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Spectrofluorometric determination and chemical speciation of trace concentrations of tungsten species in water using the ion pairing reagent procaine hydrochloride

M.S. El-Shahawi*, L.A. Al Khateeb

Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

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ABSTRACT

A highly selective and low cost extractive spectrofluorimetric method was developed for determination of trace concentrations of tungsten (VI) in water. The method was based upon solvent extraction of the developed ion associate $[(PQH^+)_2 \cdot WO_4{}^{2-}]$ of the fluorescent ion-pairing reagent [2-(diethylamino)ethyl 4 aminobenzoate] hydrochloride namely procaine hydrochloride, $PQH^+ \cdot Cl^-$ and tungstate ($WO_4{}^{2-}$) in aqueous solution of pH 6–7 followed by measuring the resulting fluorescence enhancement in n-hexane at $\lambda_{ex/em} = 270/320$ nm. The fluorescence intensity of $PQH^+ \cdot Cl^-$ increased linearly on increasing tungstate concentration in the range 25–250 μg L^{-1}. The limits of detection (LOD) and quantification (LOQ) of tungsten (VI) were found 7.51 and 24.75 μg L^{-1}, respectively. Chemical composition of the developed ion associate and the molar absorptivity at 270 nm were found to be $[(PQH^+)_2 \cdot WO_4{}^{2-}]$ and 2.7×10^4 L mol^{-1} cm^{-1}, respectively. Other oxidation states (III, IV, V) of tungsten species could also be determined after oxidation with H_2O_2 in aqueous solution to tungsten (VI). The method was applied for analysis of tungsten in certified reference material *(IAEA Soil-7)* and wastewater samples. The results were compared successfully (>95%) with the data of inductively coupled plasma-mass spectrometry (ICP-MS).

1. Introduction

Due to various processes of remobilization, heavy metals may be released and moved into the biological or food chain and concentrate in fish and other edible organisms, thereby reaching humans and causing chronic or acute diseases [1,2]. These chemicals are introduced into aquatic environment through, dumping wastes, effluents from runoff of terrestrial system and geological weathering [2]. Heavy metals are very harmful to plants and animals [3,4] and are not bio- or photodegradable and once they enter the environment, their potential toxicity depends to a large extent on their chemical forms [5–8]. Thus, the analyses of biologically essential or toxic metal ions present in the environment are of prime importance [8].

Tungsten is the elemental metal with the highest melting/boiling points, tensile strength at high temperature and a density of 19.1 g cm^{-3}. Tungsten occurs naturally in soils and sediments usually in small concentrations, e.g. in the lithosphere the average concentration values are in the range 0.2–2.4 mg/kg [9]. W also occurs in the oxidation states III, IV, V and VI, however, oxidation state VI represents the most stable one of tungsten species. These properties make tungsten suitable for a wide variety of industrial and military uses [9,10]. In spite of its extensive uses, biological and biochemical effects of tungsten and tungsten compounds are not well known [10]. Due to the resilience and biocompatibility of tungsten, it has also become very popular as a constituent of metal alloys in medical implantable devices, e.g. prostheses in orthopaedic and maxillofacial surgery, dental implants, intravascular mobilization coils, and mechanic heart valves [11,12]. However, tungsten effects on environmental systems have not been investigated extensively and published data are fragmentary. Thus, developing of novel and sensitive methods for its determination are of great importance.

A series of extractive liquid–liquid spectrophotometric methods has been reported [13–16]. Numerous analytical techniques involving the use of benzoinoximete, tributyl-phosphate, thiocyanate and dithiol and Amberlite XAD-1180 has been used effectively for the separation and/or spectrophotometric determination of tungsten (VI) species from aqueous media and industrial wastewater [13–16]. Most of these methods are not precise, expensive, and unselective and require careful experimental conditions and considerable time consuming.

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* Corresponding author. Permanent address: On leave from the Department of Chemistry, Faculty of Science at Damiatta Mansoura University, Mansoura, Egypt. Tel.: +966 2 6952000x64960; fax: +966 2 6952292.

