Talanta 84 (2011) 175–179

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Spectrofluorometric determination and chemical speciation of trace concentrations of chromium (III & VI) species in water using the ion pairing reagent tetraphenyl-phosphonium bromide

M.S. El-Shahawi[a,*], H.M. Al-Saidi[b], A.S. Bashammakh[c], A.A. Al-Sibaai[a], M.A. Abdelfadeel[a]

[a] Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[b] Department of Chemistry, University College, Umm Al-Qura University, Makkah, Saudi Arabia
[c] The Centre of Excellence in Environmental Studies, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:
Received 28 September 2010
Received in revised form
20 December 2010
Accepted 22 December 2010
Available online 8 January 2011

Keywords:
Spectrofluorimetry
Chromium speciation
Certified reference material (*IAEA Soil-7*)
Tetraphenyl-phosphonium bromide
Wastewater

ABSTRACT

A highly selective, and low cost extractive spectrofluorometric method has been developed for determination of trace concentrations of chromium (III & VI) in water samples using the fluorescent reagent tetraphenylphosphonium bromide ($TPP^+ \cdot Br^-$). The method was based upon solvent extraction of the produced ion associate [$TPP^+ \cdot CrO_3Cl^-$] of $TPP^+ \cdot Br^-$ and halochromate in aqueous HCl and measuring the fluorescence quenching of $TPP^+ \cdot Br^-$ in chloroform at $\lambda_{ex/em}$ = 242/305 nm. The fluorescence intensity of TPP^+Br^- decreased linearly on increasing the chromium (VI) concentration in the range of 1–114 $\mu g\,L^{-1}$. The limits of detection (LOD) and quantification (LOQ) of chromium (VI) were 0.43 and 1.42 $\mu g\,L^{-1}$, respectively. Chromium (III) species after oxidation to chromium (VI) with H_2O_2 in alkaline solution were also determined. Chemical speciation of chromium (III & VI) species at trace levels was achieved. The method was applied for analysis of chromium in certified reference material (*IAEA Soil-7*) and in tap- and wastewater samples and compared successfully (>95%) with the inductively coupled plasma-mass spectrometry (ICP-MS) results.

1. Introduction

Chromium occurs in the environment in two major valence states (III, VI). Due to its wide use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation, chromium (VI) exists in air, soil, and aquatic systems [1]. It can also enter the drinking water distribution system from the corrosion inhibitors used in the water pipes [2]. Although the trivalent form is an essential nutrient, its disposal as liquid effluents in natural waters or as sludge in soils has to be avoided or controlled, because it may be oxidized, especially in soils, to the hexavalent form, which is highly toxic, carcinogenic and mutagenic in nature [3]. The ability of chromium (VI) to react with other elements and its high solubility in soil and aquatic systems makes it more toxic than other heavy metal ions [4,5]. Thus, total chromium measurement cannot be used to determine the actual environmental impact and chromium (III, VI) speciation in the environmental samples is necessary to assess precisely the pollution levels [5].

The presence of chromium (VI) in the environment has resulted in the development of numerous analytical techniques for its preconcentration by solid phase extraction [6,7] and subsequent determination in different sample matrices. The most common analytical techniques for chromium determination are flow injection analysis [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], graphite furnace atomic absorption spectrometry (GFAAS) [10] and adsorptive stripping voltammetry [11]. 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. Therefore, the development of low cost method, easy to operate, highly sensitive and reliable for routine analysis e.g. spectrofluorimetry or spectrophotometry is still of great concern. The former technique is better than the later due to its high sensitivity and selectivity.

Recently, the complex ion associate of the halochromate (CrO_3Cl^-) and the ion pairing reagent tetraphenylphosphonium bromide ($TPP^+ \cdot Br^-$) in chloroform has been used for the development of a simple and accurate extractive spectrophotometric procedure for speciation of chromium (III, VI) species in water [5]. Recent literature revealed no study on the use of the fluo-

---

[*] Corresponding author. Permanent address: Department of Chemistry, Faculty of Science at Damiatta Mansoura University, Mansoura, Egypt.
Tel.: +966 2 6952000x64422; fax: +966 2 6952292.
E-mail address: mohammad_el_shahawi@yahoo.co.uk (M.S. El-Shahawi).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.12.039

Table 1
ICP-MS operational conditions for chromium 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
Pulse stage voltage	800
Quadrupole rod offset std	0
Discriminator threshold	22
Cell path voltage std (V)	−13
Cell rod offset (V)	−18
Atomic mass (am)	52.941
Sample flow rate, mL	93

rescent reagent $TPP^+\cdot Br^-$ for spectrofluorometric determination of chromium (VI). Therefore, the present article reports the use of the produced non fluorescent ion associate $[TPP^+\cdot CrO_3Cl^-]$ of $TPP^+\cdot Br^-$ and chromium (VI) for developing a simple, convenient, and low cost spectrofluorometric method for determination and speciation of chromium (III, VI) species in water.

