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ORIGINAL ARTICLE

An Ultrasensitive Detection Platform for Mercury Ions Speciation in Water Using Procaine Hydrochloride Ion Pair Coupled Extractive Spectrofluorimetry

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Abstract

A simple extractive spectrofluorimetric strategy for trace determination of mercury(II) ions in water employing procaine hydrochloride (PQ^+) as an ion pairing fluorescent tagging reagent has been established. The method was based upon the extraction of PQ^+ from aqueous iodide media onto dichloromethane as a ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ at pH 9.0–10.0 with subsequent quenching at $\lambda_{ex/em} = 268/333$ nm. The developed strategy exhibited a linear range 20–140 nM with a lower limit of detection (LOD) 6.1 nM, respectively. Intra and inter-day laboratory accuracy and precision for trace analysis of mercury(II) ions in water were performed. Complexed mercury(II) species in real water samples were evaluated along with chemical speciation and successful comparison with most of the reported methods. The method was validated by standard inductively coupled plasma-optical emission spectrometry (ICP-OES) method in terms of student's *t*- and *F* tests at 95% confidence interval. The method offers rapidity, selectivity, cost-effectiveness, robustness, and ruggedness.

Keywords Spectrofluorimetry · Mercury(II) determination · Fluorescence probe · Procaine hydrochloride · Quenching · Ternary complex ion associate

Introduction

Mercury is amongst heavy metals with highest toxicity due to its adverse impacts on the ecosystem and human health [1, 2]. The adverse effects on human health are linked with the route of exposure, chemical form, and physical features [1–3]. Mercury is one of the most toxic and dangerous chemicals in view of the wide existence of ore cinnabar in nature, its presence in chloralkali plants and use in manipulation of mercury-containing fungicides and mercury fulminate detonator in explosives [3, 4]. A variety of factors contributes to exposure together with inhalation of elemental mercury, mining processes, amalgams manufacturing, fossil-fuel processing and waste incineration [3–5]. Oral intake of mercury in fish diet, dermal penetration of mercuric salts found in different skin lightening personal care products eventually passes through biological membranes and through respiratory and gastrointestinal tissues [4, 5]. In the food chain, mercury species including methyl mercury -a highly toxic and accumulating form- from fish introduced and accumulated in tissues and brain leads to unhealthy changes in the kidney, central nervous and endocrine systems [4–6]. US Environmental Protection Agency (US-EPA) and World Health Organization (WHO) have set 10.0 nM as the maximum permissible limit (MPL) for Hg [1, 2]. Thus, it is highly desirable to establish a model methodology for monitoring and/or enrichment of mercury in environmental water.

Several analytical procedures including atomic absorption spectrometry (AAS) [7, 8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9], ion exchange chromatography [10], mechanical filtration [11], chemical precipitation [12], reverse osmosis, flotation [13, 14], membrane

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separation [15] are reported. On the other hand, among the clean-up techniques, liquid-liquid extraction (LLE) [16] and solid phase extraction methods based carbon nanotubes [17], graphene oxide [18, 19], and polymers [20, 21] have been reported for routine analysis of mercury. However, some methods require sophisticated equipment unavailable for use in developing countries with other limitations like high cost, complications in their proper operation, selectivity and sensitivity [20, 21].

Several fluorescence sensing platforms are available for mercury in literature including molecular probe based sensors using organic fluorescent chromophores [4–6]. The fluorescence, colorimetric and electrochemical methods based on quantum dots (QDs), conjugated polymers, proteins, antibodies are also reported for mercury [22–37]. Some shortcomings are associated including solubility issues, low stability, lower sensitivity and selectivity, and complicated synthesis procedures and environmentally unfriendliness to monitor it in the environmental and biological samples. The quest for developing new fluorescent probes for selective and sensitive detection of target ions and addressing the drawbacks in the previously reported methods was the chief incentive of the work. Hence, the current study reports: i) The development of a simple, highly selective, rapid and eco-friendly extractive (LLE) spectrofluorometric determination of trace mercury(II) species in water samples using the ion-pairing reagent 4-amino-N-(2-diethylaminoethyl) benzamide hydrochloride namely procaine hydrochloride, abbreviated as (PQ^+) (Fig. 1); ii) application of the proposed ion pairing reagent for trace determination of mercury(II) ions in real water samples; and finally iii) validation and assigning the most probable stoichiometry and chemical equilibria of the produced complex ion associate of $[HgI_4]^{2-}$ with the proposed ion pairing fluorescent tagging reagent.

