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A simple flow-injection chemiluminescence method for the determination of trace pentavalent vanadium in water samples

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A simple method for rapid determination of trace pentavalent vanadium in natural water was presented by flow-injection chemiluminescence (CL). Through water injection, luminol and potassium permanganate were eluted from the anion exchange column to generate the CL, which was enhanced in the presence of V(V). Under the optimum conditions, the increased CL intensity was linear with V(V) concentration in the range from 0.1 to 100 ng mL⁻¹. The limit of detection was 50 pg mL⁻¹ (3σ) and the relative standard deviation (RSD) was 2.24% (n = 5) for a 1.0 ng mL⁻¹ V(V). At a flow rate of 2.0 mL min⁻¹, one cycle of analysis could be performed in 0.5 min with a RSD of less than 3.0%. The proposed method was successfully applied to the determination of vanadium in natural water.

Keywords: on-line analysis; environmental; vanadium; chemiluminescence; water

1. Introduction

Vanadium in trace level is an essential trace element possessing specific physiological functions. Its role in physiological systems includes normalisation of sugar levels, participation in various enzyme systems as an inhibitor and a cofactor and catalysis of the oxidation of various amines. In recent years, trace metal analysis has become more and more important for environmental pollution. Vanadium is widely distributed in the earth's crust and also exists in various oxidation states and ionic forms in waters from V(II) to V(V) [1], and their presence in the atmosphere is mainly due to the combustion of fossil fuels, which have important vanadium contents [2]. However, vanadium has been recognised as a potentially dangerous pollutant when vanadium concentrations are increased to 25 ng mL⁻¹ level [3]. Different oxidation states have different toxicity to human health. The toxicity will be increased with the increase of vanadium valence, so V(V) is worst to health of humans [4]. Knowledge of speciation is important when assessing the mobility of vanadium in the environment [5]. Therefore determination of V(V) is receiving increasing attention in pollution studies.

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Since one of the routes of incorporation of vanadium into the human body is drinking water [6,7], its determination in these types of samples becomes very important. Since the concentration of V(V) in drinking water is very low [8,9], in the order of a few micrograms per litre, powerful techniques are required and only a few of them show sufficient sensitivity.

In the past years, several methods have been developed for the determination of V(V) at low concentrations including catalytic spectrophotometry [10,11], liquid chromatography [12] and electrothermal atomic absorption spectrometry [13]. To the best of our knowledge, no chemiluminescence procedure for the direct determination of V(V) in water has been published previously. In natural water, under natural conditions, VO_4^{3-} and its H-substituted forms (HVO_4^{2-} , H_2VO_4^-) is apparently specific for the vanadate anion [14,15]. Potentially interferent heavy metals are removed by passing the water sample through a cation-exchange column which would remove this species [16].

In this paper, it was found that the CL intensity from the oxidation between luminol and potassium permanganate could be enhanced in the presence of V(V). Both CL reagents were immobilised on an anion-exchange resin. This allowed for the achievement of a homogeneous mixing of CL reagents, which resulted in a more stable background and more reproducible results than those using a reagent solution. The increased CL intensity was linear within V(V) concentration in the range from 0.1 to 100 ng mL^{-1} with the reagent flow rate of 2 mL min^{-1} . The limit of detection was 50 pg mL^{-1} (3σ) and the relative standard deviation was 2.24% ($n=5$) for a 1.0 ng mL^{-1} V(V) sample. At a flow rate of 2.0 mL min^{-1} , including sampling and washing, the detection could be performed in 0.5 min with a relative standard deviation of less than 3.0%. The proposed method had been successfully applied to the determining of V(V) in water, and the results were in good agreement with results obtained by ion chromatography (IC).

2. Experimental

2.1 Reagents

All chemicals used were of analytical reagent grade. Water was deionised and redistilled and further purified with a Milli-Q water purification system (Millipore, USA). Luminol (Fluka, biochemika) was obtained from Xi'an Medicine Purchasing and Supply Station, China. Potassium permanganate and trisodium vanadate was purchased from Xi'an Chemical Reagent Plant. Anion exchange resin (Amberlyst A-27, Rohm and Haas Co.) and cation exchange resin (Dowex APA-1, Dow Chemical Co.) were purchased locally.

