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A novel flow injection chemiluminescence determination of Cr(VI) with Dichlorotris(1,10-phenanthroline)ruthenium(II)

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ABSTRACT

A selective novel reverse flow injection system with chemiluminescence detection (rFI-CL) for the determination of Cr(VI) in presence of Cr(III) with Dichlorotris (1,10-phenanthroline)ruthenium(II), (Ru(phen)$_3$Cl$_2$), is described in this work. This new method is based on the oxidation capacity of Cr(VI) in H_2SO_4 media. First, the Ruthenium(II) complex is oxidized to Ruthenium(III) complex by Cr(VI) and afterwards it is reduced to the excited state of the Ruthenium(II) complex by a sodium oxalate solution, emitting light inside the detector. The intensity of chemiluminescence (CL) is proportional to the concentration of Cr(VI) and, under optimum conditions, it can be determined over the range of 3–300 $\mu g\,L^{-1}$ with a detection limit of 0.9 $\mu g\,L^{-1}$. The RSD was 8.4% and 1.5% at 5 and 50 $\mu g\,L^{-1}$, respectively. For the rFI-CL method various analytical parameters were optimized: flow rate (1 $mL\,min^{-1}$), H_2SO_4 carrier concentration (20% w/V), Ru(phen)$_3$Cl$_2$ concentration (5 mM) and sodium oxalate concentration (0.1 M). The effect of Cr(III), Fe(III), Al(III), Cd(II), Zn(II), Hg(II), Pb(II), Ca(II) and Mg(II), was studied. The method is highly sensitive and selective, allowing a fast, on-line determination of Cr(VI) in the presence of Cr(III). Finally, the method was tested in four different water samples (tap, reservoir, well and mineral), with good recovery percentage.

1. Introduction

Chromium is common in nature, existing in various chemical, physical and morphological forms. Usually, surface and underground water contain very low levels of chromium (typical concentration range: 0.1–0.5 $\mu g\,L^{-1}$), but wastewater coming from steel, leather and textile industries exhibits much higher levels. In aqueous solution chromium exists essentially in its trivalent and hexavalent forms, being the biological effects of both species drastically different. Cr(III) is considered an essential trace element in mammals for the maintenance of glucose, cholesterol and fatty acid metabolism. In contrast, Cr(VI) is approximately 100 times more toxic, has adverse effects on the lung, liver and kidneys and it has been classified as a human carcinogen by the U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) [1]. Both oxidation states are regulated through the Dangerous Substances Directive (67/548/EEC) [2]. Therefore, EPA has regulated the maximum level allowed at 100 $\mu g\,L^{-1}$ and 50 $\mu g\,L^{-1}$ for total chromium and Cr(VI), respectively, in natural waters [3].

Most of the procedures usually employed for Cr(VI) determination involve one step separation by solid-phase extraction [4], high performance liquid chromatography [5–7] or capillary electrophoresis [8] coupled to specific detectors including atomic spectrophotometry [4,9] and plasma mass spectrometry [5,10]. Other authors use indirect determination of Cr(VI) based on the quantification of total chromium and Cr(III) with luminol or lucigenin being hexavalent chromium determined by difference [11,12].

Few authors determine Cr(VI) directly, among them Dasgupta et al. [13], through its selective reaction with diphenylcarbazide (DPC) using a long path length vis–UV spectrophotometric detector with a non-commercial portable flow-injection analyzer. Based on the same reaction, Scindia et al. [14] described a membrane optode that can be used only one time due to the irreversibility of Cr(VI)–DPC reaction.

Hassan et al. [15] determine Cr(VI) by luminescence quenching of tris(2,2′-bipyridyl) ruthenium(II), but its detection limit is too high to determine the maximum amounts allowed by the legislation for Cr(VI) in natural waters.

Recently a direct determination of Cr(VI) in water, based on a bath mode extractive spectrofluorimetric method with chloroform as solvent, has been reported [16], but it is a time consuming method.

