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Original Paper

Chemiluminescence determination of chromium(III) and total chromium in water samples using the periodate-lucigenin reaction

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Abstract. A new chemiluminescence (CL) method combined with flow injection technique is described for the determination of Cr(III) and total Cr. It is found that a strong CL signal is generated from the reaction of Cr(III), lucigenin and KIO_4 in alkaline condition. The determination of total Cr is performed by pre-reduction of Cr(VI) to Cr(III) by using H_2SO_3. The CL intensity is linearly related to the concentration of Cr in the range 4.0×10^{-10}–1.0×10^{-6} g mL^{-1}. The detection limit ($3s_b$) is 1×10^{-10} g mL^{-1} Cr and the relative standard deviation is 1.9% (5.0×10^{-8} g mL^{-1} of Cr(III) solution, $n = 11$). The method was applied to the determination of Cr(III) and total Cr in water samples and compared satisfactorily with the official method.

Key words: Chemiluminescence; flow injection; chromium; water sample.

The determination of micro amounts of chromium is of considerable interest because of the contrasting biological effects of its two common oxidation states, Cr(III) and Cr(VI), and also the growing interest in environmental problems. Cr(III) is considered as an essential trace element, whereas Cr(VI) is toxic and carcinogenic. The maximum permissible concentration of Cr(VI) in natural water at 0.05 mg mL^{-1} and Cr(III) at 0.5 mg mL^{-1} were prescribed. The determination of Cr can be performed by AAS [1, 2], AES [3, 4], spectrophotometry [5, 6], electroanalytical methods [7, 8], and so on.

Recently, chemiluminescence (CL) analysis has been frequently used for the analysis of organic and inorganic species at trace level [9–11] for its low detection limit, wide linear working range and relative simple instrumentation [12]. However, only few CL systems are available for Cr determination, they were based on luminol [13, 14], lucigenin [15], flavin mononucleotide [16], and pyrogallol [17] reactions.

In this work, it is found that strong CL signal is generated when Cr(III) is mixed with lucigenin and KIO_4 in alkaline medium. Under same conditions, Cr(VI) do not display CL behavior, whereas it can be pre-reduced to Cr(III) by using H_2SO_3. Based on these observations, a new flow injection chemiluminescence (FI-CL) method is developed for the determination of Cr(III) and total Cr. The proposed method has been applied to the determination of Cr(III) and total Cr in water sample.

Experimental

Apparatus

An IFFL-D FI-CL analyzer (Xi'an Remax Electronic Science-Tech Co. Ltd., China) is used and the schematically diagram of

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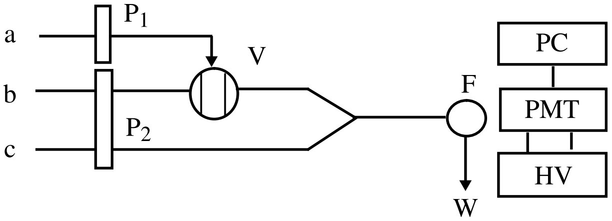

Fig. 1. Schematic diagram of CL flow system. (*a*) Lucigenin solution; (*b*) potassium periodate solution; (*c*) Cr solution; (*P_1*, *P_2*) peristaltic pump; (*V*) injection valve; (*F*) flow cell; (*PMT*) photomultiplier tube; (*HV*) high voltage; (*PC*) personal computer; (*W*) waste

CL flow system is shown in Fig. 1. PTFE tubing (0.8 mm i.d.) was used to connect all components in the flow system. One peristaltic pump delivered KIO_4 solution and lucigenin solution, each at a flow rate of $2.8\,mL\,min^{-1}$, and the other pumped Cr solution at a flow rate of $0.5\,mL\,min^{-1}$. Sample injection (50 μL) was operated by means of a six-way valve. The CL signal produced in the flow cell (a 1 mm i.d. ×20 cm length of colorless spiral glass tubing, 3.5 turns) was detected with a CR-105 photomultiplier tube (Hamamatsu). Data acquisition and treatment were performed with the type of IFFL-D data processing software (Xi'an Remax).

