Chemiluminescence Determination of Molybdenum by on–Line Reduction with a Flow Injection System

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Abstract: The chemiluminescence (CL) reaction between lucigenin (Lu) and molybdenum (III) produced by a Jones reductor was investigated using a flow injection system. On the basis of this, a novel method for the determination of trace amount of molybdenum has been established. The emission intensity was linear with molybdenum concentration in the range of 0.1—1000 ng/mL; the detection limit was 0.02 ng/mL molybdenum; the relative standard deviation was less than 2% for the determination of 0.1 ng/mL molybdenum (n=11). The method has been applied successfully to the analysis of trace molybdenum in water and steel samples.

Keywords：Chemiluminescence analysis, reductant, flow-injection, molybdenum, lucigenin.

The reactions of Lu with hydrogen peroxide catalysed by metal ions and also reaction of Lu with organic reductants such as glucose and ascorbic acid have been reported[1,2]. Our recent studies showed that some inorganic reductants such as Mo (III),V (II),U (III),W (III),Cr (II),Ti (III) and Fe (II) *etc.* can react with Lu in strong alkaline medium to generate CL. In this paper, the CL reaction between Lu and Mo (III) produced by a Jones reductor[3] has been studied in detail for the first time, and the CL reaction has been successfully applied to determine molybdenum with excellent sensitivity over a wide linear range and with the use of simple instrumentation.

All the reagents were of analytical grade; double-distilled water was used for the preparation of solutions of all dilutions. A stock solution of molybdenum (0.1mg/mL) was prepared from ammonium molybdate. Working standards were prepared from the stock solution by appropriate dilution. Lu (0.5 mmol/L) was prepared by dissolving 0.2551g of Lu in 1L of water. Other solutions were 0.4 mol/L NaOH and 0.01mol/L H_2SO_4. Strong base type anion-exchange resin (size 0.35-0.45mm) was used for separation.

A flow injection chemiluminescence analyzer, with a Jones reductor prepared according to Ref. 3 , is schematically shown in **Figure 1**. A peristaltic pump was used to deliver all flow streams at a flow rate of 3 mL/min on each flow line. The light signal produced in the flow cell was detected with a R 456 photomultiplier tube (PMT) and recorded with a XWT-204 recorder (Shanghai Dahua Instrument and Meter Plant).

Figure 1 Schematic diagram of the flow injection system for Mo determination
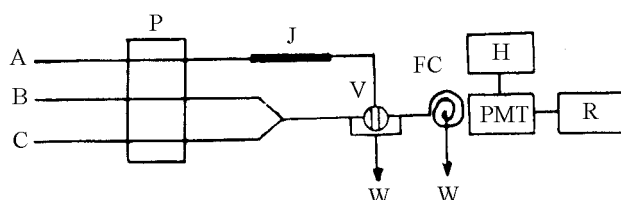
A---Sample; B---Lu; C---NaOH; P---Pump; J---Jones reductor; V---Valve; PMT---Photomultiplier tube; FC---Flow cell; H---High voltage power; R---Recorder; W---Waste.

A certain amount of standard solution or sample solution was pipetted into a 25 mL volumetric flask, an appropriate amount of 0.01 mol/L H_2SO_4 was used to adjust the acidity, and the flask was filled with water. This was used as the sample solution and its CL intensity was then measured with the flow injection system, the concentration of Mo was quantified by the CL intensity.

The kinetic characteristics of the CL reaction were examined as shown in **Figure** 2. It can been seen from **Figure** 2 that the reaction is very rapid. The CL intensity reached to maximum at one second after the reaction was started, then attenuanted quickly to baseline in 3 seconds.

Figure 2 Kinetic curve of the CL reaction in the presence of 1 μ g/mL Mo
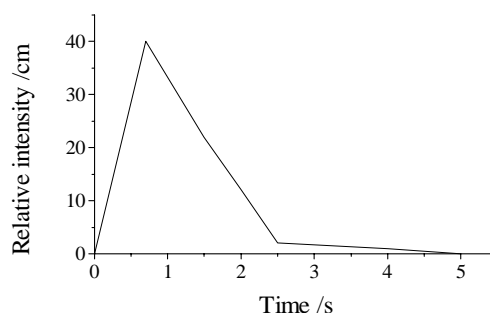
The acidity of the sample solution directly affects the efficiency of Jones reductor, and it also influences the CL reactions. The results showed that 3.5 is the best pH value, this value was used in subsequent experiments.

With the raising of Lu concentration in the range of 1×10^{-4}—1×10^{-3} mol/L, the CL intensity increases rapidly, the increase being accompanied by an increase in background signal . In order to obtain the best signal to noise ratio, a concentration of 5×10^{-4} mol/L was used for Mo determination.