2. Experimental

2.1. Reagents and materials

All chemicals and solvents used were of analytical reagent grade and were used without further purification. Stock solutions ($1000\,\mu g\,mL^{-1}$) of Cr (VI), Cr(III), As (V), MnO_4^-, NO_2^-, ClO_3^-, BrO_3^-, IO_3^- and H_2O_2 were prepared from the BDH chemicals (Poole, England) K_2CrO_4, $Cr(NO_3)_3$, $NaAsO_3$, $KMnO_4$, $NaNO_2$, $KClO_3$, $KBrO_3$, KIO_3 and H_2O_2, (30%, w/v) in water (100.0 mL), respectively. Solutions of other metal ions were prepared from their nitrate or chloride salts in deionized water. A stock solution (0.1%, w/v) of the reagent $TPP^+\cdot Br^-$ (Merk, Darmstadt, Germany) was prepared by dissolving the required weight in ethanol (3.0 mL) and the solution was completed to the mark with water.

2.2. Apparatus

All 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. The UV–visible (190–1100 nm) spectra were recorded on a Perkin-Elmer (model Lambda 25, USA) spectrophotometer with 10 mm (path width) quartz cell. A digital micropipette (Volac) and an Orion pH meter (model EA 940) were used for the preparation of more diluted chromium (VI) solutions and pH measurements, respectively. Deionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for preparation of solutions. A Perkin Elmer inductively coupled plasma–mass spectrometer (ICP–MS) Sciex model Elan DRC II (California, CT, USA) was used as a reference method for chromium determination at the optimum operational parameters (Table 1).

2.3. Recommended procedure

2.3.1. Recommended procedures for chromium (VI) determination

An appropriate concentration ($1–114\,\mu g\,L^{-1}$) of chromium (VI) in aqueous HCl ($0.5\,mol\,L^{-1}$) solution was transferred to a separating funnel (50.0 mL) containing the reagent $TPP^+\cdot Br^-$ (2.0 mL). The test solution was completed to the mark with deionized water (25 mL) and the reaction mixture was shaken twice with chloroform (2 × 2 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 242 and 305 nm, respectively against reagent blank. The quenched fluorescence intensity of the reagent $TPP^+\cdot Br^-$ by chromium (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 intensities of the $TPP^+\cdot Br^-$ reagent before and after addition of chromium (VI), respectively. A blank experiment was also carried out under the same experimental conditions.

2.3.2. Recommended procedure for chromium (III) determination

Aqueous solution (100.0 mL) containing chromium (III) ions 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 chromium (VI) in alkaline medium (KOH, $1.0\,mol\,L^{-1}$) containing H_2O_2 (2 mL, 10% w/v) [5] and boiling for 10 min. After cooling, the test solution was adjusted to the required acidity with HCl ($0.5\,mol\,L^{-1}$) and finally analyzed following the recommended procedures for chromium (VI) determination against the reagent blank under the same experimental conditions.

2.3.3. Chemical speciation of inorganic chromium (III) & (VI)

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

2.4. Applications

2.4.1. Analysis of chromium 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 0.0 with HCL and analyzed following the procedures of chromium (III) determination. The change of fluorescence intensity of the reagent $TPP^+\cdot Br^-$ by chromium added was evaluated and used for chromium determination via the linear plot of the standard addition. A blank sample was analyzed following the same digestion and analytical procedures.