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Chemiluminescence (CL) is an attractive means of detection because it presents low detection limits a wide linear working range and uses relatively simple instrumentation [17]. Ruthenium(II) complexes, such as tris(2,2′-bipyridyl)–ruthenium(II) [Ru(bpy)$_3{}^{2+}$] [18] and tris(1,10-phenanthroline)–ruthenium(II) [Ru(phen)$_3{}^{2+}$] are among the reagents most frequently used for the generation of CL. Comparison between them as chemiluminescent reagents in aqueous solution has been reported in recent years and there are conflicting reports about the relationship between the nature of the Ru complexes and their Cl emission intensity [19]. These authors support previous observations [20,21] regarding the fact that [Ru(phen)$_3{}^{2+}$] provides greater CL intensity when the reducing agent is oxalate.

In this work, it is reported that a strong CL signal, higher than that provided by [Ru(bpy)$_3{}^{2+}$], is generated when Cr(VI) is mixed with Ru(phen)$_3{}^{2+}$ and $C_2O_4{}^{2-}$ in sulfuric medium. Under the same conditions, Cr(III) does not display CL behavior. Based on these observations, a new reverse flow injection chemiluminescence (rFI-CL) method is developed for the determination of Cr(VI) using [Ru(phen)$_3{}^{2+}$]. The various parameters that affect the CL signal were carefully optimized. The method is highly sensitive and selective, allowing a fast (up to 30 injections per hour), on-line determination of Cr(VI) in the presence of 100-fold excess of Cr(III). The developed rFIA procedure was applied to the determination of Cr(VI) in different water samples.

2. Experimental

2.1. Reagents

Dichlorotris(1,10-phenanthroline)–ruthenium(II) (Ru(phen)$_3$Cl$_2$) was obtained from Aldrich with 98% purity. Stock standard (10^{-2} M) solutions were prepared by dissolving 0.1782 g of Ru(phen)$_3$Cl$_2$ in 25 mL of a 20% H_2SO_4 solution. Sodium oxalate, sulfuric acid and potassium dichromate were obtained in analytical grade from Merck.

The stock standard solution of Cr(VI) (100 mg L^{-1}) was prepared by dissolving the appropriate amount of $K_2Cr_2O_7$ and diluting to 100 mL with Milli-Q water. The cation solutions of Cr(III), Fe(III), Al (III), Cd(II), Zn(II), Hg(II), Sn(II), Pb(II), Ca(II) and Mg(II) used in the study of interferences were prepared by appropriate dilution of 1000 mg L^{-1} stock solutions.

All solutions were prepared just before use and in Milli-Q water (18.2 MΩ/cm^2).

2.2. Instrumentation

A peristaltic pump (Spetec Perimax (Erding, Germany)) was used to deliver all the chemicals. An injection valve (Omnifit, Cambridge, UK) with several sample loops was used for the injection of the Ru(phen)$_3$Cl$_2$ solution. The tygon tubes (1.2 mm i.d.) were obtained from Scharlab (Madrid, Spain). CL measurements were made with a Jasco CL-2027Plus chemiluminescence detector connected to Interface Jasco LC-Net II/ADC (Jasco Analítica, Madrid, Spain) and equipped with a flow cell, made by coiling 20 cm of colorless teflon tubing (1 mm i.d.) into a spiral disk shape, which was located directly facing the window of the photomultiplier tube.

2.3. Procedures

2.3.1. Rate of oxidation reaction of ruthenium(II) complex

The kinetics of the oxidation reaction of the ruthenium(II) complex by Cr(VI) was studied using the following procedure: 2.5 mL of a 10 mM solution of the complex were mixed in a vial with 50 μL of a 1 mg L^{-1} standard solution of Cr(VI) and with 2.4 mL of H_2SO_4 (20%). The mixture was shaken vigorously during 30 s and 100 μL was injected every 2.5 min in the flow injection system shown in Fig. 1, with H_2SO_4 (20%) flowing in channel a, water flowing in channel b, oxalate in channel c and without the reaction coil e.

