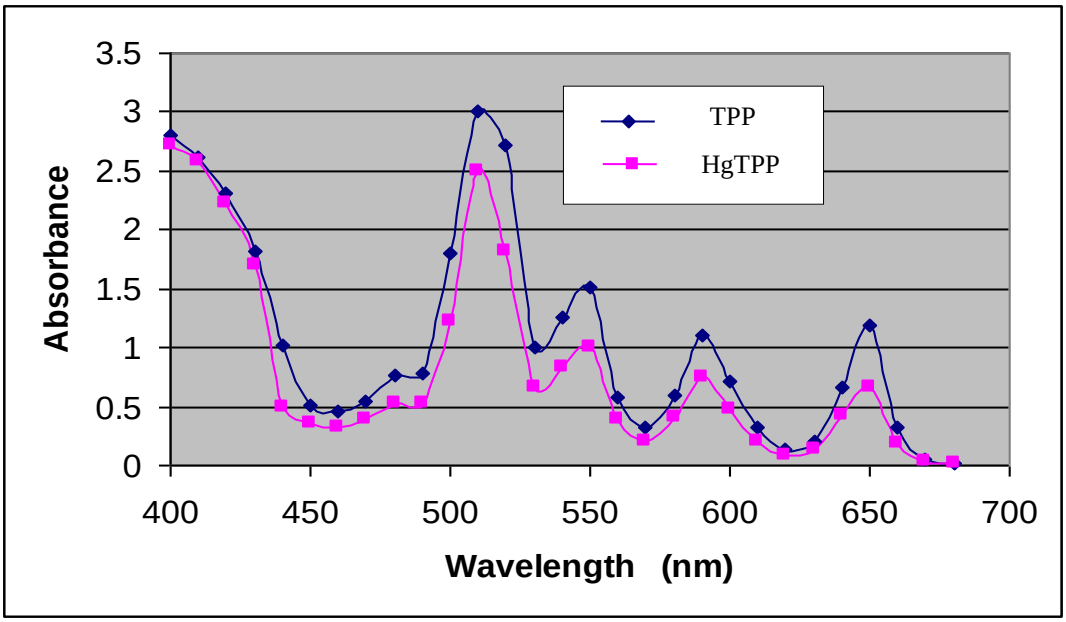

Fig.(2) Visible Spectra of TPP and HgTPP in benzene.

The Calibration Curve of the HgTPP complex is shown in fig.3 which helps in estimation of Hg^{2+} ion in the studied water samples.

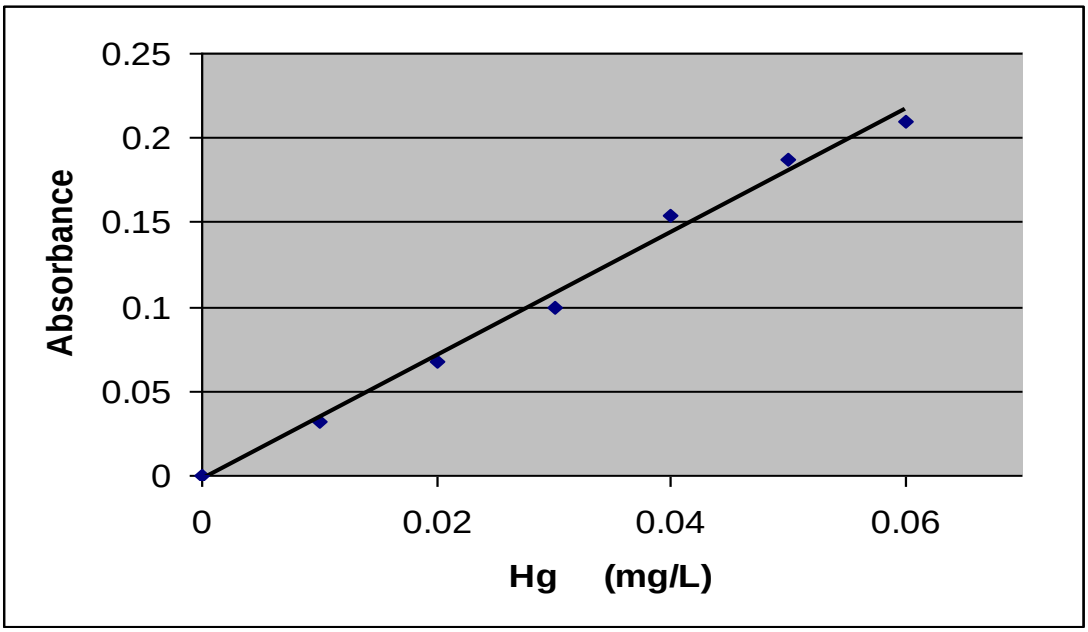

Fig.(3) Calibration Curve for mercury ion ($mg.L^{-1}$)complexed to TTP.