Experimental

Reagents and Materials

All glassware's used in this study were pre-cleaned with HNO_3 (20.0% m/v), soaked in acetone for at least 15.0 min, then washed with deionized water and dried at 120 °C. Analytical reagent grade chemicals and solvents were used as received. Nalgene low-density polyethylene (LDPE) bottles were used for storage of the stock solutions and real water samples. A stock solution (1.0 mg mL^{-1}) standard mercury(II) was prepared in ultrapure water. Stock solution (1000.0 μM) of mercury(II) was prepared from $HgCl_2$ BDH (Poole, England) in ultra-pure water. Series dilution of mercury(II) ions was achieved in deionized water. Potassium iodide solution (10.0% *w/v*) was prepared in ultra-pure water. Solutions of competent cations were prepared in deionized water from their nitrate and/or chloride salts. Britton–Robinson (B–R) (pH 2–11) buffers were made from 0.04 M from H_3BO_3, H_3PO_4, CH_3COOH, and NaOH, respectively in deionized water [38]. An accurate weight of the reagent PQ^+ (Sigma–Aldrich) in ultra-pure water was used to prepare a stock solution (1000.0 μM).

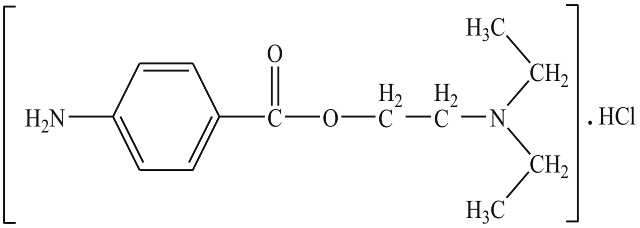


Fig. 1 Chemical structure of PQ^+ reagent

Apparatus

A Perkin-Elmer LS55 spectrofluorimeter, USA with a Hellma® fluorescence (200–2500 nm) and quartz cuvettes (Suprasil®) of 10 × 10 mm path length was used for recording emission spectra. The electronic spectra were recorded on a Perkin-Elmer (Lambda 25, Shelton, CT, USA. For method validation of mercury(II) ions, an ICP-OES (California, CT USA) purchased from Perkin Elmer was utilized. All pH measurements were performed on the pH meter (inoLap pH/ion level 2). A Milli-Q Plus system (Millipore, USA) and a digital micropipette (Plus-Sed) were used for supplying de-ionized water, preparation of stock and diluted solutions of reagent and mercury(II) ions, respectively.

Recommended Procedure

In a series of glass test tubes, appropriate concentrations (20.0–140.0 nM) of mercury(II), 100.0 μL of 10.0% KI (*w/v*) were added. The solutions were shaken gently for 1.0 min and the reagent PQ^+ (1.0 ml of 5.0 μM) was added to each mixture. The solutions were made up to the mark (10.0 mL) with the required volume of B-R buffer (pH 10.0) solution. Finally, the test solutions were shaken well for 3.0 min with dichloromethane (2.0 mL). The organic phase was separated after equilibrium and analyzed at $\lambda_{ex/em} = 268/333$ nm against a reagent blank at room temperature. The selectivity of the developed method was also examined in the presence of diverse ions Ca^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, As^{3+}, Ag^+, Al^{3+} Sn^{2+}, Cd^{2+}, Bi^{3+}, WO_4^{2-}, MnO_4^-, F^-, CO_3^{2-}, NO_3^-, SO_4^{2-} under the established conditions containing 2.0 μg L^{-1} of mercury(II) with different ratios of the interfering species.

