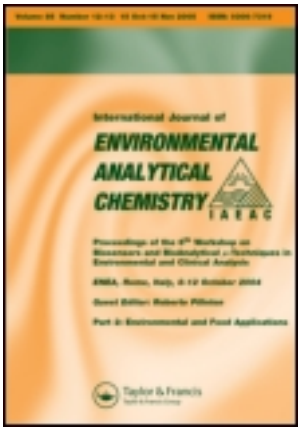

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Determination of trace amounts of chromium (VI) by flow injection analysis with chemiluminescence detection

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Determination of trace amounts of chromium (VI) by flow injection analysis with chemiluminescence detection

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A new sensitive chemiluminescence (CL) method combined with continuous flow injection analysis is described for the determination of Cr(VI). Strong CL signals were generated by Cr(VI)-catalysed oxidation of gallic acid in the presence of potassium permanganate and hydrogen peroxide. Effects of reagent concentrations, temperature, pH, flow rates, mixing coil length and mixing flow sequences on the chemiluminescence intensity were studied. Under the optimised experimental conditions, the relationship between the logarithm of concentration ($\log C$) of Cr(VI) and the logarithm of intensity ($\log I$) is linear over the range of $2 \times 10^{-11} - 5 \times 10^{-4}$ mol L^{-1}, with the detection limit (3σ) of 4×10^{-12} mol L^{-1}. Relative standard deviation of ten measurements of 1×10^{-9} mol L^{-1} Cr(VI) is 1.7%. This flow injection analysis (FIA) system proved to be able to analyse up to 40 samples h^{-1}. Effects of various interferences possibly present in the water samples were investigated. Most cations and anions, as well as organic compounds, did not interfere with the determination of Cr(VI) in water samples. The experimental results obtained for chromium in reference materials were also in good agreement with the certified values.

Keywords: chemiluminescence; flow injection analysis; trace amounts; Cr(VI)

1. Introduction

Chromium is an important element in environmental science and water pollution control. Natural levels of chromium in unpolluted water are below 3.8 μmol L^{-1} and its toxicity effects demand a maximum permissible chromium level of 9.6 μmol L^{-1} in drinking water [1]. Of its various oxidation states, Cr(VI) poses the greatest risk to human health because of its known toxicity, its high solubility in aqueous solutions and its relatively rapid mobility in soil and solid wastes. Cr(VI) is known to damage exposed skin, irritate mucous membranes, produce pulmonary sensitivity, create dental erosion, cause loss of weight, induce renal damage and target the respiratory tract and skin [2–4]. In addition, experimental evidence links Cr(VI) with various types of cancer [5]. Therefore, the direct determination of trace chromium species in environmental samples demands very sensitive analytical techniques.

Many detection protocols of Cr(VI) have been utilised by performing FIA-spectrophotometry [6], FIA-spectrofluorimetry [7], FIA-FAAS [8], FIA-fluorimetry [9], electroanalytical methods [10–14], and so on. However, the procedures are complex, time

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consuming and/or need a preconcentration step in these methods. Recently, chemiluminescence (CL) analysis has provided the basis for numerous assays of organic and inorganic species at trace level [15,16], for its low detection limit, wide linear working range and relative simple instrumentation [17]. Only a few CL systems are available for determination of chromium (III, VI); they were based on luminol [18–26], lucigenin [27], flavin mononucleotide [28] and pyrogallol [29] reactions. A comparison of the analytical performances between the previously reported techniques and the proposed method for the determination of Cr(VI) is summarised in Table 1. In this work determination of Cr(VI) by continuous flow injection analysis with chemiluminescence detection based on the catalysed effect of Cr(VI) on gallic acid–$KMnO_4$ and H_2O_2 system is described.