E-mail addresses: malsaeed@kau.edu.sa, mohammad_el_shahawi@yahoo.co.uk, mohammad_el_shahawi@hotmail.com (M.S. El-Shahawi).

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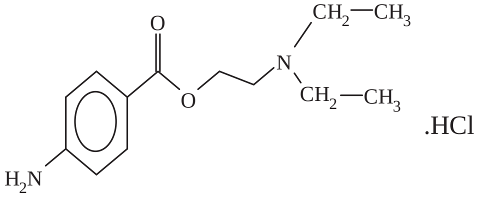

Fig. 1. Chemical structure of procaine hydrochloride ($PQH^+{\cdot}Cl^-$).

Recently, the common analytical techniques for tungsten determination are graphite furnace atomic absorption spectrometry (GFAAS) [13], energy dispersive X-ray fluorescence [18], inductively coupled plasma-atomic emission spectroscopy (ICP-OES) or ICP-mass spectrometry (ICP-MS) [19] and adsorptive stripping voltammetry [20]. The main disadvantages of these techniques are the complexity and the high cost of the instruments, and the need of some degree of expertise for their proper operation. Hence, the development of low cost method, easy to operate, highly sensitive and reliable for routine analysis, e.g. spectrofluorometry or spectrophotometry is still of great concern. The former technique is better than the later due to its high sensitivity and selectivity. To our knowledge, there has been no study on the use of the title reagent $PQH^+{\cdot}Cl^-$ (Fig. 1) on liquid–liquid extractive spectrofluorimetric determination and chemical speciation of trace amounts of tungsten species in industrial wastewater. Therefore, the present article reports the use of the reagent $PQH^+{\cdot}Cl$ for developing a simple and low cost spectrofluorimetric method for determination and/or chemical speciation of tungsten species in water.

2. Experimental

2.1. Reagents and materials

All chemicals and solvents were of analytical reagent grade and were used without further purification. Stock solutions (1000 $\mu g\,mL^{-1}$) of tungsten (VI), $AsO_4{}^{3-}$, CN^-, $MnO_4{}^-$, $NO_2{}^-$, $ClO_3{}^-$, $BrO_3{}^-$, $IO_3{}^-$, Li^+, Ni^{2+}, Cu^{2+} and H_2O_2 were prepared from the BDH chemicals (Poole, England) Na_2WO_4, Na_3AsO_4, KCN, $KMnO_4$, $NaNO_2$, $KClO_3$, $KBrO_3$, KIO_3, LiCl, $NiSO_4$, $CuSO_4$ and H_2O_2 (30% v/v) in water (100.0 mL), respectively. Solutions of other metal ions were prepared from their nitrate or chloride salts in deionized water. A series of Britton–Robinso (BR) buffer of pH (2–11) and acetate buffer (pH 2.3–5.7) were prepared as. A stock solution (0.1/0% m/v) of procaine hydrochloride (Sigma–Aldrich) chemically named as 4-aminobenzoic acid 2-diethylaminoethyl ester hydrochloride, Fig. 1 was prepared by dissolving the required weight in deionized water (100 mL) mark with water.

2.2. Apparatus

Fluorescent measurements were recorded on a Perkin-Elmer (Norwalk, CT, USA) LS 55 spectrofluorimeter, equipped with a xenon lamp and a 10 mm quartz cell. A Perkin-Elmer (model Lambda 25, USA) spectro-photometer with 10 mm (path width) quartz cell was used for recording the UV–visible spectra (190–1100 nm) and absorbance measurements. A digital micropipette (Volac) and an Orion pH-meter (model EA 940) were used for the preparation of diluted tungsten (VI) solutions and pH measurements, respectively. De-ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for preparation of solutions. A Perkin Elmer ICP-MS Sciex model Elan DRC II (California, CT, USA) was used as a reference method for tungsten determination at the operational parameters (Table 1).

Table 1
ICP-MS operational conditions for tungsten determination.