Analytical Applications

Various samples of tap water from laboratories in King Abdulaziz University and domestic samples were collected from Jeddah city, filtered with 0.45 μm filter membrane and finally stored in pre-cleaned LDPE bottle. The sample solutions were then spiked with a known concentration (20.0–100.0 nM) of mercury(II) ions. The emissions spectra were recorded at $\lambda_{ex/em} = 268/333$ nm under the optimized experimental conditions. The concentration and recoveries were computed for mercury(II) species by employing a standard addition plot.

Results and Discussion

Electronic and Emission Spectra of Procaine and its Mercury(1I) Complex

The absorbance spectrum of the ion pairing reagent PQ^+ in dichloromethane (Fig. 2) showed a well-defined band at 290 nm assigned to $n \rightarrow \pi^*$ electronic transitions [39, 40]. The spectrum of the developed complex ion associate between PQ^+ and mercury(II) in excess KI showed a well-defined absorption peak at 310 nm in dichloromethane (Fig. 2). Similarly, the reagent PQ^+ gives an intense fluorescence at $\lambda_{ex/em} = 268/333$ nm in the organic phase. The introduction of increasing content of mercury(II) to the mixture of PQ^+ and KI results in the formation of ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ eventually leading to a decrease in the fluorescence intensity at $\lambda_{ex/em} = 268/333$ nm (Fig. 3). In the ground electronic state, the formation of ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ is correlated with a negligible shift in the wavelength with increasing mercury(II) content (Fig. 3) [39, 40]. The non-existence of the formed ion associate in the excited state is linked with the absence of new emission bands (Fig. 3) [39, 40]. Hence, the principle of the change in the emission intensity of the PQ^+ reagent upon addition of mercury(II) ion was further evaluated for the determination of mercury(II) species in water.

Optimization of Analytical Parameters

The nature of the media to achieve an optimum microenvironment for the species under study is a key parameter to be investigated. Hence, pH effect for the formed ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ was studied in B-R buffer of pH 3.0–12. Maximum quenching by mercury(II) quencher was achieved at pH ≈ 9–10 (Fig. 4). The extraction of mercury(II) at pH higher than 10.0 for was lower attributed to hydrolysis, instability and/or incomplete extraction. The slow dissociation of the complex $K_2[HgI_4]^{2-}$ accounts for the decrease in the amount of mercury extracted at pH other than pH ≈ 9–10 [40, 41]. Thus, in the subsequent work, the solution media was adopted to pH ≈ 10.

To select the most suitable organic solvent and its volume required for extracting complex ternary ion associate of mercury(II) and PQ^+ in maximum amounts, different solvents toluene, cyclohexane, n-hexane, dichloromethane, and trichloromethane were utilized. Consistent and efficient extraction was carried out in dichloromethane with the optimized volume of 2.0 mL. Moreover, the stability of the fluorescence signal for the formed ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ was examined and found to depend on the reaction time. The fluorescence intensity was recorded at various time intervals (0.5–14 min). Maximum stability and signal intensity were achieved after 2.0 min and remained constant up to 14.0 min.

Lastly, the influence of PQ^+ content was also studied and the results are demonstrated in Fig. 5. An observed increase in