Reagents and solutions

All the reagents used were of analytical-reagent grade and all solutions were prepared with doubly distilled water. Lucigenin was purchased from Sigma (St. Louis, MO). Sulfurous acid (H_2SO_3, $SO_2 \geq 6\%$) was purchased from Tianjing Chemical Reagent Plant (Tianjing, China). Other chemicals were obtained from Xi'an Chemical Reagent Company (X'an, China). Stock standard solutions ($1.0 \times 10^{-3}\,g\,mL^{-1}$) of Cr(III) and Cr(VI) were prepared by dissolving appropriate amounts of $CrCl_3 \cdot 6H_2O$ and $K_2Cr_2O_7$ in doubly distilled water, respectively. More dilute solutions were prepared by the minimum number of dilution steps possible. A $5 \times 10^{-4}\,mol\,L^{-1}$ lucigenin solution was prepared in water. A $3 \times 10^{-4}\,mol\,L^{-1}$ KIO_4 solution was prepared by transferring 7.5 mL of $0.01\,mol\,L^{-1}$ KIO_4 solution into a 250 mL calibrated flask, to which 12.5 mL of $5\,mol\,L^{-1}$ NaOH solution was added and then diluting to the mark with water.

Procedure

Flow lines were inserted into Cr standard/sample solution, lucigenin solution and KIO_4 solution, respectively. Fifty microlitres of Cr standard/sample solution was injected into $5 \times 10^{-4}\,mol\,L^{-1}$ lucigenin by using the six-way valve, and then merged with $3 \times 10^{-4}\,mol\,L^{-1}$ KIO_4 solution (containing $0.25\,mol\,L^{-1}$ NaOH) stream just prior to reaching the flow cell for producing CL. The concentration of Cr was quantified by the CL signal (peak height).

Results and discussion

A series of experiments were conducted to establish optimum conditions using $5.0 \times 10^{-8}\,g\,mL^{-1}$ Cr(III) standard solution.

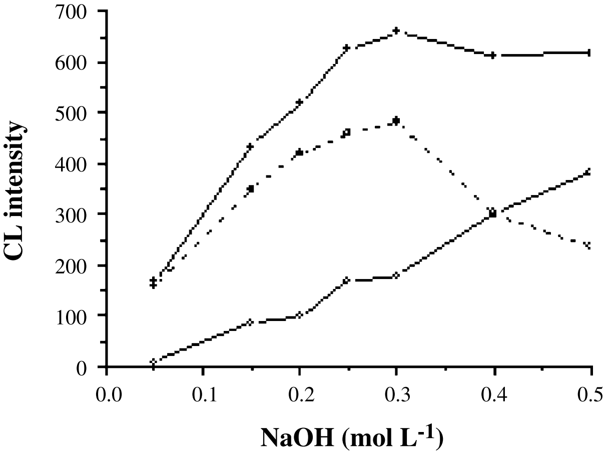

Fig. 2. Effect of sodium hydroxide concentration. Conditions: $5 \times 10^{-4}\,mol\,L^{-1}$ lucigenin, $3 \times 10^{-4}\,mol\,L^{-1}$ KIO_4 and $2.8\,mL\,min^{-1}$ of flow rate. (•): $5.0 \times 10^{-8}\,g\,mL^{-1}$ Cr (pH 5, $5 \times 10^{-3}\,mol\,L^{-1}$ EDTA); (○): blank; (⊕): net CL signal

Effect of NaOH concentration

Lucigenin CL reaction occurs in alkaline medium. To avoid lucigenin reacting with dissolved oxygen in alkaline medium and also to simplify the flow system, sodium hydroxide was added into KIO_4 solution. The effect of NaOH concentration on the CL reaction was examined in the range $0.05–0.5\,mol\,L^{-1}$ (Fig. 2). The CL signal continued to increase with increasing NaOH concentration up to $0.3\,mol\,L^{-1}$. The CL signal decreased when NaOH concentration was higher than $0.3\,mol\,L^{-1}$. Therefore, $0.3\,mol\,L^{-1}$ NaOH was selected.