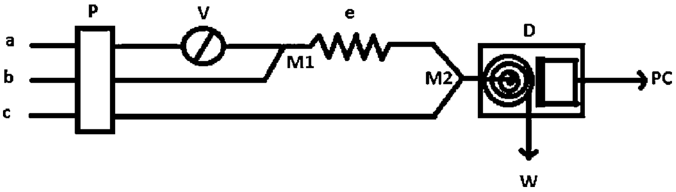

Fig. 1. Schematic diagram of the FI-CL system—M1, M2: merging points; V: injection valve; P: peristaltic pump; PC: personal computer; D: chemiluminescence detector with spiral colorless teflon tubing flow cell and photomultiplier tube; a: carrier H_2SO_4 20%; b: samples or standard solutions; c: sodium oxalate solution 0.1 M; e: reaction coil (3 m); W: waste.

2.3.2. rFI-CL method

After its injection in the rFI-CL system shown in Fig. 1, the reagent is mixed with samples or standard solutions (channel b) in the first merging point (M1), and it is oxidized to the ruthenium(III) complex by Cr(VI) in reaction coil (e). Just before entering the detector, the ruthenium(III) complex is mixed in the second merging point (M2) with the oxalate solution (channel c), and it is reduced to the excited state of the ruthenium(II) complex, emitting light inside the detector. The measured luminescence intensity is a function of Cr(VI) concentration.

3. Results and discussion

3.1. Preliminary study of oxidation reaction rate of tris(1,10-phenanthroline)ruthenium(II)

To obtain a preliminary idea of the rate of the oxidation reaction of tris(1,10-phenanthroline)ruthenium(II) to tris(1,10-phenanthroline)ruthenium(III) by Cr(VI) in sulfuric medium, the change in the intensity of CL was studied as a function of reaction time, following the procedure described in Section 2.3. As shown in Fig. 2, the intensity remains constant only after the reaction has proceeded for 14 min. This indicates that it is rather slow, therefore requiring a relatively long reaction coil and a strict control of the flow rate in order to obtain greater interaction between the reagents.

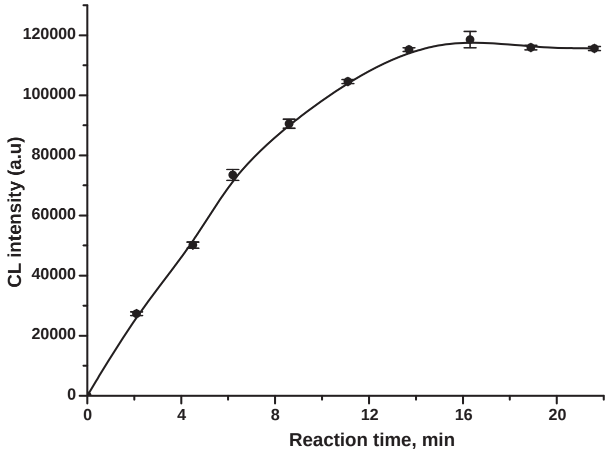

Fig. 2. Influence of the oxidation reaction time on the CL intensity.

3.2. *Optimization of experimental parameters*

Experiments were carried out to establish the optimum experimental conditions, employing a Cr(VI) solution of 100 μg L^{-1}. This study was carried out varying each parameter one at a time, while the others were maintained constant.

3.2.1. *Effect of flow rate, injection volume, length of reaction coil and distance to detector*

In order to allow the oxidation reaction to proceed in a large extent and so that the delivered sample reaches the detector at the point of maximum CL signal, the flow rate was optimized.

Flow rates per channel from 0.5 to 3 mL min^{-1} were studied, using a 3 m reaction coil (Fig. 1). The results showed that when the flow rate decreased, allowing longer reagent contact, CL signal increased; but for very slow flow rates the CL signal peak is too wide and the total time of analysis is too long. For these reasons, 1 mL min^{-1} was selected as optimum.