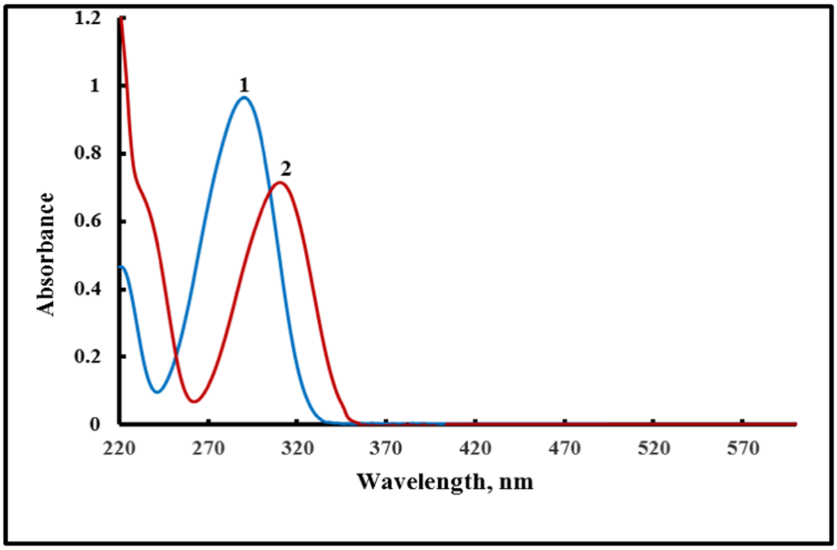


Fig. 2 Electronic spectra of the fluorescence probe PQ^+ (4×10^{-5} M) (1) and its ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ in dichloromethane (2). Condition: Mercury(II) ions $= 1 \times 10^{-5}$ M

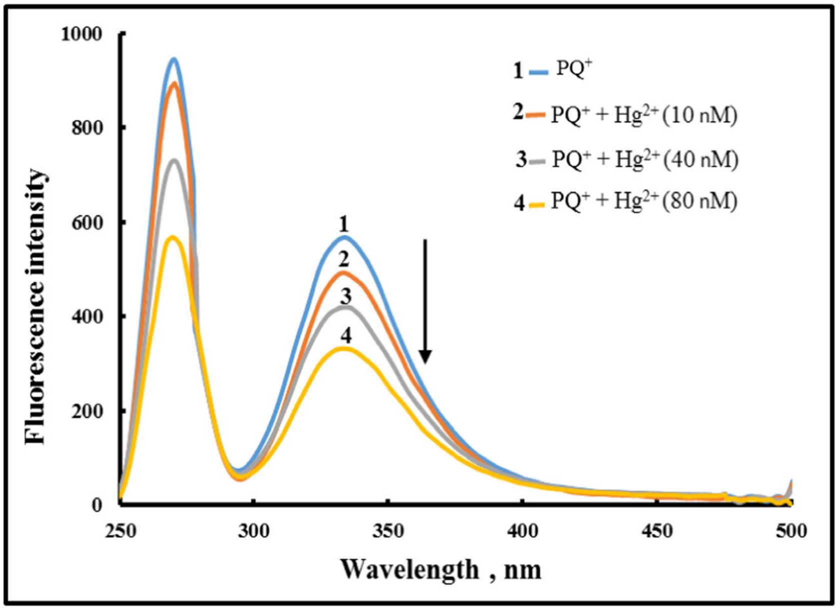


Fig. 3 Fluorescence spectra of PQ^+ (5.0 μM, 0.1% *w/v*) and its ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$ in dichloromethane at $\lambda_{ex/em} = 268/333$ nm. [Hg] = 10, 40, 80 nM

ΔF value was achieved till the addition of 5.0 μM fraction from PQ+ (0.1% *v/v*) solution and leveled off with the continuous increase. This behavior was correlated with the self-absorption and possible aggregation of the reagent at high concentration.[40,41] Thus, a concentration of 5.0 μM (0.1% *v/v*) of PQ^+ was selected.

Selectivity

The applicability of the developed method was further validated by studying the proposed method in the presence of several interfering ions in excess concentration. To evaluate the selectivity of the proposed $[(PQ^+)_2.(HgI_4)^{2-}]$ probe, the change in fluorescence intensity was examined at $\lambda_{ex/em} = 268/333$ nm in the presence of metal ions including Ca^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, As^{3+}, Ag^+, Al^{3+} Sn^{2+}, Cd^{2+}, Bi^{3+}, WO_4^{2-}, MnO_4^-, F^-, CO_3^{2-}, NO_3^-, SO_4^{2-} at 50–500 μg L^{-1} ratios under the optimum experimental conditions. The tolerance limits (*w/v*) less than ±5% change in the fluorescence intensity of mercury(II) was considered as free from interfering species. The results indicate negligible changes on the quenching of fluorescence intensity for all the tested metal ions compare to the emission spectra of mercury(II) ions (Table 1), under identical conditions revealing good selectivity of the proposed method for mercury(II) determination.