2. Experimental

2.1 *Reagents*

All the reagents used were of analytical-reagent grade and all solutions were prepared with doubly deionised water having resistivity higher than 18 $M\Omega cm^{-1}$. Standard stock solution (1×10^{-3} mol L^{-1}) of Cr(VI) was prepared by dissolving an appropriate amount of potassium dichromate (Tianjin Bohai Chemical Reagents Factory, China) in doubly deionised water. Standard working solutions of Cr(VI) were prepared in 1×10^{-3} mol L^{-1} ethylenediaminetetraacetic acid (North Beijing Fine Chemicals Co., China). EDTA was added to all sample solutions to remove the interference of other metal ions [22]. NaOH, gallic acid, $KMnO_4$, HCl, $HClO_4$ and HNO_3 were obtained from Tianjin Fuchen (Chemical Reagent Factory, China). Concentration of hydrogen peroxide (30%, Beijing Chemical Plant, China) in the stock solution was determined by titration using the thiosulfate-iodide method [30]. Resin used in this study was a strongly basic anion-exchange resin (Type 717, produced in China). Before using, the resin was first washed with water and soaked in 2 mol L^{-1} HCl overnight so as to convert it into Cl^- form, then it was washed with deionised water until it became neutral. Certified reference materials used in this work were BH1203-1 and BH1203-5, obtained from Dalian Steel Co., China. Standard working solutions were prepared by accurate dilution of the standard stock solution just before use. All glassware were cleaned with 10% (v/v) nitric acid and then rinsed with doubly distilled water before use.

2.2 *Apparatus*

Flow Injection Analysis Processor FIA-3110 (Beijing Titan Instruments Co., China) consists of two peristaltic pumps, a sixteen-hole eight-way valve and a digital-system to maintain the time of flow and pressure of each pump. The CL detection system is a computerised ultra-weak luminescence analyser (Type BPCL manufactured at the Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). Emitted CL light was measured with the photomultiplier tube (PMT, which is installed in the BPCL analyser) operating at 1080 V and 30°C with no wavelength discrimination. The BPCL analyser has a temperature control system, which can adjust the temperature of CL reaction chamber automatically. Resulting peaks were recorded with a FIA monitor/data processing apparatus. The CL spectra of the proposed system were obtained by a series of optical filters (425, 440, 460, 490, 515, 535, 555, 575, 595, 620, 640 nm).

Table 1. Comparison of various techniques for the determination of Cr(VI).

Detection technique (analyte species)	Reagent solution	Analytical ranges[a] (mol L^{-1})	Detection limit[a] (mol L^{-1})	Reference
FIA-spectrophotometry Cr(VI)	1,5 Diphenylcarbazide	1.92×10^{-6}–3.84×10^{-4}	1.5×10^{-8}	[6]
FIA-spectrofluorimetry Cr(III, VI)	8-Hydroxyquinoline	1.92×10^{-9}–9.6×10^{-9}	3.8×10^{-9}	[7]
FIA-FAAS Cr(III, VI)	8% NH_4NO_3		1×10^{-8}	[8]
FIA-flourimetry Cr(VI)	$[Ru(bpy)_3]^{2+}$	3.84×10^{-8}–1.92×10^{-6}	6.3×10^{-7}	[9]
FIA-ETAAS Cr(III, VI)	Formic acid	9.6×10^{-9}–1.15×10^{-7}	2.5×10^{-9}	[11]
IC-CL Cr(III,VI)	Luminol–H_2O_2	1.92×10^{-8}–7.69×10^{-6}	1.7×10^{-9}	[20]
CL Cr(III)	Luminol–H_2O_2		5×10^{-8}	[23]
FIA-CL Cr(III,VI)	Lucigenin	9.6×10^{-8}–1.92×10^{-6}	1.9×10^{-8}	[27]
CE-CL Cr(III,VI)	Luminol–H_2O_2	2×10^{-11}–5×10^{-9}	8×10^{-12}	[21]
FIA-CL Cr(VI)	Luminol–$Fe(CN)_6^{4-}$	7.7×10^{-7}–1.9×10^{-5}	2.7×10^{-7}	[26]
FIA-CL Cr(III,VI)	Flavin mononucleotide		5×10^{-8}	[28]
FIA-CL Cr(VI)	$KMnO_4$–gallic acid–H_2O_2	2×10^{-11}–5×10^{-4}	4×10^{-12}	This method

Note: [a]Analytical ranges and detection limits are provided only for Cr(VI).