2.2 Preparation of resin with immobilised reagents

Amberlyst A-27 resin 2.0 g was shaken with 50 mL of 0.025 mol L^{-1} luminol or 0.04 mol L^{-1} potassium permanganate for 12 h, and then the resin was filtered, washed with deionised water and dry-stored. The most convenient method to determine the amounts of luminol and potassium permanganate immobilised was to measure the losses of these reagents from the immobilisation solutions. The concentration was detected at 360 nm for luminol and at 546 nm for potassium permanganate by UV-vis. In the proposed method, the amounts of luminol and potassium permanganate immobilised were 1.99 ± 0.03 ($n=3$) mmol g^{-1} and 1.66 ± 0.02 ($n=3$) mmol g^{-1} resin, respectively.

2.3 Instrument

The flow-injection (FI) system used in this work is shown in Figure 1. A peristaltic pump (Shanghai meter electromotor plant, Model ND-15, 15 rpm) was used to generate the flows. PTFE tubing (1 mm i.d.) was used in the flow system. The anion-exchange resins contain immobilised luminol (0.05 g) and potassium permanganate (0.10 g) were mixed together and packed into a glass column (3 mm i.d. and total volume of about 0.5 mL), and another loaded with cation exchange resins is placed in the sample pipeline. And both of the columns were plugged with glass wool at both ends to prevent the resins from leaking. A six-way valve injected 100 μL of eluant. Before reaching the flow cell, the streams of luminol, potassium permanganate, sodium hydroxide and analyte were combined in a mixing tube (50 mm in length). The CL emission cell is a spiral glass tube (1 mm i.d., 15 cm length) producing a large surface area exposed to the adjacent photomultiplier tube (PMT) (Hamamatsu, Model IP28). Extreme precautions were taken to ensure that the sample compartment and PMT were light-tight. The CL signal produced in the flow was detected without wavelength discrimination, and the PMT output was amplified and quantified by a luminosity meter (Xi'an Remax Electronic Science-Tech. Co. Model GD-1) connected to a recorder (Shanghai Dahua Instrument and Meter Plant, Model XWT-206). All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-600 ion chromatograph.

2.4 Analytical procedure

The carrier water and the solutions (NaOH, sample and eluant) were propelled at a constant flow rate on each flow line. The pump was started to wash the whole flow system until a stable baseline was recorded. Then 100 μL of eluant solution was injected into the carrier stream, luminol and potassium permanganate were eluted quantitatively, which was then mixed with the sample stream, the mixed solution was delivered to the CL cell, and the peak height of the CL signal was detected with the PMT and the luminometer. The concentration of sample was quantified by increased CL intensity, $\Delta I = I_o - I_s$, where I_o and I_s were CL signals in the absence and in the presence of V(V), respectively.

3. Results and discussion

3.1 The CL chemical kinetics curve

Before the FI method was carried out, the batch method for the CL profiles was used. Without any special eluant, the mixture of luminol and potassium permanganate rinsed

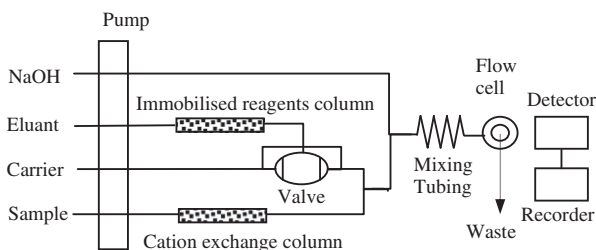


Figure 1. Schematic diagram of the flow-injection system for V(V) determination.

by water gave an evident CL signal. The CL intensity reached a maximum 10 s after injection, and then died within 25 s. When the sample was added into the above mixing solution, an increased CL signal was recorded. The peak heights of the CL emission were proportional to V(V) concentration.