The determined concentrations of mercury are presented in Table (2).

Table 2. The concentrations of Hg^{2+} (mg/l) in water from selected stations.

Location	Water dried (L)	Time of reaction (hr)	Color of complex after reaction	Absorbance at 440 nm	Found conc. From Calibration curve
5 km north of Basrah paper factory	20	1	No change	ND	0.0000
Discharging Chlorine production unit in factory	20	1	Color change	0.185	0.0492
5 km south of Basrah paper factory	20	1	No change	ND	0.0000
Karmatt Ali bridge	20	1	No change	ND	0.0000

ND= not detected.

As could be seen from Table 2, the only detected concentration for mercury in Shatt Al-Arab River is from water samples at the discharging point of the pulp and mill factory in Basrah, with a value of 0.0492 mg/l. This could be rationalized as this point receives industrial effluents expected to be contaminated with mercury [10] especially when it discharged directly to water ways with out any treatments [11]. This value is comparable to values recorded spectrofluorometrically earlier in Tigris and Shatt Al-Arab Rivers which were 0.05 and 0.023 mg/l respectively [12]. This value is little bit high, but it is acceptable and still lower than values reported in some sites at risk all over the world. Mercury values recorded in Mersey estuary in the UK which was 5.185 mg/l [13]. Moreover, they are lower than or within the allowable concentration of mercury in fresh water of 0.05 mg/l [14]. Mercury values reported in water samples from sites at a distance from the discharging point of Basrah paper factory were undetectable. These stations are much affected by dilution with water of Shatt Al-Arab River and the reduced concentration [12].

Table 3. shows some analytical parameters for the HgTPP complex which supported the correctness of this methodology for the determination of mercury ion in this study.

Table (3) Some Analytical Parameters for HgTPP Complex.

Complex	Sensitivity gm.cm.L^{-1}	Accuracy	Stander Deviation S.D	Detection Limit D.L
HgTPP	0.0134	0.9×10^{-6}	0.00317	0.75×10^{-7}

Conclusion

Accordingly the method is suitable to determine mercury in water samples in a range below ppm.

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طريقة معدّ لة لتقدير ايون الزئبقيك اعتماداً على تكوين معقد مع البورفرين

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الخلاصة

استخدمت طريقة جديدة لتقدير ايون الزئبق الثنائي في عينات مياه اعتماداً على تكوين معقد بين الزئبق والبورفرين(TPP) والذي يحضر من تفاعل البايرول والبنزالديهايد. تم التحري على وجود الزئبق في ثلاث عينات من مياه شط العرب قرب نقطة تصريف مخلفات معمل الورق في البصرة، 1) على بعد 5 كم شمال نقطة التصريف، و 2) عند نقطة التصريف، و 3) على بعد 5 كم جنوب نقطة التصريف، فظلاً عن موقع رقم (4) قناة كرمة علي كمحطة سيطرة. وتم تقدير الزئبق بعد تكوين معقد Hg-TPP الذي تمت دراسته طيفياً عند الطول الموجي 440 نانو متر . وتم قياس تركيز الزئبق في مياه شط العرب عند نقطة تصريف مخلفات معمل الورق في البصرة ووجد انه يساوي 0.0492 ملغم \ لتر بينما لم يسجل اي تركيز في اي من المواقع الاخرى. يمكن الاعتماد على هذه الطريقة لكونها تتميز بحساسية تصل الى 0.0134 غم سم \ لتر ود قة 0.9×10^{-6} وانحراف معياري 0.00317 وحدود قياس 0.75×10^{-7} .

كلمات دالة: زئبق، معقد بورفرين– زئبق، معمل ورق البصرة، شط العرب،مطيافية.