A newly packed column was washed with deionised water to condition the column and to remove trace amounts of analyte from the ion-exchange material and the plastic foam. Column was regenerated after every 3 hours. This was done by washing the resin 3–5 times with 3 mol L^{-1} HCl and then 4–5 times with deionised water. Flow lines were made of PTFE tubing (0.5 mm i.d. Shenyang Zhaofa Institute of Automatic Analysis, China).

2.3 *Sample preparation*

Certified reference samples (0.1 g) were taken into beaker with about 12 mL HCl (36% v/v), 4 mL HNO_3 (65% v/v) and 1 mL $HClO_4$ (70% v/v) and boiled for about 30 minutes with regular stirring until the sample was completely decomposed. After the dissolved sample solution was cooled down to room temperature, 5 mL, 5 mol L^{-1} HCl was added to it for the iron to form anion complexes $FeCl_4^-$. Then the dissolved sample was eluted through the anion exchange column. In this way interference from the iron in the certified reference steel sample was eliminated by adsorption of $FeCl_4^-$. The effluent from the column was collected in a volumetric flask and diluted with doubly-deionised water so as to make the concentration of Cr(VI) within the detection range.

Tap waters were collected from our laboratory and hostel; lake waters were collected from different locations of South Lake, Changchun, China. All water samples were filtered through a 0.45 μm membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) and were stored at 4°C. Water samples must not be acidified before storage, because this would change the chemical species [31].

2.4 *Flow injection analysis procedure*

A schematic diagram of the FIA-CL system employed is presented in Figure 1 (sequence C). Quantities of 0.2 mol L^{-1} H_2O_2, 0.05 mol L^{-1} gallic acid and 0.02 mol L^{-1} $KMnO_4$ solutions were carried through pump A collectively, at a flow rate of 2.7 mL min^{-1}. Sample solution (prepared in 1×10^{-3} mol L^{-1} EDTA) was introduced to the reaction valve through pump B with loop volume of 150 μL, and flow rate of 0.9 mL min^{-1}. Finally, the mixture from pump A was taken to the reaction valve, from where this mixture along with the sample solution was carried to the chemiluminescent detection chamber. Running time for pump A was 30 s; for pump B it was 10 s.

For the flow injection analysis system described here, the minimum cycle time (load plus inject) necessary to prevent carry-over between successive samples is 50 s, which leads to maximum throughput rate of more than 40 samples h^{-1}.

3. Results and discussion

3.1 *Kinetic study of the proposed CL system*

Kinetic curves for different CL systems are shown in Figure 2. It is obvious from Figure 2 that very low or almost no CL signals were obtained for both $KMnO_4$–gallic acid (Figure 2a) and gallic acid–H_2O_2 (Figure 2b) systems. $KMnO_4$–gallic acid–Cr(VI) (Figure 2c) and gallic acid–H_2O_2–Cr(VI) (Figure 2d) systems produced higher CL signals, which is possibly due to the catalysis of Cr(VI). Addition of H_2O_2 to the $KMnO_4$–gallic acid system enhanced the CL intensity (Figure 2e). Further addition of Cr(VI) to the