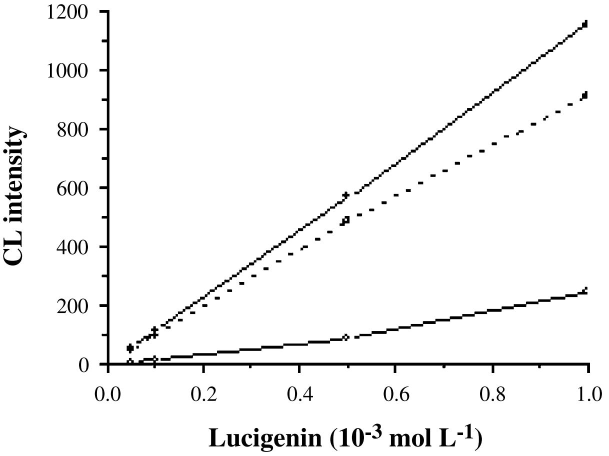

Fig. 3. Effect of lucigenin concentration. Conditions: $3 \times 10^{-4}\,mol\,L^{-1}$ KIO_4, $0.3\,mol\,L^{-1}$ NaOH and $2.8\,mL\,min^{-1}$ of flow rate. (•): $5.0 \times 10^{-8}\,g\,mL^{-1}$ Cr (pH 5, $5 \times 10^{-3}\,mol\,L^{-1}$ EDTA); (○): blank; (⊕): net CL signal

Effect of lucigenin concentration

The effect of lucigenin concentration on the CL reaction was examined in the range 5×10^{-5}–1×10^{-3} mol L^{-1} (Fig. 3). The results showed that both the CL signal gradually increased as lucigenin concentration increasing within the examined concentration range, but the blank was also increased. The maximum S/N and higher CL signal were obtained with 5×10^{-4} mol L^{-1} lucigenin. Therefore, 5×10^{-4} mol L^{-1} lucigenin was employed.

Effect of KIO_4 concentration

The effect of KIO_4 concentration on the CL reaction was shown in Fig. 4. As can be seen, the CL signal increased with increasing KIO_4 concentration up to 3×10^{-4} mol L^{-1}. Further increasing KIO_4 concentrations decreased the CL signal. Therefore, 3×10^{-4} mol L^{-1} KIO_4 was employed.

Effect of EDTA concentration

EDTA can react with many metal ions to form stable complex compound. Compared with other metal ions, the rate of reaction of EDTA with Cr(III) is relatively slow. This characteristic can be used to effectively eliminate the interference from other metal ions on the CL determination of Cr(III) [13]. The effect of EDTA concentration on the CL reaction was examined. The experiments showed that EDTA didn't influence the CL signal from Cr(III) solution when its concentration was not higher than 0.01 mol L^{-1}. Finally, 5×10^{-3} mol L^{-1} EDTA was employed.

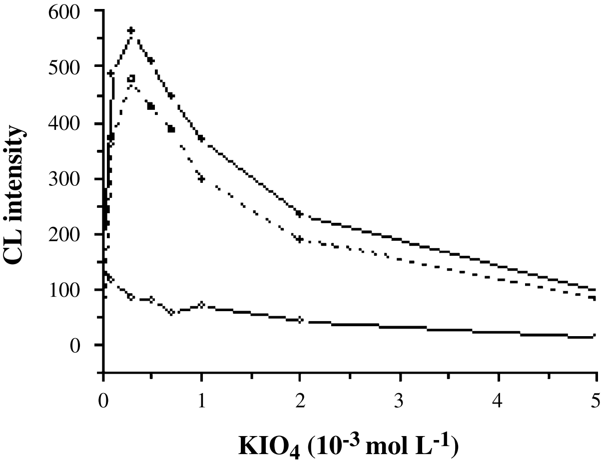

Fig. 4. Effect of potassium periodate concentration. Conditions: 5×10^{-4} mol L^{-1} lucigenin, 0.3 mol L^{-1} NaOH and 2.8 mL min^{-1} of flow rate. (●): 5.0×10^{-8} g mL^{-1} Cr (pH 5, 5×10^{-3} mol L^{-1} EDTA); (○): blank; (⊕): net CL signal