Lu reacts with Mo (III) to produce CL light in basic solution, but Lu also reacts with oxygen to produce CL slowly in basic medium, in order to decrease Lu consumption by dissolved oxygen, NaOH was added in flow line C. Since the sodium hydroxide concentration *versus* CL intensity plot shows a maximum for sodium

hydroxide levels around 0.4 mol/L, so this concentration was used in subsequent experiments.

The kinetic property shows that Mo (Ⅲ) reacts with Lu very quickly. So the time interval from mixing Lu and Mo (Ⅲ) to signal appearance completely depends on the valve-cell distance. At a flow rate of 3 mL/min. 5.0 cm was selected as the valve-cell distance in our work.

EDTA is usually used as a masking reagent in CL analysis, so it is in this reaction. A concentration of 0.015% was used in our work.

The linear relationship between CL intensity and concentration of Mo (Ⅵ) was examined under optimized conditions. In order to improve the precision, the standard curves were plotted according to quantitative levels. The parameters of standard curves are listed in **Table 1**.

Table 1 The parameters of standard curves

Linear range of Mo(Ⅵ) (g /mL)	Regression equation	Correlation coefficient（γ）	Instrumental parameters	
			Voltage(V)	Range(V)
$1 \times 10^{-10} \sim 1 \times 10^{-9}$	$I = 1.52C + 0.60$	0.9986	750	0.02
$1 \times 10^{-9} \sim 1 \times 10^{-8}$	$I = 1.21C - 0.09$	0.9988	700	0.05
$1 \times 10^{-8} \sim 1 \times 10^{-7}$	$I = 1.07C + 0.01$	0.9996	700	0.50
$1 \times 10^{-7} \sim 1 \times 10^{-6}$	$I = 0.81C - 0.01$	0.9992	600	0.50

The detection limit of the method is 0.02 ng/mL, and the relative standard deviation is less than 2% for 0.1 μ g/mL (n=11) Mo.

Interference of foreign ions was tested by analysing a standard solution of Mo (0.02 μ g/mL) . The tolerable concentrations of some interfering ions are listed in **Table 2.**

Table 2 Tolerable concentration ratios with respect to Mo (Ⅵ) for some interfering species (± 5% error)

Foreign ions	Tolerable concentration ratio
K^+, Na^+, NH_4^+, Al^{3+}, Ba^{2+}, Zn^{2+},Sr^{2+},Hg^{2+}, F^-, Br^-,NO_3^-,SO_4^{2-},IO_3^-	>1000
Ca^{2+}, Ti^{3+}, Mg^{2+} Cu^{2+}, Pb^{2+}, Ni^{2+}, Se(Ⅳ),As(Ⅲ)	100
Cr^{3+},Cd^{2+},Co^{2+},Sn^{2+},U(Ⅵ),W(Ⅵ), Ti(Ⅳ), Mn^{2+},Fe^{2+}	10
Fe^{3+}, V(Ⅴ), Cr(Ⅵ)	2

A certain amount of strongly basic anion exchange resin was imbibed with 2 mol/L NaOH solution for 24 hours, and washed to neutral with water, then put into a small glass column (Φ =15×150 mm).

50—100 mL of water sample was poured into the column, 10 mL of 0.1 mol/L HCl solution was added to remove impurities, then 20 mL of 1 mol/L HCl solution was used to elute molybdenum, and adjusted the acidity for the analysis. The results are given in **Table 3**.

0.50—1.50 mg of standard steel sample was weighed accurately, dissolved and diluted in 100 mL of 0.1 mol/L HCl solution, poured into the column, 10 mL of 0.1 mol/L HCl solution was added to remove impurities, then 20 mL of 1 mol/L HCl solution

was used to elute molybdenum, and the acidity was adjusted for the analysis. The results are given in **Table 4**.

Table 3　Determination results of Mo in water samples

Sample	Content (ng/mL）			Added (ng/mL)	Found (ng/mL)	RSD (%)	Recovery (%)
Tap　water	4.0	4.2	4.3	4.0	3.9	3.6	97.5
Lake water	3.0	3.2	3.4	4.0	4.1	5.2	102.5
River water	7.0	7.2	7.1	4.0	4.2	1.4	105.0

Table 4　Determination results of Mo in standard steel samples

Sample	Component	Content (%)	Found (%)			Mean (%)	RSD (%)	RE (%)
BH6628	$25Cr_2Mo_2V$	1.034	1.15	1.036	1.049	1.033	1.7	-0.10
BH79	35MnVAlTiRe	0.544	0.549	0.554	0.543	0.549	1.0	0.92
6814	Low alloy steel	0.70	0.67	0.69	0.71	0.69	2.9	0.01

References

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