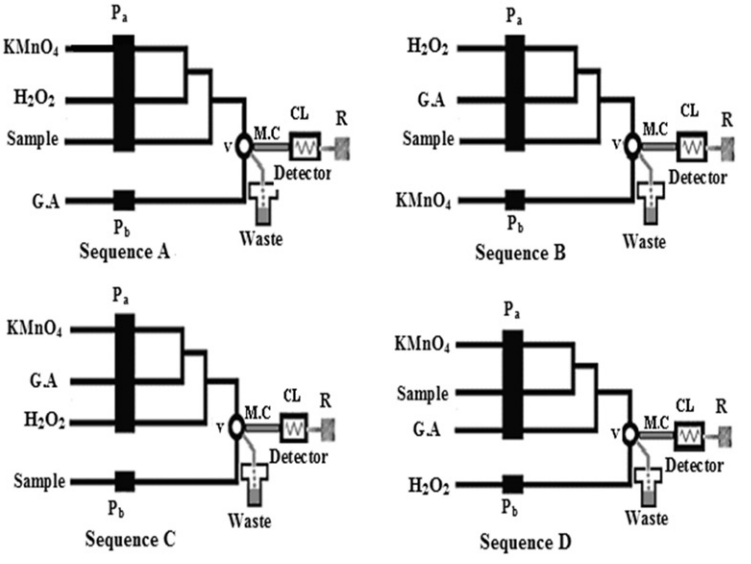

Figure 1. Various mixing sequences. 1×10^{-8} mol L^{-1} Cr(VI); 0.05 mol L^{-1} gallic acid; 0.02 mol L^{-1} $KMnO_4$; 0.2 mol L^{-1} H_2O_2; V, 8-way valve; M.C, Mixing Coil 10 cm; R, recorder; pump A = 2.7 mL min^{-1}; pump B = 0.9 mL min^{-1}.

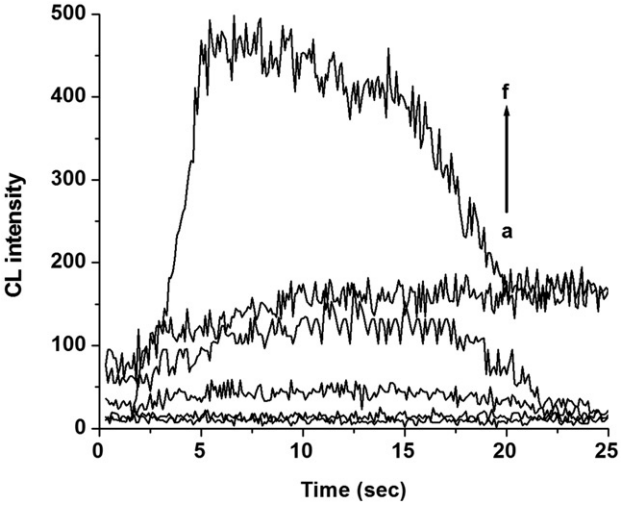

Figure 2. CL kinetic curves for the systems of $KMnO_4$–gallic acid (a); gallic acid–H_2O_2 (b); $KMnO_4$–gallic acid–Cr(VI) (c); gallic acid–H_2O_2–Cr(VI) (d); $KMnO_4$–gallic acid–H_2O_2 (e); $KMnO_4$–gallic acid–H_2O_2–Cr(VI) (f); Conditions: 1×10^{-9} mol L^{-1} Cr(VI); 0.05 mol L^{-1} gallic acid; 0.02 mol L^{-1} $KMnO_4$; 0.2 mol L^{-1} H_2O_2.

$KMnO_4$–gallic acid–H_2O_2 system enhanced the CL intensity greatly (Figure 2f), which indicates the catalysis of Cr(VI) on the $KMnO_4$–gallic acid–H_2O_2 CL system.

3.2 *Possible reaction mechanism*

CL phenomena of the oxidation of pyrogallol and other polyhydroxyl compounds with a variety of oxidants, such as molecular oxygen, hydrogen peroxide or periodate, in aqueous solution has been extensively investigated. It is generally accepted today that the CL-emission during oxidation of pyrogallol by H_2O_2 is due to the formation of $(^1O_2{}^*)_2$ which is formed through the collision of two peroxide species [32]. $(^1O_2{}^*)_2$ then transfers energy to the oxidized polyhydroxyl compound and generates CL [33–38].