2.4.2. Analysis of chromium 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-fold with rotary evaporator and finally digested

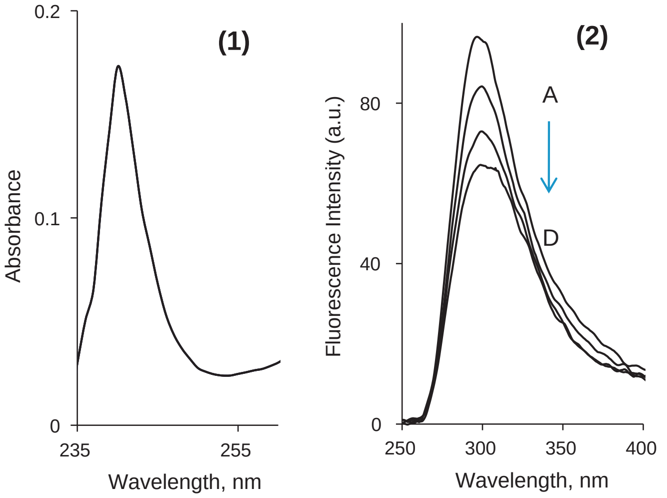

Fig. 1. UV–visible absorption spectrum (1) of TPP⁺·Br⁻ reagent and its emission spectra in chloroform (2) upon addition of various concentrations of chromium (VI): 0.00 (A); 5.0 (B), 20.0 (C) and 80.00 μg L^{-1} (D) at $\lambda_{ex/em}$ = 242/305 nm.

with concentrated nitric acid to remove the coexisting organic substances. The solution was adjusted to the required acidity and analyzed following the recommended procedures of chromium (III) determination. For the chemical speciation of chromium (III & VI), the sample solution was oxidized to chromium (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 chromium (III) and to remove excess H_2O_2. After centrifugation and filtration, an accurate volume (10 mL) of the sample was analyzed following the recommended procedure of chromium (VI) determination against a reagent blank. Chromium (III) species was obtained by subtracting the measured chromium (VI) from the total chromium content.

3. Results and discussion

On mixing chromium (VI) with the reagent TPP^+Br^- in aqueous HCl solution and shaking with chloroform, a yellow-colored complex ion-associate of the formula [$TPP^+ \cdot CrO_3Cl^-$] was developed [5]. In absence of chromium (VI), the reagent TPP^+Br^- has intense fluorescence at $\lambda_{ex/em}$ = 242/305 nm in chloroform phase and the formation of the ion associate [$TPP^+ \cdot CrO_3Cl^-$] caused fluorescence quenching at the same wavelength (Fig. 1). The fluorescence intensity of $TPP^+ \cdot Br^-$ was quenched on raising chromium (VI) concentration with negligible shift in the wavelength confirming the formation of the associate [$TPP^+ \cdot CrO_3Cl^-$] [5] in the ground electronic state. The absence of new emission band in the spectrum (Fig. 1) indicates that, the formed ion associate in the excited state does not exist under the experimental conditions [12]. Hence, the developed quenching was successfully used for developing a new spectrofluorometric method for determination of chromium (VI) and total inorganic chromium (III) & (VI) species in water.

3.1. Influence of analytical parameters

The effect of acidity on the fluorescence quenching of the ion associate was tested in H_2SO_4, HCl, HNO_3 or CH_3COOH (1.0 mol L^{-1}). Maximum and constant fluorescence quenching was achieved using HCl. Therefore, the effect of HCl concentration (0.1–2.0 mol L^{-1}) was critically studied. The results are shown in Fig. 2. Maximum and constant fluorescence quenching was achieved in HCl concentration in the range 0.4–0.6 mol L^{-1}. Thus, HCl was adjusted at 0.5 mol L^{-1} in the subsequent work.

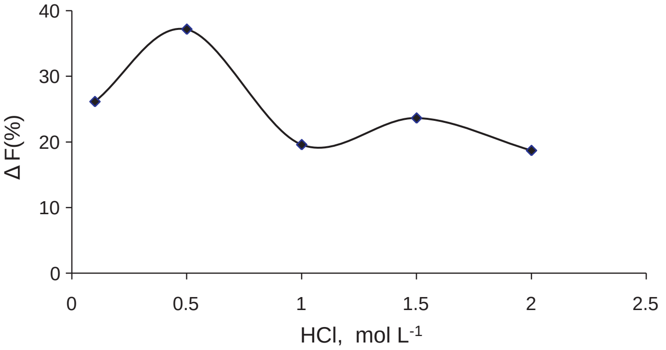

Fig. 2. Influence of HCl concentration (0.1–2.5 mol L^{-1}) on the fluorescence quenching of the ion associate.

The influence of shaking time on the fluorescence quenching intensity of the reagent $TPP^+ \cdot Br^-$ by the developed ion associate [$TPP^+ \cdot CrO_3Cl^-$] in the organic phase was investigated. Maximum and constant quenching intensity was achieved at 3 min shaking with $CHCl_3$ (Fig. 3). Thus, a shaking time of 3 min was adopted in the in the next work.