The injection volumes studied varied from 20 to 200 μL of the reagent, resulting 80 μL as the optimum signal to blank ratio. Larger volumes produced wider peaks, while smaller ones decreased the sensitivity.

In order to select the most convenient length of the reaction coil, reactors of 1, 2 and 3 m were used with a flow rate of 1 mL min^{-1}. The maximum CL intensity was obtained when the reaction coil was 3 m long. Longer reaction coils produce wider FI peaks. The 3 m coil was selected for further experiments.

The distance between merging point M2 and the detector was also studied, in a range from 1 to 20 cm, while using a 3 m reactor and a flow rate of 1 mL min^{-1}. The smallest distance, 1 cm, resulted the optimum and was selected.

3.2.2. *Effect of concentration of sulfuric acid in the carrier solution*

As it is well known, the oxidation potential of Cr(VI) increases when the proton concentration increases. The influence of H_2SO_4 present in the carrier solution was investigated over the range 10–40%, maintaining constant the concentrations of Ru(phen)$_3{}^{2+}$ and Cr(VI), 1 mM and 100 μg L^{-1}, respectively. The oxalate concentration was 0.1 M. The optimal signal to blank ratio was found at 20% of sulfuric acid. At lower concentrations a decrease in this relation was observed, while the use of a carrier solution over 20% produces an unstable signal probably due to the increase in the temperature when this highly concentrated solution is merged with the samples or the standards in the first merging point (Fig. 1).

3.2.3. *Effect of tris(1,10 phenantroline)ruthenium(II) concentration*

It is well known that in the CL system containing Ru(phen)$_3{}^{2+}$, the CL is due to the reaction of Ru(phen)$_3{}^{3+}$ with reductants (intermediate radicals) to give [Ru(phen)$_3{}^{2+}$]* [22]. In order to obtain Ru(phen)$_3{}^{3+}$ several oxidants, such as Ce(IV) [22] and $S_2O_8{}^{2-}$ [23], have been used. Based on these redox characteristics, in the present work the analyte itself, Cr(VI), is used as oxidant, something which has not been reported. A possible reaction mechanism is the following:

$$6\,\mathrm{Ru(phen)_3}^{2+} + \mathrm{Cr_2O_7}^{2-} + 14\,\mathrm{H}^+ \rightarrow 6\,\mathrm{Ru(phen)_3}^{3+} + 2\,\mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \quad (1)$$

$$\mathrm{Ru(phen)_3}^{3+} + \mathrm{C_2O_4}^{2-} \rightarrow \mathrm{Ru(phen)_3}^{2+} + \mathrm{C_2O_4}^{-\bullet}$$

$$\mathrm{C_2O_4}^{-\bullet} \rightarrow \mathrm{CO_2}^{-\bullet} + \mathrm{CO_2} \quad (2)$$

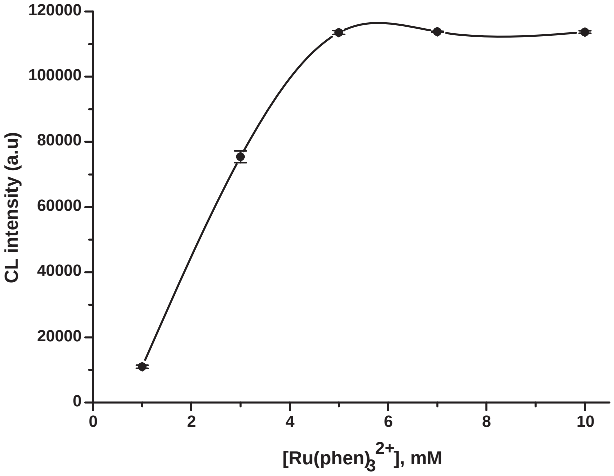

Fig. 3. Influence of Ru(phen)$_3{}^{2+}$ concentration on the CL intensity.

$$\mathrm{Ru(phen)_3}^{3+} + \mathrm{CO_2}^{-\bullet} \rightarrow \mathrm{Ru(phen)_3}^{2+}* + \mathrm{CO_2}$$

$$\mathrm{Ru(phen)_3}^{2+}* \rightarrow \mathrm{Ru(phen)_3}^{2+} + h\nu \quad (3)$$