Gallic acid, which has several phenolic hydroxyl groups, could also react similarly as pyrogallol. Gallic acid works as good receptor for oxygen from hydrogen peroxide [36].

Under the almost neutral conditions of the proposed FIA-CL system, the reductive product of $KMnO_4$ is MnO_2 rather than Mn^{2+} [32]. Therefore it is expected that CL is most probably produced from the oxidation products of gallic acid, this can also be confirmed via Figure 3. From Figure 3, it can be seen that the photoluminescence spectrum of gallic acid/H_2O_2 system matches the CL spectrum of the studied CL system, thus showing that the oxidation products of gallic acid actually generate CL within the studied CL system (the maximum peak of CL is at ~510 nm). Possible CL reaction mechanism is summarised as follows:

$$\text{G.A} + \text{permanganate} + H_2O_2 \xrightarrow{\text{Cr(VI)}} (^1O_2{}^*)_2 + \text{P} + MnO_2 + \text{other products}$$

$$(^1O^*{}_2)_2 + \text{P} \xrightarrow{\text{Energy Transfer}} 2\,^3O_2 + \text{P}^*$$

$$\text{P}^* \rightarrow \text{P} + h\nu$$

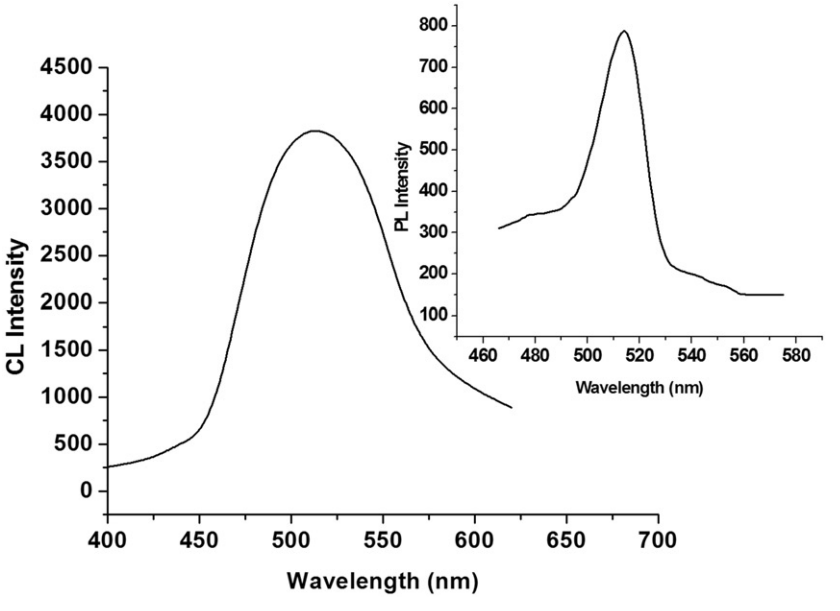

Figure 3. CL spectrum of the proposed CL system, inset shows the PL spectrum for gallic acid–H_2O_2 system.

where G.A denotes gallic acid, P stands for oxidation products of gallic acid and P* represents excited state of oxidation products of gallic acid.

Based upon above discussion about kinetic study and possible reaction mechanism of proposed CL system, it is clear that Cr(VI) act as catalyser of the CL reaction of $KMnO_4$–gallic acid–H_2O_2 system, resulting in the production of $(^1O_2^*)_2$. $(^1O_2^*)_2$ transfers its energy to oxidation product of gallic acid and forms P*, which returns to ground state under emission of CL radiation.

3.3 *Optimisation of flow system*

During the optimisation, effects of flow rates of liquids as well as concentration of reagents on the CL signal were studied. For this purpose, at first we investigated the various mixing sequences to find the optimal one that could produce the highest CL signal. All examined mixing sequences are schematically presented in Figure 1 and results are shown in Table 2. It is clear from Table 2 that the mixing sequence C showed the highest CL signal and low relative standard deviation (1.1%, $n=4$) compared with other three mixing sequences. Therefore we chose sequence C to carry out further experiments.