Parameter	
ICP RF power (W)	1100
Nebulizer gas flow ($L\,min^{-1}$)	0.94
Plasma gas (Ar) flow rate ($L\,min^{-1}$)	15
Auxiliary gas (Ar) flow rate ($L\,min^{-1}$)	1.2
Lens voltage (V)	0.9
Analog stage voltage (V)	−1750.0
Pulse stage voltage	800
Quadrupole rod offset std	0.0
Discriminator threshold	22
Cell path voltage std (V)	−13
Cell rod offset (V)	−18.0
Atomic mass (am)	52.9407
Sample flow rate, mL	093

2.3. Recommended procedure

2.3.1. Recommended spectrofluorimetric procedures for tungsten (VI) determination

An appropriate concentration (25–200 $\mu g\,L^{-1}$) of tungsten (VI) in aqueous solution of pH 6–7 was transferred to a separating funnel (50.0 mL) containing the reagent ($PQ^+{\cdot}Cl^-$) (2.0 mL). The test solution was completed to the mark with deionized water (25.0 mL) and the reaction mixture was shaken twice with n-hexane (2 × 2.5 mL) for 3 min. After separation of the layers, the organic phase was subjected to the fluorescence measurement at the excitation and emission wavelengths of 270 and 320 nm, respectively against reagent blank. The enhanced fluorescence intensity of the reagent $PQH^+{\cdot}Cl^-$ by tungsten (VI) added was represented by the equation:

$$\Delta I\ (\%) = \frac{I_0 - I_f}{I_0} \times 100 \qquad (1)$$

where I_0 and I_f are the fluorescence intensity of the $PQH^+{\cdot}Cl^-$ reagent before and after addition of tungsten (VI), respectively. A blank experiment was also carried out under the same experimental conditions.

2.3.2. Recommended procedure for tungsten (V) determination

Aqueous solution (100.0 mL) containing tungsten (V) ions prepared as reported [13] at concentration in the range 0.05–100 $\mu g\,L^{-1}$ was transferred to a conical flask (250 mL). The solution was oxidized to tungsten (VI) by adding few drops of concentrated nitric acid–H_2O_2 (2 mL, 10% w/v) and boiling for 10 min. After cooling, the test solution was adjusted to the required pH 6–7 with few drops of dilute HCl and/or NaOH and analyzed following the recommended procedures for tungsten (VI) determination against reagent blank.

2.3.3. Chemical speciation of inorganic tungsten (V) & (VI)

An aqueous solution (0.5 L) containing the binary mixture of tungsten (V) and tungsten (VI) species at a total concentration of tungsten species $\leq$100 $\mu g\,L^{-1}$ was first analyzed following the recommended procedures for tungsten (VI) determination. Another aliquot sample (0.5 L) was oxidized to tungsten (VI) and analyzed as mentioned for tungsten (V) determination. The fluorescence intensity of the first aliquot (ΔI_1, %) is equivalent to tungsten (VI) ions, while the fluorescence intensity of the second aliquot (ΔI_2, %) is a measure of the sum of tungsten (V) and (VI) ions in the mixture. Thus, the fluorescence intensity ($\Delta I_2 - \Delta I_1$) is a measure of tungsten (III) ions in the binary mixture (Fig. 3).

2.4. Applications

2.4.1. Analysis of tungsten in certified reference material (IAEA Soil-7)

The validation of the developed procedure was investigated by determination of chromium in CRM (IAEA Soil-7) as follows: an accurate weight (0.20–0.30 ± 0.001 g) of the CRM sample was transferred into a Teflon beaker (50.0 mL) containing HF (7.0 mL), concentrated HCl (2.0 mL), and concentrated HNO_3 (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture was heated slowly for 1 h at 100–150 °C on a hot plate. After evolution of NO_2 fumes had ceased, the reaction mixture was evaporated almost to dryness and mixed again with concentrated HNO_3 (5.0 mL). The process was repeated twice and the solid residue was re dissolved in dilute HNO_3 (10.0 mL, 1.0 mol L^{-1}), transferred to volumetric flask (25.0 mL) and completed to the mark with deionized water. An accurate volume of the sample solution (10.0 mL) was adjusted to pH 6–7 with few drops of dilute HCl and/or NaOH and analyzed following the procedures of tungsten (V) determination. The change of the fluorescence intensity of the reagent $PQH^+{\cdot}Cl^-$ by tungsten added was evaluated and used for tungsten determination via the linear plot of the standard addition method. Blank sample was analyzed following the same digestion and analytical procedures.