In the proposed mechanism, [Ru(phen)$_3{}^{2+}$]* is the luminophor responsible of the emission [22]. So, the effect of its concentration on CL was investigated. Solutions containing increasing concentrations of Ru(phen)$_3{}^{2+}$ in the range from 1 mM to 10 mM were studied keeping the oxalate and Cr(VI) concentrations constant, 0.1 M and 100 μg L^{-1}, respectively. As is shown in Fig. 3, the intensity of CL increases with increasing Ru(phen)$_3{}^{2+}$ concentration, up to 5 mM, being constant at higher values of concentration. This concentration is a very critical aspect because it determines, together with the acid media, the kinetics of the oxidation reaction of the ruthenium(II) complex. If a concentration lower than 1 mM was used, the reaction coil should be lengthened in order to increase the reaction time. An optimum concentration of 5 mM of Ru(phen)$_3{}^{2+}$ was used throughout this study.

3.2.4. *Effect of oxalate concentration*

The influence of $C_2O_4{}^{2-}$ concentration on CL was studied at constant concentrations of Ru(phen)$_3{}^{2+}$ and Cr(VI), 5 mM and 50 μg L^{-1}, respectively. The range studied was from 10 to 120 mM, and the highest CL signal to blank ratio was obtained when the reagent concentration was 100 mM (Fig. 4).

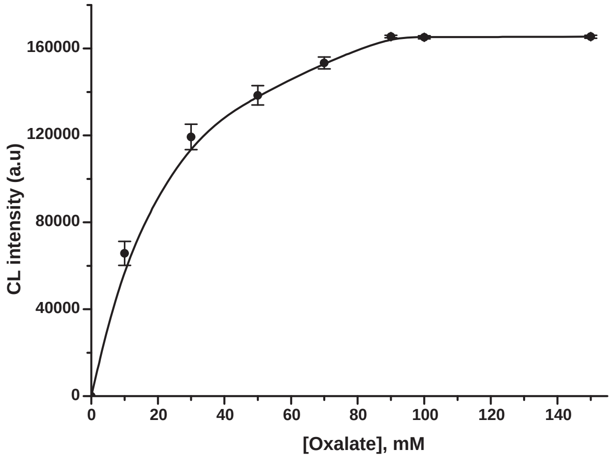

Fig. 4. Dependence of the CL intensity with oxalate concentration.

Table 1
Optimum FI-CL experimental conditions.

Parameter	Range studied	Optimum value
$Ru(phen)_3{}^{2+}$ concentration (mM)	1–10	5
Oxalate concentration (mM)	10–120	100
Flow rate per channel (mL min^{-1})	0.5–3	1
Carrier concentration (H_2SO_4) (%)	10–40	20
Injection volume (μL)	20–200	80
Distance from M2 to detector (cm)	1–20	1
Length of reaction coil (m)	1–3	3

Table 1 shows the selected optimum experimental conditions for the FI-CL method.

3.3. Analytical performance

3.3.1. Calibration curve, limit of detection and precision

Based on the optimized experimental conditions described above, a calibration curve for the determination of Cr(VI) was obtained. Cr(VI) solutions up to 50 μg L^{-1} were prepared in aqueous medium and were measured following the procedure presented in Section 2.3. By plotting CL intensities as a function of Cr(VI) concentration, non-linear calibrations graphs were obtained. The data can be adjusted to the following exponential function:

$$I_{CL} = a\,e^{x/b} + c$$

being $a = (1.27 \pm 0.05) \times 10^4$, $b = 36.6 \pm 0.9$, $c = (-1.21 \pm 0.06) \times 10^4$ and x the analyte concentration expressed in μg L^{-1}. The correlation coefficient was 0.9998. Fig. 5(a) and (b) shows the fiagram and the calibration curve obtained, respectively.