The highest CL signal was obtained only when the sample was carried through pump B, which may be due to the catalysis of Cr(VI) on the $KMnO_4$–gallic acid–H_2O_2 CL system.

3.4 *Optimisation of reagent concentrations*

Effect of gallic acid concentration on the CL reaction was studied in the range of 5×10^{-3}–6×10^{-2} mol L^{-1}. It was observed that the CL intensity increased gradually along with the increase of gallic acid concentration. Maximum S/N and higher CL signals were obtained when we used 0.05 mol L^{-1} gallic acid. Therefore, 0.05 mol L^{-1} gallic acid was employed for further studies. The effect of $KMnO_4$ concentration on the CL reaction was studied in the range of 5×10^{-3}–5×10^{-2} mol L^{-1}. Highest CL signal was observed when the concentration of $KMnO_4$ was 0.02 mol L^{-1}. Effect of H_2O_2 concentration on the CL reaction was studied in the range of 0.1–0.5 mol L^{-1}. CL signals increased with the increasing concentration of H_2O_2 up to 0.2 mol L^{-1}. Further increase in H_2O_2 concentration showed no considerable effects on the CL signal. Therefore, 0.2 mol L^{-1} H_2O_2 was employed for further studies. As EDTA has property to form stable complexes with metal

Table 2. Effect of mixing order of reagents on the FI-CL signal.[a]

	Reagent sequence	
Manifold	1-2-3-4	S/S_{max}
A	$KMnO_4$–H_2O_2–sample–GA	0.61
B	H_2O_2–GA–sample–$KMnO_4$	0.47
C	$KMnO_4$–GA–H_2O_2–sample	1.00
D	$KMnO_4$–sample–GA–H_2O_2	0.55

Notes: S/S_{max} is CL signal of sequence C.
[a]Cr(VI); 1×10^{-8} mol L^{-1}, gallic acid; 0.05 mol L^{-1}, $KMnO_4$; 0.02 mol L^{-1}, H_2O_2; 0.25 mol L^{-1}.

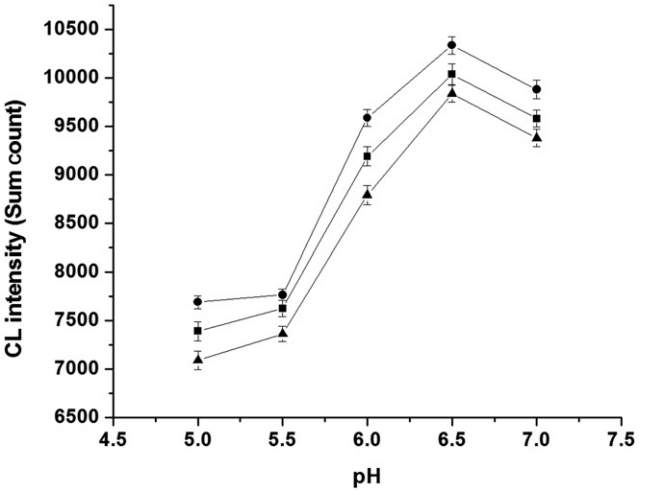

Figure 4. Effect of pH on CL signal intensity. Cr(VI) concentration: 1×10^{-8} mol L^{-1} (•); 5×10^{-9} mol L^{-1} (■); 1×10^{-9} mol L^{-1} (▲).

ions, so this characteristic was used to effectively eliminate the interference from other metal ions along with Cr(III) on the CL determination of Cr(VI). Effect of EDTA concentration on the CL reaction was examined in the range of 2×10^{-2}–5×10^{-4} mol L^{-1}. It was seen that CL intensity became maximum when EDTA concentration was 1×10^{-3} mol L^{-1}. Therefore, 1×10^{-3} mol L^{-1} EDTA was chosen for further experiments. In the reaction of Cr(VI) with the proposed reagents, pH of the sample solution is very important for the reaction efficiency. The effect of pH on the chemiluminescent intensity was investigated from 5–7. The pH was adjusted by the addition of an appropriate amount of 0.01 mol L^{-1} NaOH or HCl in 1×10^{-3} mol L^{-1} EDTA solution. Results are shown in Figure 4. It is evident from Figure 4 that the highest CL signals were obtained when pH of sample solution was 6.5. So pH of 6.5 was employed for further experiments.