The influence of the reagent $TPP^+ \cdot Br^-$ concentration on the fluorescence intensity was investigated. Maximum and constant fluorescence intensity was achieved using 2.0 mL of the reagent (0.1%, w/v). High concentration of $TPP^+ \cdot Br^-$ makes the fluorescence quenching so small that it cannot be detected.

The extraction performance of the ion associate [$TPP^+ \cdot CrO_3Cl^-$] was tested in a series of organic solvents, e.g. *n*-hexane, dichloromethane, carbon tetrachloride, toluene, chloroform and methyl isobutyl ketone. The extraction performance of the ion associate increased in the following order: dichloromethane > chloroform > toluene > methyl isobutyl ketone > *n*-hexane ≈ carbon tetrachloride in agreement with the order of the dielectric constant. However, maximum extraction and constant fluorescence signal was achieved in chloroform. Therefore, chloroform was chosen as a preferred solvent.

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 chromium (VI) was considered as free from interfering species. Solutions containing 50.0 μg L^{-1} of chromium (VI) and the interfering species in different ratios were subjected to complete analysis. The results are summarized in Table 2. Complete extraction of chromium (VI) was achieved as indicated from the ICP-MS and fluorescence measurements. The anions BrO_3^-, IO_3^-,

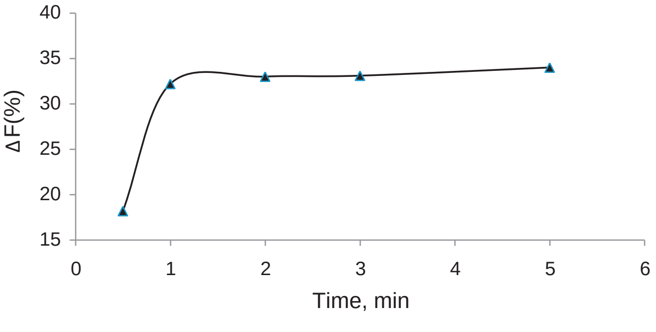

Fig. 3. Effect of shaking time on the fluorescence quenching of $TPP.^+Br^-$ in presence of chromium (VI) (100.0 μg L^{-1}) in aqueous solution of HCl (0.4–0.6 mol L^{-1}).

Table 2
Tolerance limits of interfering species in chromium (VI) (50.0 ng 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^{+}, $CO_3{}^{2-}$, $SO_4{}^{2-}$, $NO_3{}^{2-}$, CN^{-}	1000:1
Fe^{3+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Cl^{-}, F^{-},	100:1
$NO_2{}^{-}$, H_2O_2	50:1
$MnO_4{}^{-}$, $BrO_3{}^{-}$	5:1
$IO_3{}^{-}$	0.5:1

and $MnO_4{}^-$ interfered seriously with the fluorescence intensity of the $TPP^+{\cdot}Br^-$ reagent and chromium (VI) determination. 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). After this modification, the tolerance of the interfering ions was improved to acceptable limit (98 ± 2%). The results denoted that, the method has good selectivity even in the presence of high concentration of chromium (III) species. Thus, the method was found suitable for the chemical speciation of chromium (VI & III) in a variety of environmental water samples.

3.3. Figure of merits

Under the optimized experimental conditions, the plot of chromium (VI) concentration vs. fluorescence quenching by the formation of the ion associate $[TPP^+{\cdot}CrO_3Cl^-]$ was linear in the concentration range 1–114 μg L^{-1} (1.9×10^{-8} to 2.19×10^{-6} mol L^{-1}) with the regression equation:

$$\Delta I\,(\%) = 0.660\,C\,(\mu g\,L^{-1}) + 5.56$$

with a correlation coefficient of 0.998 ($n = 6$). Based on the IUPAC [13], the values of LOD and LOQ of chromium (VI) species were 0.43 and 1.42 μg L^{-1}, respectively. The relative standard deviation at concentration 15 μg L^{-1} chromium (VI) was ±1.6% ($n = 5$).