2.4.2. Analysis of total and chemical speciation of tungsten in wastewater

Wastewater samples were collected from the industrial effluent collection points in the industrial zones of chemicals, tanning, and dyes industries (Jeddah city, KSA). The water samples were filtered, condensed 100-folds with rotary evaporator and finally digested with concentrated nitric acid to remove the coexisting organic substances. The solution was adjusted to the required pH and analyzed following the recommended procedures of tungsten (III) determination. For the chemical speciation of tungsten (III &VI), the sample solution was oxidized to tungsten (VI) by H_2O_2 (0.5 mL, 30%, w/v) in alkaline solution (pH ∼9) adjusted with drops of KOH and heated for 10 min to assure complete oxidation of tungsten (III) and to remove excess H_2O_2. An accurate volume (10 mL) of the sample after centrifugation and filtration was analyzed following the recommended procedure of tungsten (VI) determination against blank. Tungsten (III) species was obtained by subtracting the measured tungsten (VI) from the total tungsten content.

3. Results and discussion

Preliminary study has shown that, on mixing tungsten (VI) with the ion pairing reagent $PQH^+{\cdot}Cl^-$ (Fig. 1) in aqueous solution of pH 6–7 and shaking with n-hexane, a colorless – complex species was developed. In the absence of tungsten (VI), the absorption UV spectrum of the reagent $PQH^+{\cdot}Cl^-$ (1×10^{-5} M) showed no absorption bands in n-hexane. Similar trend was also obtained on shaking tungstate ions with n-hexane. The electronic absorption spectra of the developed ion associate of $PQH^+{\cdot}Cl^-$ (1×10^{-5} M) and tungsten (VI), $PQH^+{\cdot}Cl^-$ and tungstate ions in n-hexane are shown in Fig. 2. The spectrum of the developed associate in n-hexane showed two bands at 280 (like shoulder) and 270 nm confirming the associate formation. The value of the molar absorptivity (ε) at λ_{max} 270 nm of the associate formed was found equal 2.7×10^4 L mol^{-1} cm^{-1} in n-hexane suggesting the possible use of the title reagent for spectrofluorimetric determination of tungsten. The composition of the produced ion associate was determined by Job's continuous variation and molar ratio methods at λ_{max} 270 [21]. The results revealed that, the ration of tungstate: $PQH^+{\cdot}Cl^-$ was 1:2 molar ration Thus, the most probable composition of the extracted species $[(PQH^+)_2{\cdot}WO_4{}^{2-}]$.

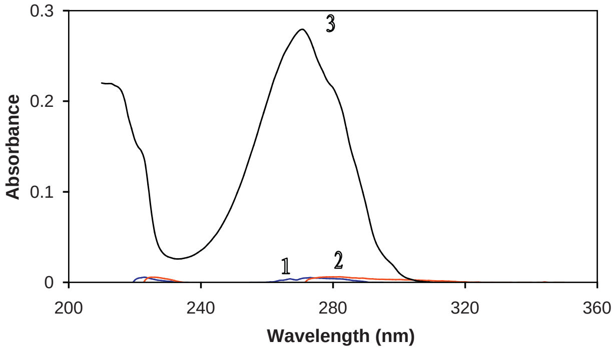

Fig. 2. Electronic spectra of $PQH^+{\cdot}Cl^-$ (1), tungstate (2) and the developed ion associate $[(PQH^+)_2{\cdot}WO_4{}^{2-}]$ in n-hexane (3). Aqueous phase (10 mL) of pH 6–7 containing tungsten (100 μg L^{-1}) 0.2 mL $PQH^+{\cdot}Cl^-$ (0.01% w/v) and n-hexane (10 mL).