3.5 *Optimisation of manifold parameters*

Effect of temperature on CL signal intensity was examined by varying the temperature of CL detection chamber from 10°C to 50°C using a temperature control system. It was seen that chemiluminescent intensity increased gradually with the increase in temperature. In order to select a suitable temperature, the relative standard deviation within three measurements at fixed temperature was determined. At 30°C, the R.S.D. of 1.2% was found and it was the least one. Therefore, 30°C was chosen as the appropriate temperature for further measurements. Effect of mixing coil length was examined by varying the length from 5 to 30 cm. Sharp decrease in the chemiluminescence intensity was observed when the mixing coil length was above 10 cm. High CL intensity at coil length of 10 cm suggested that the chemiluminescent reaction was completed within the CL detection chamber, resulting in a higher signal. For coil lengths longer than 10 cm, the chemiluminescent reaction was supposed to be completed within the mixing coil, prior to reaching the CL detection chamber, thus affecting the CL detection. Therefore a reaction coil length of

10 cm was chosen for further experiments. Flow rate is an important parameter in CL detection, because the time taken to transfer the excited product into the flow cell is critical for maximum collection of the emitted light [39]. Relative light emission was found to increase with increasing flow rates for pump A. Increase in chemiluminescence intensity suggested that the chemiluminescent reaction was completed within the cell. At higher flow rates, more light was emitted per unit time, resulting in higher CL signal. However, an increase in flow rates had a negative effect on reproducibility. The method could be made more sensitive to Cr(VI) concentration but only at the sacrifice of precision. Therefore, accepting a reasonable compromise, the total flow rate of 2.7 mL min^{-1} was chosen collectively for 0.02 mol L^{-1} $KMnO_4$, 0.05 mol L^{-1} gallic acid and 0.2 mol L^{-1} H_2O_2 through pump A. The sample loop through pump B carried 150 μL solution. For this purpose time of flow of 10 s for pump B was enough to fill the sample loop and also to avoid sample wastage.

3.6 *Analytical performance of the system for Cr(VI) measurements*

Under the selected conditions described above, calibration graph between the logarithm of concentration (log *C*) of Cr(VI) versus the logarithm of intensity (log *I*) was linear over the concentration range of 2×10^{-11}–5×10^{-4} mol L^{-1}. (Lowest concentration of the linear range was calculated as 10 times the SD of the blank signal.) Linear regression equation was $\log I = 5.80 + 0.46 \log C$ and correlation coefficient for 12 measurements was 0.9998. Detection limit (3 times the SD of the blank signal) was calculated to be 4×10^{-12} mol L^{-1}, and relative standard deviation of ten measurements of 1×10^{-9} mol L^{-1} Cr(VI) was 1.7%.

3.7 *Interferences from foreign substances*

Influences of foreign species were examined by adding a certain amount of interfering species in 1×10^{-9} mol L^{-1} Cr(VI) solution. Tolerable concentrations, defined as the concentrations of foreign species causing less than ±5% relative error, were examined. Results show that the tolerable concentration ratios of foreign substances to 1×10^{-9} mol L^{-1} Cr(VI) is over 50,000-fold for Na^+, K^+, and Cl^-, 10,000-fold PO_4^{3-} and CO_3^{2-}, 5000-fold Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-} and ethanol, 1000-fold Ba^{2+}, Zn^{2+}, Sn^{2+}, Pb^{2+}, $C_2O_4^{2-}$, Co^{2+} and iso-propanol, 500-fold glucose, HCHO, pyrogallic acid, Ni^{2+}, ClO^-, W^{4+} and Cd^{2+}, 400 fold for Fe^{3+}, 100-fold toluene, ClO_4^-, V^{4+}, Cr^{3+} and 50-fold for tannic acid. As for tannic acid (hydrolysable tannins), it can be totally hydrolysed with weak acid; in this way interference from excess tannic acid can be removed [40]. Therefore the proposed method is free from interference during the determination of Cr(VI) in water samples.