The fluorescence quenching of the reagent TPP by chromium (VI) added under the optimum experimental conditions suggested application of the $TPP^+{\cdot}Br^-$ reagent for the preconcentration and determination of chromium (VI) from large sample volumes of deionized water. Thus, aqueous solutions (0.5 L) of deionized water samples containing various concentrations (20.0–50.0 μg L^{-1}) of chromium (VI) and HCl (0.5.0 mol L^{-1}) were shaken with chloroform as described above. Analysis of aqueous solutions by ICP-MS against a reagent blank revealed complete extraction (96–98 ± 1.6) of chromium (VI). The concentration of chromium (VI) species in the organic phase was quantitatively determined (97% ± 2.6) by measuring the fluorescence quenching of $TPP^+{\cdot}Br^-$ in chloroform at optimum $\lambda_{ex/em}$. Chromium (III) species in aqueous solutions (0.1 L) in the concentrations range 0.05–50 μg mL^{-1} was also determined by the $TPP^+{\cdot}Br$ reagent after oxidation to chromium (VI) species as described. Satisfactory extraction percentage (96 ± 2.7–102 ± 1.9%, $n = 5$) of chromium (III) species was also achieved.

3.4. Analytical applications

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

The validation of the developed method was performed by the analysis of chromium in the certified reference materials (*IAEA Soil-7*). Good agreement between the total chromium content determined by the developed spectrofluorometric (55.7 ± 2.9 μg g^{-1}), and ICP-MS (58.4 ± 1.3 μg g^{-1}) methods and the recommended value (60 μg g^{-1}) based on dry weight in the range of 95% confidence interval (49–74 μg g^{-1}). These data demonstrated that, the described method is accurate and precise for trace analysis of chromium in complex matrices.

3.4.2. Analysis of chromium in water

The proposed method was applied for the chemical speciation of chromium (III & VI) in tap and wastewater samples. Total

Table 3
Analysis of chromium species in water by the developed pectrofluorimetric (A) and ICP MS (B) methods (mean ± standard deviation, $n = 5$).

Sample	Chromium added (μg L^{-1})		Chromium found (μg L^{-1})		Total chromium (μg L^{-1})		Total recovery (%)	
	Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}	A	B	A	B
Wastewater	–	–	642 ± 8.1	39.8 ± 3.4	682 ± 10.1	684 ± 6.4	–	–
	50	50	794.3 ± 9	90.1 ± 4.1	785.2 ± 8	783 ± 10.1	100.4 ± 1.02	99.9 ± 1.3
Tap water	–	–	10.47 ± 1.6	ND	10.47 ± 1.6	11 ± 1.2	–	–
	10	10	20.50 ± 2.1	9.85	30.40 ± 1.1	32 ± 1.3	99.7 ± 3.6	103 ± 4.1

Table 4
Figure of merits of the developed and some of the reported spectrofluorometric methods for chromium (μg L^{-1}) determination in water.

Method	Disadvantages	Linear range	LOD (μg L^{-1})	Reference
Cr^{6+} – PTQA	Low sensitivity, interference of Ag^+, Cr^{3+}, Fe^{3+}, Cu^{2+}	100–1.0×10^4	50	[14]
Cr^{6+} – 8-hydroxy quinoline-5-sulfonic acid benzophenone	Moderate sensitivity, low sensitivity with Pb^{2+}, Hg^{2+}, Ce^{4+}, Sc^{3+}, $BrO_3{}^-$	291–780	–	[15]
Magnetic Fe_3O_4/Py/PAM nanocomposite	Low sensitivity	100–14×10^3	10	[16]
Cr^{6+} – polyvinyl alcohol keto – derivatives nanoparticles	Low sensitivity	100–13×10^3	20	[17]
Cr^{6+} – rhodamine 6G	Interference of Cu^{2+}, Ce^{4+}, Sc^{3+}, $NO_2{}^-$	8.0–80	0.8	[18]
Cr^{6+} – quercetin	Interference of $MnO_4{}^-$, $BrO_3{}^-$, $IO_3{}^-$	5.2–104	0.47	[19]
Cr^{6+} – 1,4-diaminoanthraquinone	Interference of $MnO_4{}^-$, $BrO_3{}^-$, $IO_3{}^-$	5.2–208	0.12	[20]
Diperoxo chromium–ethylacetate extract	Time consuming, expensive, interference of $MnO_4{}^-$, $BrO_3{}^-$		0.2	[22]
Cr^{6+} – $TPP^+{\cdot}Br^-$	Interference of $MnO_4{}^-$, $BrO_3{}^-$, $IO_3{}^-$	1.0–114	0.42	Present work

chromium content in water samples was determined via the developed spectrofluorometric (A) and ICP-MS (B) methods (Table 3). The recovery percentage of the developed method was in good agreement with the data obtained by ICP-MS data and always higher than 95% confidence level (Table 3). These data confirm the precision of the proposed method and its independence from matrix interference. Statistical treatment of data using *F* test [13] 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 [13] was also applied to the analytical data of the developed and ICP-MS methods. The results revealed that, no significance difference between the two methods, since the tabulated *t* value at 95% confidence limit is 2.306, while the calculated *t* value by applying Student *t*-test to the results of wastewater sample was found lesser (0.79) for five measurements.