In the absence of tungsten (VI), the reagent $PQH^+{\cdot}Cl^-$ has no fluorescence at $\lambda_{ex/em}$ = 270/305 nm in n-hexane. The fluorescence intensity of $PQH^+{\cdot}Cl^-$ was enhanced on raising tungsten (VI) concentration with negligible shift in the wavelength confirming the formation of the complex ion associate in the ground electronic state. Representative results are demonstrated in Fig. 3. The absence of new emission band in the spectrum indicates that, the formed ion associate in the excited state does not exist under the experimental conditions [12]. The developed enhancement in the fluorescence intensity was successfully used for developing a new spectrofluorimetric method for determination of tungsten (VI) and total inorganic tungsten (V) and (VI) species in water.

3.1. Influence of analytical parameters

The effect of pH on the enhancement of the fluorescence intensity of the developed ion associate in n-hexane was tested at various pH ranges employing BR buffer (2–11) and acetate (2.3–5.7). The results revealed the interference of the BR buffer on the signal therefore it was excluded. Maximum and constant fluorescence

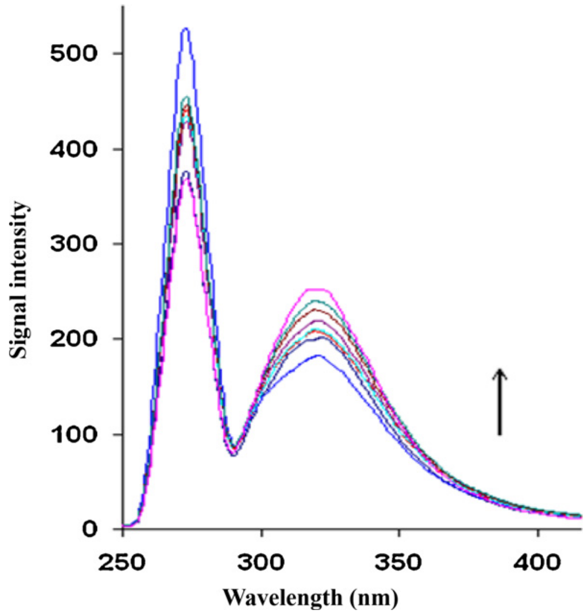

Fig. 3. Emission spectra of $PQH^+{\cdot}Cl$ in n–hexane upon addition of various concentrations (25–100 μg L^{-1}) of tungsten (VI).

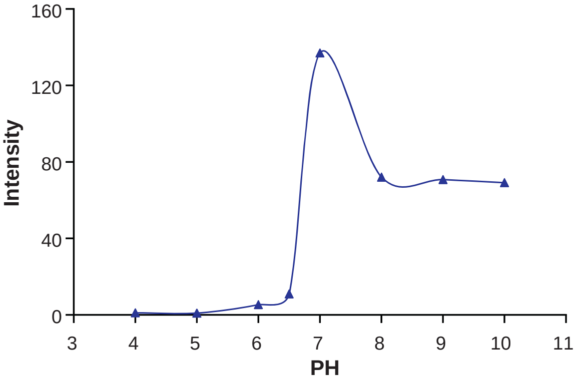

Fig. 4. Influence of pH on the fluorescence enhancement of the developed ion associate $[(PQH^+)_2\cdot WO_4^{2-}]$ in n-hexane.

enhancement was achieved in acetate media in the pH range 6–7. Representative results are shown in Fig. 4. Therefore, in the subsequent work, the solution pH was adjusted to pH 6–7 using few drops of dilute HCl and/or NaOH.

The influence of shaking time on the fluorescence quenching intensity of the reagent $PQH^+\cdot Cl^-$ by the developed ion associate in the organic phase was investigated. Maximum and constant quenching intensity was achieved at 3 min shaking with n-hexane (Fig. 5). Thus, a shaking time of 3 min was selected in the in the next work.