The relative standard deviation for 5 μg L^{-1} and 20 μg L^{-1} of Cr(VI) was 8.4% and 1.5%, respectively ($n = 5$).

The limit of detection, calculated as the concentration of Cr(VI) that produces an analytical signal three times the standard deviation of the blank, was 0.9 μg L^{-1}.

3.3.2. Influence of interfering species

In order to study the selectivity of the FI-CL method for the determination of Cr(VI), the effect of some common metal ions on CL intensity was studied. The CL signals of a Cr(VI) solution and of Cr(VI) solutions that contain each foreign species were compared. When the effect of the foreign species on the peak area was less than ±3 s, being s the standard deviation of Cr(VI) in the absence of interfering ion, the ion was considered non-interfering. The experimental results indicated that for 25 μg L^{-1} of Cr(VI), up to 100 times excess of Cr(III), Fe(III), Cd(II), Zn(II), Sn(II), and Pb(II) do not interfere and 10 times excess of Hg(II) and Al(III) are also tolerated. Ca(II) and Mg(II) were tolerated when present at levels up to 1000-fold excess over Cr(VI). This procedure has been designed for natural waters with low contents of organic compounds; therefore the samples were analyzed without previous treatment. At low concentrations of organic concomitants their influence can be taken into account in the matrix effect and corrected using the standard addition method proposed.

3.4. Analysis of natural water samples

Different, well, reservoir, mineral and tap water samples, collected in several zones near Madrid and containing no Cr(VI) according to ICP-AES and AAS results, were used for the preparation of calibration curves. These were then compared with an external calibration prepared in Milli-Q water. The obtained curves are shown in Fig. 6 and, as can be seen in Table 2, they adjust to an exponential equation. The different coefficients obtained clearly show there is a strong matrix effect.

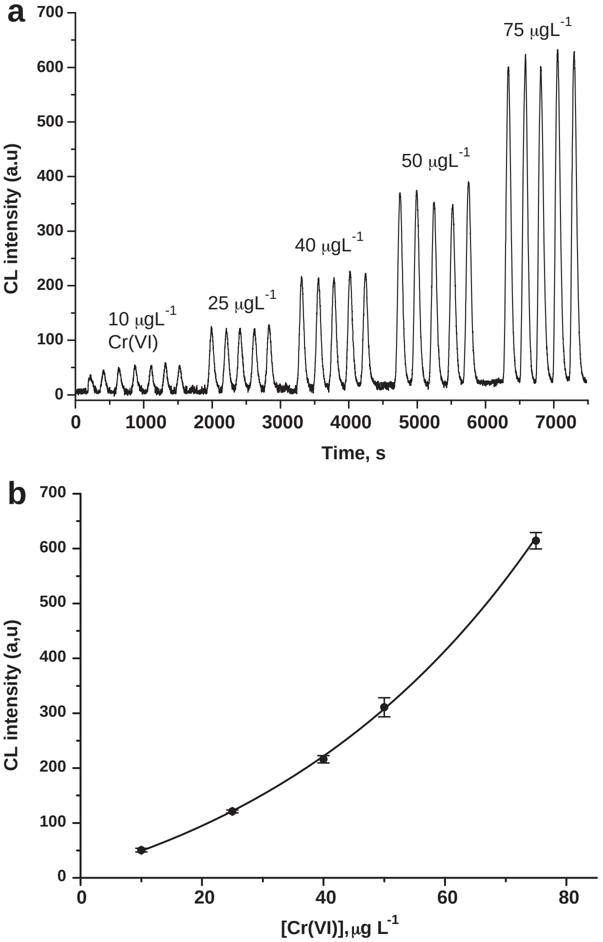

Fig. 5. Diagram (a) and calibration curve (b), obtained in optimum experimental conditions.