3.2 Activity of eluant

One hundred microlitres of different eluants was injected through the resin column and releasing different amounts of luminol and potassium permanganate, thus producing the CL emission. It was found that sodium sulfate gives a maximum CL emission while sodium carbonate shows some inhibitory effects on the CL reaction. Nevertheless, it was observed that a continuous flow of eluant through the column results in a rather short lifetime of sensor down to only a few hours. It was shown that the immobilised luminol and potassium permanganate anions on the anion exchange resin undergo dissociation with water, thus releasing trace amounts of luminol and potassium permanganate from the column, and the increase of V(V) CL signal could be easily observed. In this case, the column could be used for more than 80 h. As a compromise between higher CL intensity and longer lifetime of the column, water was used as eluant in subsequent work.

3.3 Effect of molar ratio of immobilised luminol and potassium permanganate

In order to test the influence of the mixing ratio, 0.15 g resins with different mixing ratios were packed into the same type of column. By injecting 100 μ L water, different amounts of luminol and potassium permanganate were eluted from the resins and emitted CL signals with different intensities. As Figure 2 shows, the CL intensity dropped drastically from the beginning to the next day, and then it went down slowly. The most stable CL signal was found with a molar ratio of 1:2 (luminol to potassium permanganate), and a middling CL intensity is in favour of measuring an enhancement effect of V(V) on CL reaction.

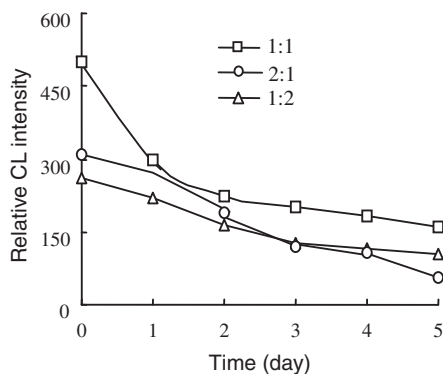


Figure 2. Effect of molar ratio of luminol and potassium permanganate on CL intensity and sensor lifetime.

3.4 Determination of pH on CL and sensor lifetime

The best pH of eluant (water) on the performance of the system was evaluated. As seen from Figure 3, along with the increase of pH in eluant, the CL intensity increased while the lifetime of sensor decreased considerably. This phenomenon is probably due to the increasing quantities of hydroxide ions in the eluant. A pH of 6.5 was then chosen as a compromise between column lifetime and sufficient CL intensity. Therefore, the deionised water had a compatible pH and was used as eluant directly throughout. In this case, as seen from Figure 4, the column with immobilised CL reagents could be used for more than 80 h in continuous-injection system.

3.5 Determination of molar ratio of immobilised luminol and potassium permanganate

To examine the influence of the mixing ratio, resins (0.15 g) with different mixing ratios were packed into a column with the same internal diameter and volume. By the injection of water at a fixed volume of 100 μL , different amounts of luminol and potassium

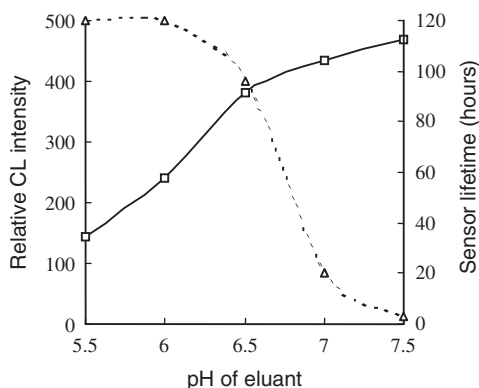


Figure 3. Effect of eluant pH on CL intensity and effect of eluant pH on sensor lifetime.

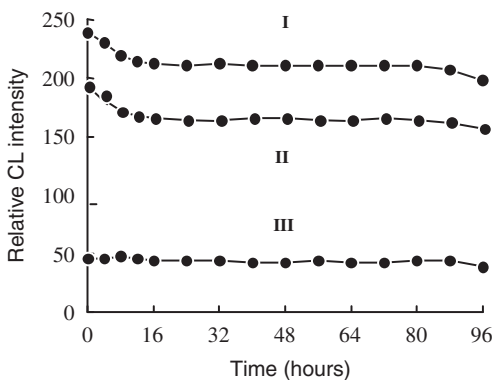


Figure 4. Stability of the column; I: CL intensity in presence of 2.0 $\text{ng} \cdot \text{mL}^{-1}$ V(V) (I_s); II: CL intensity in absence V(V) (I_0); III: The increase of CL intensity ($\Delta I = I_s - I_0$).