The influence of the reagent $PQH^+\cdot Cl^-$ concentration on the fluorescence intensity was investigated. The results are demonstrated in Fig. 6. Maximum and constant fluorescence intensity was achieved using 2.0 mL of the reagent (0.1% w/v). High concentration of $PQH^+\cdot Cl^-$ makes the fluorescence quenching so small that it cannot be detected.

The extraction performance of the ion associate $[(PQH^+)_2.WO_4^{2-}]$ was tested in a series of organic solvents, e.g. n-hexane, dichloromethane, carbon tetrachloride, toluene, chloroform and methyl isobutyl ketone. The extraction of the ion associate increased in the following order: n-hexane > toluene > dichloromethane > chloroform > methyl isobutyl ketone in agreement with the order of lowering the dielectric constant. Maximum extraction and constant fluorescence signal intensity was achieved in n-hexane. Therefore, in the subsequent work n-hexane was chosen as a preferred solvent.

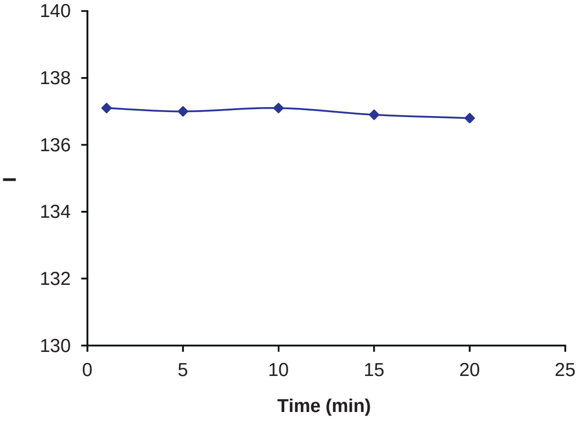

Fig. 5. Effect of shaking time on the fluorescence enhancement of $PQH^+\cdot Cl^-$ in the presence of tungsten (VI) (100.0 $\mu g\,L^{-1}$) in aqueous solution of pH 6–7.

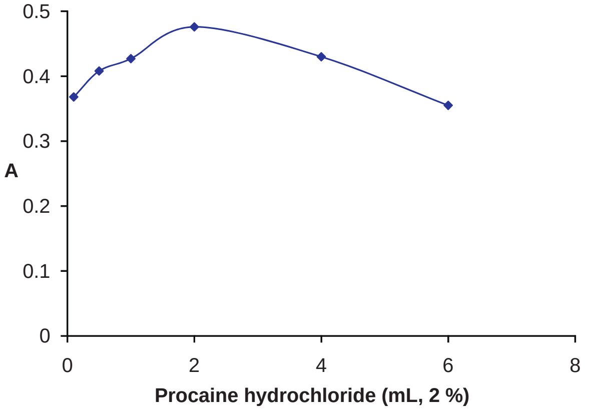

Fig. 6. Influence of reagent $PQH^+\cdot Cl^-$ concentration on the signal of fluorescence intensity of the developed ion associate with tungsten (VI).

3.2. *Selectivity*

The selectivity of the developed method was examined in the presence of a series of foreign ions under the established conditions. The tolerance limits (w/w) less than ±4% change in the fluorescence intensity of tungsten (VI) was considered as free from interfering species. Solutions containing 1.0 $\mu g\,L^{-1}$ of tungsten (VI) and the interfering species in different ratios were subjected to complete analysis. The results are summarized in Table 2. Complete extraction of tungsten (VI) was achieved as indicated from the ICP-MS and fluorescence measurements. The anions $BrO_3{}^-$, $IO_3{}^-$, and $MnO_4{}^-$, CN^- and Cu^{2+} interfered seriously with the fluorescence intensity of the $PQH^+\cdot Cl^-$ reagent and tungsten (VI) determination. The interference of cyanide and copper was eliminated by adding few drops of, KOH (0.1% mL V) $-H_2O_2$ and sodium thiosulphate, respectively. The interference of $MnO_4{}^-$ was eliminated by the addition of few drops (0.1% m/v) NaN_3 to reduce manganese (VII) to manganese (II) and the tolerance was improved to acceptable limit (98 ± 2%). The results denoted that, the method has good selectivity even in the presence of high concentration of tungsten (III) species. Thus, the method was found suitable for the chemical speciation of tungsten (V, VI) in a variety of environmental water samples.