3.8 *Analysis of water samples and certified reference samples*

The developed FIA-CL procedure was applied to the determination of Cr(VI) in different water (tap water, lake water) samples.

Data summarised in Table 3 shows good agreement of *results acquired by the proposed FIA-CL method with those obtained by GF-AAS*. Data obtained from these two methods were evaluated by Paired *t*-test and calculated *t* value (1.64) did not exceed the tabulated value (2.57 for degrees of freedom of 5 and the level of significance of 0.05), which shows

Table 3. Determination of Cr(VI) in water samples with the proposed method and comparison with GF-AAS method.

	Contents of Cr(VI) in water samples ($mol\,L^{-1}$) (mean ± SD, $n = 3$)	
Sample	This technique	GF-AAS method
Tap water 1	$2.4 \times 10^{-8} \pm 1.1$	$2.34 \times 10^{-8} \pm 2.1$
Tap water 2	$3.1 \times 10^{-8} \pm 1.2$	$3.05 \times 10^{-8} \pm 1.8$
Tap water 3	$3.6 \times 10^{-8} \pm 1.1$	$3.62 \times 10^{-8} \pm 1.7$
Lake water 1	$7.0 \times 10^{-8} \pm 0.9$	$6.75 \times 10^{-8} \pm 1.2$
Lake water 2	$7.0 \times 10^{-7} \pm 1.3$	$6.9 \times 10^{-7} \pm 1.6$
Lake water 3	$6.5 \times 10^{-8} \pm 0.9$	$6.53 \times 10^{-8} \pm 1.3$

Table 4. Analytical results for the determination of Cr(VI) in certified reference steel samples.

Sample	Certified (%)	Determined (%)	R.S.D. (%, $n = 3$)
BH1203-1	4.12	4.10	±1.3
BH1203-5	5.41	5.38	±1.8

that the results are not significantly different. It is evident that proposed method is highly sensitive and fully sufficient for the analysis of Cr(VI) in water samples. Results offer the application of the proposed FIA-CL method as a suitable and efficient alternative to other existing methods for the determination of Cr(VI).

Accuracy of the developed method was checked by the determination of Cr(VI) in two kinds of certified reference steel samples. The analytical results are listed in Table 4. Results show that, for both certified samples, concentrations of Cr(VI) determined with the proposed FIA-CL method are in good agreement with the certified values.

4. Conclusion

A simple FIA-CL system, consisting of a pumping system, sample injection valve, reaction chamber and a chemiluminescent detector for the determination of Cr(VI) is developed. Continuous CL flow technique and high-standard electronic equipment make it possible to increase the sensitivity and to shorten the time of analysis to less than 1 minute. In comparison with other recently elaborated methods for Cr(VI) determination [14,16,18], the FIA-CL technique offers several advantages. As the CL reaction is essentially instantaneous, Cr(VI) analysis is not delayed by long reaction times. Pump system maintains uniform, continuous flow and time control is also fully automated. Instrumentation is minimal; only a pump system and a photo-multiplier with basic electronic equipment are required. Reagents used are normally found in the laboratory and their cost is very low. Amount of sample required for the detection of Cr(VI) is 150 μL, which is far less than other methods. Experimental results show that the method is highly

sensitive for the determination of Cr(VI) in drinking and lake water samples. Experimental results obtained for chromium reference materials are also in good agreement with the certified values. This method is expected to be especially useful for continuous and trace level routine determination of hazardous Cr(VI) in different water samples and offers possibilities of automation.

Acknowledgements

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