Analytical Performance

Under the optimal parameters, the analytical figure of merits were computed. Based on the influence of

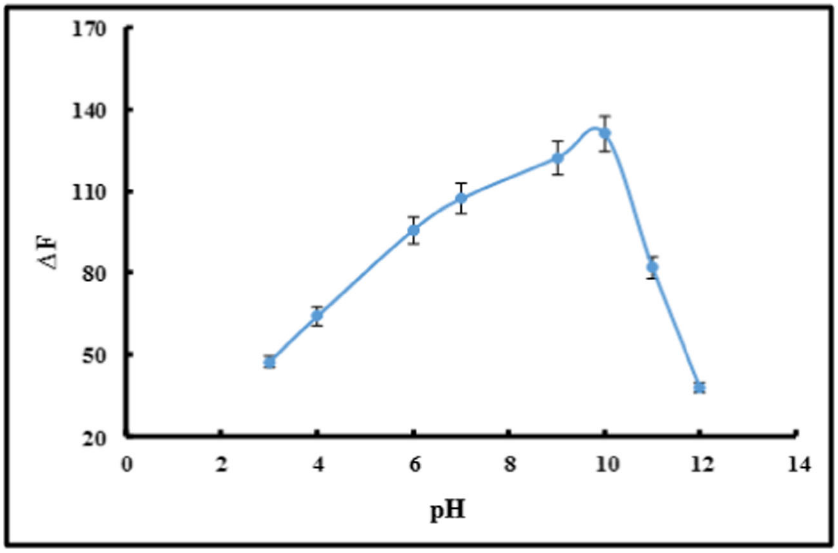
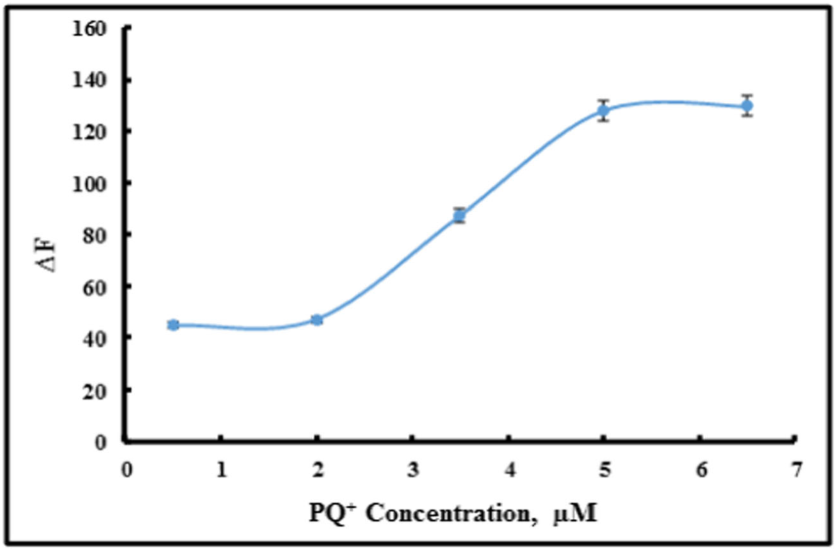


Fig. 4 Plot of pH vs. the fluorescence quenching of PQ^+ reagent by mercury(II) in aqueous iodide media

Fig. 5 Effect of PQ^+ concentration on the fluorescence quenching at $\lambda_{ex/em} = 268/333$ nm by mercury(II) (80 nM) in KI (0.1% *w/v*) media



various standard concentrations (20–140 nM) of mercury(II) on the fluorescence spectra of the ternary complex ion associate of mercury $[(PQ^+)_2.(HgI_4)^{2-}]$, the repeatability, linear range, LOD, LOQ and correlation coefficient (R^2) were evaluated. The plot of known mercury(II) concentration versus the fluorescence quenching (ΔF) was linear in the concentration range 20–140 nM. A R^2 of the linear plot was 0.9924 (n = 5) and the following regression equation was obtained:

$$\Delta F = 1.6354[C](nM) - 3.3971 \quad (1)$$

where C represents the concentration of mercury and ΔF as the quenched fluorescence intensity, respectively.