Table 1. Determination of V(V) in different water samples.

Samples	Results by the proposed method ^a					Results by IC	
	Found (ng·mL ⁻¹)	Added (ng·mL ⁻¹)	Total (ng·mL ⁻¹)	Recovery (%)	RSD (%)	Concentration (ng·mL ⁻¹)	SD
water 1	1.07	0		89.0	1.61	1.0	0.1
		2.0	2.85		3.87		
water 2	2.33	0	4.24	96.9	1.99	2.3	0.2
		2.0			3.18		
water 3	2.79	0		103.2	1.51	2.6	0.3
		2.0	4.85		2.82		
water 4	2.34	0	4.29	97.8	3.21	1.8	0.2
		2.0			1.97		
water 5	0.88	0	2.93	102.3	1.94	0.9	0.1
		2.0			3.51		
water 6	1.22	0	3.11	94.4	3.34	1.3	0.1
		2.0			3.90		
water 7	1.11	0	3.01	95.0	2.22	1.3	0.1
		2.0			3.14		
water 8	1.84	0	3.80	95.4	3.22	2.5	0.3
		2.0			1.45		

^aThe average of five determinations.

permanganate were eluted from the resins and emitted CL signals with different intensities. The most stable CL signal was found with a molar ratio of 1:2 (luminol to potassium permanganate), and a middling CL intensity is in favour of measuring an enhancement effect of V(V) on CL reaction.

3.6 Calibration curve

Under the above optimum conditions, the linearity of V(V) was tested by determining a series of standard solutions with the flow sensor. The enhancement CL intensity was found to be proportional with the V(V) ion concentration. The linear range is from 0.1 to 100 ng mL⁻¹ and the regression equation is $\Delta I = 14.88 C_{V(V)} + 12.68$, $R^2 = 0.9995$. The relative standard deviation (RSD) of five determinations was 2.24% with V(V) concentration of 1.0 ng mL⁻¹, and the limit of detection was 0.05 ng mL⁻¹. At a flow rate of 2.0 mL min⁻¹, the determination of analyte could be performed in 0.5 min, including sampling and washing, giving a throughput of about 120 times per hour with a RSD of less than 3.0%.

3.7 Interference studies

The effect of foreign ions was tested by analysing a standard solution of V(V), to which increasing amounts of interfering ions were added. The tolerable concentration ratios with respect to 1.0 ng mL⁻¹ V(V) for interference at 5.0% level were over 1800 for Cl⁻, NO₃⁻, Ac⁻, I⁻, SO₄²⁻, PO₄³⁻, Cr₂O₇²⁻, borate, and oxalate, 1200 for NH₄⁺, Mg²⁺, Ca²⁺, Ba²⁺, Zn²⁺, Ni²⁺, and Cr³⁺, 600 for methanol, and ethanol, 50 for Cu²⁺, and Fe³⁺.

Common metal ions existing in water and causing interference in V(V) determination were effectively eliminated by a column cation exchanger.

3.8 Determination of V(V) in water samples

Following the procedure detailed in the Experimental section, the proposed method was applied with preliminary success to the determination of V(V) in various water samples, including underground water, spring water, distilled water, tap water and drinking water, and the results of trial determinations are summarised in Table 1. The recovery studies were performed on each of the analysed samples by adding a known amount of V(V) to the sample before the recommended treatment. The result is well with the ones by ion chromatography.

4. Conclusions

The proposed method is the first flow-injection chemiluminescence method for direct determination of free V(V) in water, and it is rapid, accurate, precise, easily handled and with low operational cost. Compared with other methods, the proposed method offers advantages in instrumental simplification, high sensitivity and reducing reagent consumption.

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