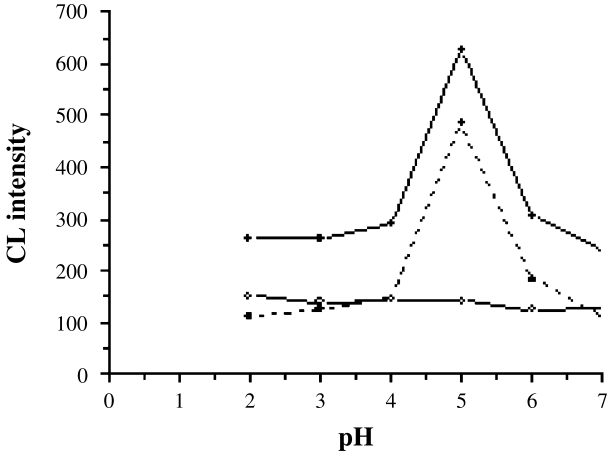

Fig. 5. Effect of the acidity of Cr(III) solution. Conditions: 5×10^{-4} mol L^{-1} lucigenin, 3×10^{-4} mol L^{-1} KIO_4, 0.3 mol L^{-1} NaOH and 2.8 mL min^{-1} of flow rate. (●): 5.0×10^{-8} g mL^{-1} Cr (5×10^{-3} mol L^{-1} EDTA); (○): blank; (⊕): net CL signal

Effect of pH of Cr solution

Cr(III) can exist as Cr^{3+}, $Cr(OH)_3$ or hydroxylation complex compounds under different pH conditions [18]. The effect of the pH of Cr(III) solution on the CL reaction was examined and the results were shown in Fig. 5. The CL signal increased by increasing pH value of Cr(III) solution up to 5, whereas higher pH values decreased the CL signal. Therefore, the pH 5 was selected as the suitable acidity of Cr(III) solution.

Effect of flow rate

The effect of flow rate on the CL reaction was also investigated. Flow rate is an important parameter in the CL determination because it influences the time that taken to transfer the reaction mixture into the flow cell and on the maximum collection of the CL signal. The effect of flow rate on the CL reaction in the range 1.4–3.5 mL min^{-1} was examined. It was observed the CL signal increased with increase in flow rate within the examined range, which indicated this CL reaction was a fast process. Finally, as a compromise between reagents consumption and sensitivity, 2.8 mL min^{-1} of flow rate was employed.

Selection of reductant

It is very important for the completely reducing of Cr(VI) to Cr(III). The reduction of Cr(VI) to

Table 1. A comparison of various methods for the determination of chromium (Unit: 10^{-9} g mL^{-1})

Methods	Reagents used	Analytical ranges	Detection limit	Reference
AAS	ammonium pyrrolidinedithiocarbamate		0.3	[1]
	pyrrolidinedithiocarbamate	0.02–0.4	0.003	[2]
AES	1-phenyl-3-methyl-4-benzoylpyrazol-5-one		0.81	[3]
	activated carbon	0.029–60	0.029	[4]
Spectrophotometry	CrO_3Cl^-, $TPAs^+Cl^-$	52–2600		[5]
	2-[2-(4-methoxy-phenylamino)-vinyl-1,3,3-trimethyl-3H-indolium chloride	260–7280		[6]
Potentiometry	rhodamine B	260–5200	52	[7]
Ion-selective electrode	2-hydroxybenzaldehyde-O,O′-(1,2-dioxetane-1,2-diyl)oxime	26–156000	13	[8]
CL	luminol-H_2O_2 reaction	0.1–260	0.026	[13]
	flavin monoucleotide		2.6	[16]
	pyrogallol-IO_4^- reaction	5–100	1	[17]
	lucigenin-KIO_4 reaction	0.4–1.0	0.1	this method

Cr(III) may be performed by using H_2SO_3, Na_2SO_3, $NaHSO_3$, and so on [19–22] and these compounds were tested to reduce Cr(VI) to Cr(III) under respective reported optimum conditions. The experimental results showed that H_2SO_3 was the suitable one. When 0.12% (v/v) H_2SO_3 was employed and heated for 10 min at 100 °C, no significant differences between the CL signal from Cr(VI) and the same concentration of Cr(III) have been found with 95% confidence level.

Performance of the system for Cr measurements

Under the selected conditions described above, the calibration graph of CL intensity (ΔI, relative unit) versus Cr concentration was linear in the range 4.0×10^{-10}–1.0×10^{-6} g mL^{-1}. The regression equation was $\Delta I = 10.46 + 2.11\ C$ (where C is the concentration of Cr in 10^{-10} g mL^{-1}) with a correlation coefficient of 0.9984 ($n = 11$). The detection limit ($3s_b$) was 1×10^{-10} g mL^{-1} and the relative standard deviation for 5.0×10^{-8} g mL^{-1} of Cr(III) solution was 1.9% ($n = 11$).