The molar absorptivity was found equal to 2.09×10^4 L mol^{-1} cm^{-1}. The precision of the method was also checked by analysis of variance (ANOVA) as an extremely powerful statistical technique which can be used to separate and estimate the different causes of variation. The results of ANOVA test for 5.0 successive replicates per day for 5 days, for a typical sample containing 100 nM mercury(II) ions are shown in Table 2. The value of the calculated F ($F_{cal} = 1.64$) at the 95% confidence (Tables 3) was found lower than the critical value of F ($F_{crit} = 2.87^{43}$ confirming the precision of the proposed method.

The values obtained for LOD for mercury(II) species was 6.1 nM lower than the permissible range in drinking water established according to US Environmental Protection Agency (EPA) guidelines [1, 2, 10]. The analytical features of the proposed method was successfully compared with a wide number of the published literature including fluorescence [2–26, 28, 29], electrochemical sensor [27], spectrophotometric [32], colorimetry [19, 30, 33], chemiluminescence [31, 34], single-crystal X-ray diffraction [31], X-ray fluorescence(XRF) [35] electrochemical [21, 36, 37], ICP-OES [9]. The developed probe provides high sensitivity, the simplicity of operations and might be employed as a routines analysis method (Table 4).

Fluorescence Quenching Mechanism

The fluorescence quenching process of the PQ^+ ($\lambda_{ex/em} = 268/333$ nm) by $[HgI_4]^{2-}$ was critically studied at room temperature by varying mercury content (0.3–1.0 µg L^{-1}). The results indicate the fluorescence intensity of PQ^+ decreases regularly with increasing quencher concentration. The Stern-Volmer constant was calculated employing the equation [39, 42]:

$$F_0/F = 1 + K_{SV}[Q] \quad (2)$$

where F_0 and F are fluorescence intensities with and without mercury(II) quencher, respectively. Ksv is the Stern-Volmer constant and [Q] is the concentration of the quencher i.e. mercury(II) ions. The Stern-Volmer quenching constant value from the plot of fluorescence quenching (ΔI) of PQ^+ versus $[Hg^{2+}]$ was found equal to 1.87×10^6 L g^{-1} mol^{-1} with a correlation factor of 0.9909, respectively.

Table 1 Tolerance limits of interfering species in mercury(II) (2.0 µgL^{-1}) determination by the developed method

Interfering species	Interfering ion to analyte ratio
Ca^{2+}, K^+, Ba^{2+}, CO_3^{2-}, F^-	200:1
Zn^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Ag^+, As^{3+}, Sn^{2+}, SO_4^{2-}, NO_3^-	50:1
Bi^{3+}, Cd^{2+}, WO_4^{2-}, MnO_4^-	40:1

Table 2 Five replicates per day determined by the proposed mercury(II) determination method (100 nM)

Replicate	First day ΔF	Second day ΔF	Third day ΔF	Fourth day ΔF	Fifth day ΔF
1	167.00	163.88	166.10	159.40	167.59
2	164.47	168.70	163.75	162.32	165.55
3	161.81	166.43	167.99	166.78	166.34
4	160.53	166.45	161.69	164.76	164.00
5	165.70	162.44	165.08	161.13	169.45
Mean	163.90	165.58	164.92	162.88	166.59
SD[†]	2.69	2.45	2.38	2.93	2.06

[†] SD: Standard Deviation

The apparent binding constant (K_A) and the number of binding sites (n) were successfully determined by employing Benesi- Hildebrand fluorescence model [43, 44]. The plot described the molecules of the reagent PQ^+ that actively and independently binds to a set of equivalent sites on a macromolecule. The apparent binding Benesi- Hildebrand model can be expressed by the following equation [43, 44]:

$$\log\left(F_0 - F/F\right)/F = \log K_A + n \log [Q] \tag{3}$$

The plot of log (F_0-F)/F versus log [Hg^{2+}] of Benesi-Hildebrand of fluorescence confirmed the formation of 2:1 stoichiometry of the ion pairing and mercury(II) ions molar ratio in the produced ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$. K_A was found equal 3.32×10^4 L mol^{-1}. The value of n indicates the participation of one molecule of PQ^{++} as a binding site on $[(PQ^+)_2.(HgI_4)^{2-}]$.