3.3. *Figure of merits*

Under the optimized experimental conditions, the plot of tungsten (VI) concentration *vs.* fluorescence enhancement by the developed ion associate $PQH^+\cdot Cl^-$ was linear in the concentration range 25–250 $\mu g\,L^{-1}$. A regression equation of:

$$\Delta I = 636.51\ C(\mu g\ L^{-1}) + 1.5179 \quad (2)$$

with a correlation coefficient of 0.998 ($n = 6$) were achieved. Based on the IUPAC [13], the values of LOD and LOQ of tungsten (VI) species were 7.51 and 24.75 $\mu g\,L^{-1}$, respectively. The LOD

Table 2
Tolerance limits of interfering species in tungsten (VI) (1.0 $\mu\,mL^{-1}$) determination by the developed method.

Interfering species	Interfering to analyte ratio
As^{3+}, Ni^{2+}, Bi^{3+}, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ag^+, $CO_3{}^{2-}$, $SO_4{}^{2-}$, $NO_3{}^-$	1000:1
Fe^{3+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Cu^+, Cr^{3+}, Cl^-, F^-,	100:1
$NO_2{}^-$, H_2O_2	50:1
$MnO_4{}^-$, and $BrO_3{}^-$	50:1
$IO_3{}^-$	0.5:1
CN^-	10:1[a]

[a] Interference was minimized by adding few drops of diluted KOH (0.1%) and hydrogen peroxide.

(7.51 $\mu g\,L^{-1}$) lower than the instrumental detection limits of flame AAS (750 $\mu g\,L^{-1}$), ICP-OES radial (17.0 $\mu g\,L^{-1}$) and energy dispersive X-ray fluorescence spectrometry (157.51 $\mu g\,mL$) for tungsten determination. The method provides LOD lower than the maximum allowable level (<15.0 $\mu g\,L^{-1}$) of tungsten recommended by WHO [9]. The present method has a limit of detection lower than some of the reported methods of tungsten determination and ICP-OES [13–15,18]. The LOD of the developed was found higher than the reported method [12]. The relative standard deviation at concentration 50 $\mu g\,L^{-1}$ tungsten (VI) was ±3.6% ($n = 5$). The figures of merits of the proposed method were compared successfully with many of the published electrochemical, chromatographic and spectrometric methods [12,13,17–20]. Thus, the method presents an effective approach in pre concentration and separation of tungsten from natural waters. The method could be extended to be on-line for the pre concentration of ultra traces concentrations of tungsten (VI) from sea water samples. However, most of the reported methods [12,17–20] suffered from time consuming, selectivity and reproducibility. The fluorescence enhancement of the reagent by tungsten (VI) added under the optimum experimental conditions suggested use of the $PQH^+{\cdot}Cl^-$ reagent for the preconcentration and determination of tungsten (VI) from large sample volumes of deionized water. Thus, aqueous solutions (0.5 L) of deionized water samples containing various concentrations (5.0–50.0 $\mu g\,L^{-1}$) of tungsten (VI) at pH 6–7 were shaken with n-hexane as described above. Analysis of aqueous solutions by ICP-MS against reagent blank has revealed complete extraction (96–98 ± 1.6) of tungsten (VI). The concentration of tungsten (VI) species in the organic phase was quantitatively determined (94% ± 3.6) by measuring the enhancement in the fluorescence of $PQH^+{\cdot}Cl^-$ in n-hexane at optimum $\lambda_{ex/em}$. Tungsten (III) species in aqueous solutions (0.1 L) in the concentrations range 0.05–50 $\mu g\,mL^{-1}$ was also determined by the $PQH^+{\cdot}Cl^-$ reagent after oxidation to tungsten (VI) species as described. Satisfactory extraction percentage (96 ± 2.7–102 ± 1.9%, $n = 5$) of tungsten (V) species was also achieved.