A comparison of the analytical performances between the previously reported methods and the proposed method for the determination of Cr were summarized in Table 1. The proposed method is more sensitive than spectrophotometry [5, 6] and electroanalytical methods [7, 8], and rapid than AAS [1, 2] and AES [3, 4]. Compared with other CL methods, the detection limit of the proposed method was one order of magnitude lower than that of flavin monoucleotide reaction [16] and pyrogallol-IO_4^- reaction [17].

Interference

The effect of the foreign species on the determination of 5.0×10^{-8} g mL^{-1} Cr(III) was studied. A foreign species was considered not to interfere when its effect on the peak height was less than 5%. The tolerance ratios were as follows: 1000 for Na^+, K^+, Pb^{2+}, Zn^{2+}, SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, SO_3^{2-}; 100 for Al^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, NO_2^-, NH_4^+, CO_3^{2-}, PO_4^{3-} and equal amount of Fe^{3+}, Co^{2+}, Fe^{2+}. To eliminate the effect of these metal ions, different masking agents were examined. The experimental results showed triethanolamine was the most suitable one. When 0.05% (v/v) triethanolamine was used as the masking agent, the tolerance ratios for Co^{2+}, Fe^{3+} and Fe^{2+} was improved to 500, 100 and 50, respectively.

Application

The proposed method was applied to the determination of Cr in several water samples collected from different sources from Xi'an area. The collected water samples were filtered using a membrane filter (pore size: 0.45 μm) and stored in the polyvinyl alcohol bottles for analysis.

To determine Cr(III), 25.00 mL water samples, 5 mL of 5×10^{-2} mol L^{-1} EDTA, 2.5 mL of 1% (v/v) triethanolamine and appropriate amount of doubly distilled water were added into a small beaker, after adjusting the pH of the solution to 5 with diluted HCl, the solution was diluted to 50 mL with doubly distilled water.

To determine total Cr, 25.00 mL water samples and 1 mL of 6% (v/v) H_2SO_3 was added into a small bea-

Table 2. Results of Cr determination in water samples

Water samples	Proposed method (g mL^{-1}) ($n = 3$)					Official method (g mL^{-1})		
	Cr(III)	RSD (%)	Cr(VI)	Total Cr	RSD (%)*	Cr(III)	Cr(VI)	Total Cr
1	1.0×10^{-8}	3.3	2.2×10^{-8}	3.2×10^{-8}	2.4	1.1×10^{-8}	2.0×10^{-8}	3.1×10^{-8}
2	2.0×10^{-8}	2.5	3.6×10^{-9}	2.4×10^{-8}	2.2	1.9×10^{-8}	4.5×10^{-9}	2.4×10^{-8}
3	1.8×10^{-8}	2.7	3.3×10^{-8}	5.1×10^{-8}	1.9	2.0×10^{-8}	3.2×10^{-8}	5.2×10^{-8}
4	5.1×10^{-8}	2.1	2.5×10^{-8}	7.6×10^{-8}	2.0	5.2×10^{-8}	2.6×10^{-8}	7.8×10^{-8}
5	1.1×10^{-8}	3.2	1.6×10^{-8}	2.7×10^{-8}	2.8	1.0×10^{-8}	1.6×10^{-8}	2.6×10^{-8}
6	3.2×10^{-8}	2.2	2.5×10^{-8}	5.7×10^{-8}	1.8	3.2×10^{-8}	2.4×10^{-8}	5.6×10^{-8}

ker, after heating at 100 °C for 10 min and cooling to room temperature, 5 mL of 5×10^{-2} mol L^{-1} EDTA, 2.5 mL of 1% (v/v) triethanolamine and appropriate amount of doubly distilled water were added and adjusted the pH of the solution to 5 with diluted HCl. The resultant solution was further diluted to 50 mL with doubly distilled water.

Table 2 showed the results obtained by the proposed method and those obtained by the official method [23]. It could be seen that the data obtained by both methods were not different significantly with 95% confidence level.

Conclusion

A new CL reaction, lucigenin-KIO$_4$-Cr(III) reaction, has been found. The experimental conditions that affected the CL reaction were optimized and a simple FI-CL method for the determination of Cr was developed. The proposed method is sensitive (The detection limit was 1–3 order of magnitude lower than spectrophotometry [5, 6], electroanalytical methods [7, 8] and other CL methods, flavin monoucleotide reaction [16] and pyrogallol-IO$_4^-$ reaction [17]), rapid. The application of the method was validated by the determination of Cr(III) and total Cr in water samples.

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