Analytical Applications

The applicability of the current method was finally evaluated in various real water samples. A range of known mercury(II) concentrations (20.0–100.0 nM) were spiked onto real water sample followed by the recommended procedure (Table. 5). The method was validated by the standard ICP-OES method. The validation was performed with statistical analysis using student's *t* and *F* tests at 95% confidence. The percentage for mercury(II) ions recovery in several tap water samples for the developed method (97.78–104.7%) and standard method (98.05–102.7%) was insignificant with recoveries higher than 95.0%. The calculated value of *t* and *F* were lower than their respective tabulated values. This indicates, the suitability and reliability of the current label-free PQ^+ assay system possessing strong sensing affinity towards mercury(II) ions.

Conclusion

A simple and direct extractive spectrofluorimetric method for rapid determination of mercury(II) ions has been developed based on the formation of ternary complex ion associate $[(PQ^+)_2.(HgI_4)^{2-}]$. The detection process offers rapidity at room temperature without any catalyst or oxidizer with excellent affinity and selectivity towards mercury(II) ions. The proposed method provides LOD (6.1 nM) significantly lower than the value set by the US-EPA in drinking water [1, 2]. The proposed method has been successfully validated by standard ICP-OES method for analysis of mercury(II) ions in tap water samples. It represents a milestone in developing low cost, simple and ultrasensitive determination strategies applicable in technologically less advanced labs. The potential toxicity of mercury(II) could be evaluated without tedious processes and technologically advanced instrumentations. Moreover, the current trend could be adopted and expanded for developing fluorescent probes for species of environment, health and security concerns. The current methodology of mercury(II) speciation could be extended to routine analysis method as opposed to most of the successful and promising methods in the literature. The rapidity, simplicity and high sensitivity recommend the current work to be an approachable and model strategy compared to a number of reliable studies (Table 4). The extension of the work for ultra-trace levels of mercury(II) ions in water could be its immobilization on-line nanosized solid phase extractors (SPEs) (e.g, nanosized Au, Ag, Fe_3O_4 chemically and/or physically treated polyurethane foams, Chitosan) packed column for pre-concentration from large sample volumes of water and subsequent determination at surface modified electrodes.

Table 3 Analysis of the results by ANOVA[†]

Source of Variation	Sum of Squares (SS)	Degrees of Freedom (df)	Mean Square (MS)	F Value S_1/S_2
Between measurements	41.55	4	10.39	1.64
Within days	126.77	20	6.34	
Total	168.32	24		

[†] S1: Regression mean square. S2: Mean square error, SS = Sum of squares, df = Degrees of freedom

Analysis of variance (frequently abbreviated to ANOVA)

Table. 4 Comparison of analytical features from different methods employed for mercury determination