3.4. Analytical applications

3.4.1. Analysis of tungsten in the certified reference material (IAEA Soil-7)

The validation of the developed method was performed by the analysis of tungsten in the certified reference materials (*IAEA Soil-7*). Good agreement between the total tungsten content added and analyzed by the developed spectrofluorometric, and ICP-MS methods based on dry weight in the range of 95% confidence interval. These data demonstrated the accuracy and precision of the developed method for trace analysis of tungsten in complex matrices.

3.4.2. Analysis of tungsten in water

The proposed method was applied for the chemical speciation of tungsten (V & VI) in tap and wastewater samples. Total tungsten content in water samples was determined via the developed spectrofluorimetric (A) and ICP–MS (B) methods (Table 3). Good agreement between the percentage recovery determined by the developed spectrofluorimetric and ICP-MS methods was achieved and always higher than 95% confidence confirming the precision of the independence of the method from matrix interference. Statistical treatment of data using *F* test [21] revealed that, no significant differences between the two variances of the developed and the ICP-MS methods. The calculated value of F (2.78) is lesser than the tabulated *F* value (6.39) for five replicate measurements. The student *t* test [21] was also applied to the analytical data of the developed and ICP-MS methods. No significance difference between the two methods. The tabulated *t* value at 95% confidence limit was 2.306 and the calculated *t* value by applying *Student's t*-test to the results of wastewater sample was found lesser (0.79) for five measurements.

Table 3
Analysis of tungsten ($\mu g\,L^{-1}$) species in water by the developed spectrofluorimetric (A) and ICP MS (B) methods (mean ± standard deviation, $n = 5$).

Sample	Tungstate added	Tungstate found	Total tungsten	
			A	B
Wastewater	–	6.92 ± 0.7	7.1 ± 0.34	6.24 ± 0.57
	50	59.3 ± 2.4 9	60.7 ± 4.1	60.34 ± 1.9
Tap water	–	nd	nd	2.4 ± 1.2
	10	10.8 ± 2.6	11.3 ± 1.1	10.93 ± 2.1

4. Conclusion

The analytical merits of the proposed method were successfully compared with some of the reported spectrofluorimetric methods. The method provides LOD lower than the maximum allowable level (50.0 $\mu g\,L^{-1}$) of tungsten recommended by WHO [12]. The reagent $PQH^+{\cdot}Cl^-$ appears to be promising as the basis of a sensitive and clean spectrofluorimetric procedure for tungsten speciation. The LOD of the method could be improved to lower value by prior pre concentration onto $PQH^+{\cdot}Cl^-$ immobilized polyurethane packed column before determination. Most of reported methods exhibited a relatively high LOD (10.0–50.0 $\mu g\,L^{-1}$), and serious interferences of Ag^+, Hg^{2+}, Pb^{2+}, Cr^{3+}, and Ni^{2+} [18–20]. The method could be applied easily for the analysis of polytungstic acids, and other oxo after digestion in alkaline solution [2]. Work is continuing for on-line determination and speciation of inorganic tungsten and different polyoxotungstate such as heteropoly acids, paratungstate A $[W_6O_{20}(OH)_2]^{6-}$ and $[W_7O_{24}(OH)_2]^{6-}$ and paratungstate B $[H_2W_{12}O_{42}]^{-10}$ and $[H_3W_{12}O_{42}]^{9-}$, and metatungstate, e.g. α,β-Keggin ion isomers B $[HW_{12}O_{40}]^{7-}$, $[H_2W_{12}O_{40}]^{6-}$ $[W_7O_{24}(OH)_2]^{6-}$ after decomposition in alkaline conditions of pH 8–9 [2].

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