4. Conclusion

The reagent $TPP^+ \cdot Br^-$ was successfully used for the chemical speciation of chromium (III, VI) species without previous separation step. The method has the following advantages: high selectivity, good reproducibility, stable fluorescence up to 4 h, simple spectrofluorimeter and procedure. The analytical merits of the proposed method were successfully compared with some of the reported spectrofluorometric methods [14–20,22] (Table 4). Most of the reported methods exhibited a relatively high LOD (10.0–50.0 $\mu g\,L^{-1}$) [14,16,17], and serious interferences of Ag^+, Hg^{2+}, Pb^{2+}, Cr^{3+}, and Ni^{2+} [18–20]. The method provides LOD lower than the maximum allowable level (50.0 $\mu g\,L^{-1}$) of chromium recommended by WHO [21].

Acknowledgement

The authors would like to thank the Deanship of Scientific Research, King Abdul Aziz University, Kingdom of Saudi Arabia forthe financial support under the grant number 3 -108 - 430 and Mr. Mr. O. N. Rathaw (Chairman of the Chemistry Department, University College, Umm Al-QuraUniversity) for his support and excellent advices.

References

[1] K. Umesh, M.P. Kaur, D. Sud, V.K. Gary, Desalinization 249 (2009) 475.
[2] A. Zhenga, J. Chenb, G. Wub, G. Wua, Y.G. Zhangb, H.P. Wei, Spectrochim. Acta A 74 (2009) 265.
[3] M.M. Araujo, J.A. Teixeira, Int. Biodeteriorat. Biodegrad. 40 (1) (1997) 63.
[4] P.K. Ghosh, J. Hazard. Mater. 171 (2009) 116.
[5] M.S. El-Shahawi, S.S.M. Hassanb, A.M. Othmanc, M.A. Zyadaa, M.A. El-Sonbati, Anal. Chim. Acta 534 (2005) 319.
[6] M. Narin, M. Soylak, K. Kayakirilmaz, L. Elci, M. Dogan, Anal. Lett. 35 (2002) 1437.
[7] M. Tuzen, M. Soylak, J. Hazard. Mater. 129 (2006) 266.
[8] P. Singer, A. Melissa, J.H. Aldstadt, Microchem. J. 74 (2003) 47.
[9] Y.R. Li, N.K. Pradhan, R. Foley, G.K.C. Low, Talanta 57 (2002) 1143.
[10] X.S. Zhu, B. Hu, Z.C. Jiang, M.F. Li, Water Res. 39 (2005) 589.
[11] O. Dominguez, M.J. Arcos, Anal. Chim. Acta 470 (2002) 241.
[12] P.M. Jayaweeraa, T. Sanjeewaa, K. Tennakone, Solar Energy Mater. Solar Cell. 91 (2007) 944.
[13] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, 4th Edn., Ellis Horwood, New York, 1994, p. p.115.
[14] E.K. Paleologos, S.I. Lafis, S.M. Tzouwara-Karayanni, M.I. Karayannis, Analyst 123 (1998) 1005.
[15] N.Q. Jie, J. Jiang, Analyst 116 (1991) 395.
[16] S. Hong, H. Chen, L. Wang, Lun Wang, Spectrochim. Acta A 70 (2008) 449.
[17] S. She, Y. Zhou, L. Zhang, L. Wang, L. Wang, Spectrochim. Acta A 62 (2005) 711.
[18] N. Jie, Q. Zhang, J. Yang, X. Huang, Talanta 46 (1998) 215.
[19] M.S. Hosseini, F. Belador, J. Hazard. Mater. 165 (2009) 1062.
[20] M.S. Hosseini, M. Asadi, Anal. Sci. 25 (2009) 807.
[21] WHO Guidelines for Drinking Water Quality, World Health Organization, Geneva, 2003.
[22] A. Beni, R. Karosi, J. Posta, Microchem. J. 85 (2007) 103.