Now, in order to demonstrate the reliability of the proposed FI-CL method, the original samples, containing no chromium, were spiked with different quantities and a standard addition procedure was used for the determinations. According to Koscielniak [24] this procedure is especially useful if the calibration dependence, i.e. the analytical signal vs. the analyte concentration, is linear. If not, special caution against employment is suggested. These authors

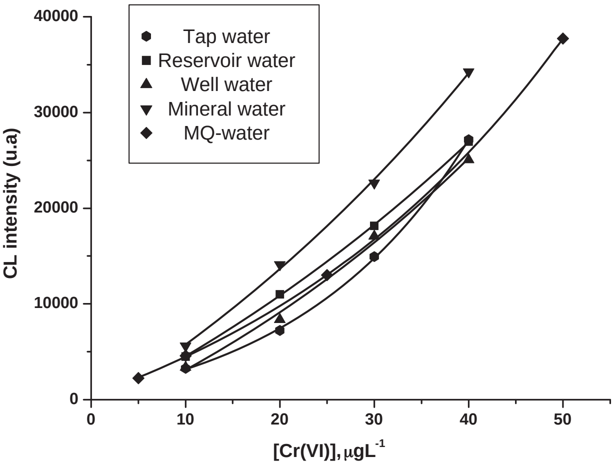

Fig. 6. Calibration curve in presence of different water samples.

Table 2
Different coefficients of exponential functions due to matrix effect.

Matrix	Coefficient of exponential function	Value ± standard deviation	*R*-Square
Milli-Q water	*c*	$(-1.2 \pm 0.6)\ 10^4$	0.9999
	a	$(1.3 \pm 0.6)\ 10^4$	
	b	$(3.7 \pm 0.1)\ 10$	
Tap water	*c*	$(-4.1 \pm 0.8)\ 10^3$	0.9991
	a	$(4.3 \pm 0.6)\ 10^3$	
	b	$(2.0 \pm 0.1)\ 10$	
Reservoir water	*c*	$(-2.3 \pm 0.4)\ 10^4$	0.9993
	a	$(2.3 \pm 0.4)\ 10^4$	
	b	$(5.1 \pm 0.5)\ 10$	
Well water	*c*	$(-1.3 \pm 0.7)\ 10^4$	0.9916
	a	$(1.3 \pm 0.6)\ 10^4$	
	b	$(3.6 \pm 0.9)\ 10$	
Mineral water	*c*	$(-2.8 \pm 0.7)\ 10^4$	0.9986
	a	$(2.8 \pm 0.6)\ 10^4$	
	b	$(4.9 \pm 0.8)\ 10$	

Table 3
Percentage (%) recoveries in water samples.

Water sample	Cr(VI) added ($\mu g\ L^{-1}$)	Cr(VI) found ($\mu g\ L^{-1}$)	% Recovery	RSD
Reservoir	10	8.30	83.0	7.2
	20	18.4	91.4	5.1
	30	28.3	94.3	3.4
	40	38.3	95.8	3.6
Well	10	8.95	89.5	4.1
	20	18.8	94.4	5.5
	30	28.8	96.0	3.5
	40	38.7	96.8	2.6
Tap	10	13.6	136	7.3
	20	23.6	118	7.1
	30	33.6	112	5.2
	40	41.6	104	1.8
Mineral	10	8.60	86.0	4.3
	20	18.7	93.0	2.7
	30	28.6	95.3	3.1
	40	38.7	96.7	1.6

recommend the standard addition method if the curvature of the represented function is not very sharp, as is our case.

The water samples were stored without adjustment of pH (the pH of sample solution as received was 6.5) because usual acidification would change the chromium chemical species. The concentrations were obtained by applying the following extrapolation:

$$\mathrm{Xo} = b \ln\left(\frac{-c}{a}\right)$$

The results are satisfactory and are summarized in Table 3. In all the cases, the recoveries of Cr(VI) were found to be >83%.