Technique	Brief description of the method	Linear Range, M	LOD, M	Ref
Fluorescence	NBD-based sensor bearing a dipicolylamine derivative, (2-pyridylmethyl) (2-quinolylmethyl) amine	$4.0–100 \times 10^{-6}$	2.6×10^{-8}	[22]
Fluorescence	Rhodamine hydrazine and 2-hydroxy-acetophenone was designed	$0–55 \times 10^{-6}$	150×10^{-9}	[23]
Fluorescence	Fast-responsive fluorescent phenylamine-oligothiophene sensor 3TDDA	$0–10 \times 10^{-6}$	4.39×10^{-7}	[24]
Fluorescence	Coordination-induced signaling by introducing rhodamine-B group linkage into squaraine-diamine	–	6.47×10^{-6}	[25]
Fluorescence	Rhodamine (R-2) is designed and synthesized to detect mercury(II)	–	1×10^{-8}	[26]
Electrochemical sensor	Exploiting the catalytic formation of gold amalgam and of silver nanoparticles	$0–80 \times 10^{-9}$	0.002×10^{-9}	[27]
Fluorescence	Turn-on sensor developed by coupling gold nanoparticle (AuNPs) with the rhodamine 6G derivative FC1s*	$2–12 \times 10^{-9}$	0.75×10^{-9}	[28]
Fluorescence	An ionic conjugated oligoelectrolye (M1Q) based on 1,4-bis(styryl)benzene	$10–180 \times 10^{-9}$	7×10^{-9}	[29]
Colorimetry	Chemically initiated aggregation of gold nanoparticles	$0.002–0.1 \times 10^{-9}$	0.008×10^{-9}	[30]
Chemiluminescence	Chemiluminescence system composed of permanganate, rhodamine B and gold nano prisms	$0.67–33.3 \times 10^{-9}$	0.027×10^{-9}	[31]
Single-crystal X-ray diffraction	1-[(5-Benzyl-1,3-thiazol-2yl)diazenyl]naphthalene-2-ol: X-ray structure, spectroscopic characterization, dissociation studies	–	0.41×10^{-6}	[31]
Spectrophotometry	Electromembrane extraction-preconcentration followed by microvolume UV–Vis spectrophotometry	$11–4700 \times 10^{-9}$	3.5×10^{-9}	[32]
Colorimetry	Carrageenan-functionalized Ag/AgCl nanoparticles	$1–100 \times 10^{-6}$	1×10^{-6}	[33]
Electrochemiluminescence biosensor	"Off-On"switching electrochemiluminescence biosensor by tris-(bipyridine) (Ru(bpy) 32+)/Cyclodextrins-Au nanoparticles(CD AuNps)/Nafion	$0.1–4000 \times 10^{-9}$	0.1×10^{-9}	[34]
X-ray fluorescence	Handheld X-ray fluorescence	$5–2900 \times 10^{-6}$	37×10^{-6}	[35]
Differential pulse voltammetry	polypyrrole decorated graphene/_-cyclodextrin composite for low level electrochemical	$1–1000 \times 10^{-9}$	0.47×10^{-9}	[21]
ICP-OES**	Spectrometric method	–	0.15×10^{-9}	[9]
Differential pulse voltammetry	Copper-cobalt hexacyanoferrate modified glassy carbon electrode	$0.5–3 \times 10^{-6}$	80×10^{-9}	[36]
Electrochemical and XPS***	Ion selective electrode based on 1-undecanethiol assembled Au substrate	$0.01–100 \times 10^{-6}$	4.5×10^{-9}	[37]
Fluorescence	Reusable DNA-functionalized-graphene	$0–500 \times 10^{-9}$	4.1×10^{-9}	[18]
Fluorescence	Fluorescent probe based on procaine hydrochloride	$20–140 \times 10^{-9}$	1.3×10^{-9}	Present work

* FC1s; Fluorimetric chemodosimeter, ** ICP-OES: Inductively coupled plasma optical emission spectrometry, *** XPS; X-ray photoelectron spectroscopy

Table 5 Analysis of the mercury(II) (nM) in tap water samples by the developed (A) and standard ICP-OES method (B)[†]

Samples	Added, (nML^{-1})	Found, ($nM\ L^{-1}$)		Recovery (%)		*t* (2.78)[*]	*F* (6.39)[*]
		A	B	A	B		
Tap water 1	20	20.97 ± 0.50	20.54 ± 0.63	104.7	102.7	2.24	0.62
Tap water 2	40	39.11 ± 1.25	39.22 ± 0.92	97.78	98.05	0.38	1.85
Tap water 3	60	61.74 ± 3.07	62.58 ± 0.72	102.2	104.3	0.98	1.82
Tap water 4	80	78.51 ± 1.63	77.88 ± 1.21	98.14	97.35	0.64	1.82
Tap water 5	100	97.74 ± 3.51	98.37 ± 1.30	97.74	98.37	2.8	6.29

[†] Mean of five measurements± standard deviation

[*] The values in parenthesis are the corresponding critical values at 95% ($P = 0.05$) confidence

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