4. Conclusions

The proposed FI-CL method for the direct determination of Cr(VI) is very sensitive, with a limit of detection of $0.9\ \mu g\ L^{-1}$, and is therefore among the more sensitive methods for hexavalent chromium found in the literature. It allows the determination of contents of this species at the maximum permissible level of concentration ($50\ \mu g\ L^{-1}$) recommended by EPA. The results obtained in this study show that it is possible to determine Cr(VI) with the proposed rFI-CL method in natural waters. On the other hand, it is important to highlight that this can be done in the presence of a 100-fold excess of Cr(III), which confers the method the possibility of determining the most toxic chromium species directly. Furthermore, the instrumentation is simple, no pretreatment of water samples is necessary and it is fast, since up to 30 injections per hour can be made.

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References

[1] USEPA (Ed.), Environmental Engineering: Environmental Health and Safety for Municipal Infrastructure, Land Use and Planing and Industry, U.S. Government Printing Office, Washington, 1998.
[2] Official Journal of the European Communities, Council Directive 67/548/EEC of 27 June, 1967.
[3] N. Unceta, F. Séby, J. Malherbe, O.F.X. Donard, Anal. Bioanal. Chem. 397 (2010) 1097–1111.
[4] J. Chwastowska, W. Skwara, E. Sterlinska, L. Pszonicki, Talanta 66 (2005) 1345–1349.
[5] H. Hagendorfer, W. Goessler, Talanta 76 (2008) 656–661.
[6] S. Cathum, C.E. Brown, W. Wong, Anal. Bioanal. Chem. 373 (2002) 103–110.
[7] S. Meseguer-Lloret, P. Campíns-Falco, L.A. Tortajada-Genaro, F. Blasco-Gomez, Int. J. Environ. Anal. Chem. 85 (2003) 405–416.
[8] M. King, M. Macka, B. Paull, Anal. Lett. 37 (2004) 2771–2787.
[9] L. Machckova, M. Semberyova, Int. J. Environ. Anal. Chem. 89 (2009) 705–715.
[10] N.N. Meeravali, J.S. Jen, Talanta 80 (2009) 173–178.
[11] W. Som-Aum, J. Threeprom, H. Li, J.M. Lin, Talanta 71 (2007) 2062–2068.
[12] D. Jian-Xiu, L. Yin-Huan, R. Guan, Microchim. Acta 158 (2007) 145–150.
[13] Q. Li, K.J. Morris, P.K. Dasgupta, I.M. Raimundo, H. Tenkin, Anal. Chim. Acta 479 (2003) 151–165.
[14] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, S.B. Manohar, Anal. Chim. Acta 515 (2004) 311–321.
[15] S.S.M. Hassan, A.A. Abdel-Shafi, A.H.K. Mohammed, Talanta 67 (2005) 696–702.
[16] M.S. El-Shahawi, H.M. Al-Saidi, A.S. Bashammakh, A.A. Al-Sibaai, M.A. Abdelfadeel, Talanta 84 (2011) 175–179.
[17] P. Fletcher, K.N. Andrew, A.C. Calokerinos, S. Forbes, P.J. Worsfold, Luminescence 16 (2001) 1–23.
[18] B.A. Gorman, P.S. Francis, N.W. Barnett, Analyst 131 (2006) 616–639.
[19] M.M. Cooke, E.H. Doeven, C.F. Hogan, J.L. Adcock, G.P. McDermott, X.A. Conlan, N.W. Barnett, F.M. Pfeffer, P.S. Francis, Anal. Chim. Acta 635 (2009) 94–101.
[20] M.M. Karim, S.H. Lee, H.S. Lee, Z.U. Bae, K.H. Choi, J. Fluoresc. 16 (2006) 535–540.
[21] B.H. Kim, D.N. Lee, H.J. Park, J.H. Min, Y.M. Jun, S.J. Park, W.-Y. Lee, Talanta 62 (2004) 595–602.
[22] F. Yu, F. Chen, L. Chen, Microchim. Acta 163 (2008) 297–303.
[23] F.E.O. Suliman, M.M. Al-Hinai, S.M.Z. Al-Kindy, S.B. Salama, Luminescence 24 (2009) 2–9.
[24] P. Koscielniak, Chemom. Intell. Lab. Syst. 47 (1999) 275–287.