

Flow Injection Chemiluminescence Analysis of Low Level Concentration of Hydrazine

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Abstract: Combined with flow-injection (FI) technology, a simple chemiluminescence (CL) method was developed for hydrazine determination in this paper. It was found that hydrazine could greatly decrease the strong CL signal produced by the reaction between luminol and hexacyanoferrate (III) in alkaline medium. The decreased CL intensity was linear with hydrazine concentration in the range of 5.0×10^{-9} g mL⁻¹ to 4.0×10^{-5} g mL⁻¹, and the limit of detection was 2.0×10^{-9} g mL⁻¹ (3 σ) with a relative standard deviation of 2.4~4.1% (n=5).

Keywords: Hydrazine, flow injection, chemiluminescence.

Introduction

Hydrazine is often used as high-energy propellant in space shuttle program, and it is an important precursor in polymer industry, pesticides, and pharmaceuticals^{1,2}. However, owing to its intensive mammalian toxicity, the monitoring of hydrazine residues in environment matrices has become a priority field in industrial laboratories.

Siontorou *et al.*^{3,4} and Marrazza *et al.*⁵ recently designed a kind of DNA biosensor for monitoring pollutant including hydrazine. Some electrochemical methods using modified electrode⁶⁻⁸ were also reported. Flow injection (FI) spectrophotometric methods⁹⁻¹³ have also been employed for the determination of hydrazine based on its inhibitive effect on the reaction of a certain dyestuff with nitrite. However, the expense, operator expertise, sensitivity, and/or detector lifetime has been the primary disadvantages for these techniques.

The application of chemiluminescence (CL) to quantitative analysis of hydrazine has recently received much more attention. Collins *et al.*^{14,15} described a real-time CL detector for monitoring hydrazine vapor, and it is capable of monitoring sub ppb levels of hydrazine in air. In the present work, it was found that hydrazine could greatly decrease the strong CL signal produced by the reaction of luminol with hexacyanoferrate (III) in alkaline medium. The decreased CL intensity is linear with the concentration of hydrazine. Thus, hydrazine could be quantified via the CL intensity and FI-CL system has been applied to the hydrazine determination in air samples.

Experimental

All reagents used were of analytical-reagent grade. A peristaltic pump (Shanghai Meter Electromotor Plant, Model ND-15, 15 r/min) and PTFE tubing (1 mm i.d.) was used in manifold. The reacted solutions of hydrazine and $K_3Fe(CN)_6$ in reaction cell were injected into the carrier stream with the aid of a six-way valve having a 200- μ L loop. The mixed solution was passed to the CL cell and the luminometer (Northwest Non-ferrous Geology Institute of China, Model GD-1) connected to a recorder (Shanghai Dahua Instrument and Meter Plant, Model XWT-206) was used as the light detection system. The concentration of hydrazine was quantified by decreased CL intensity, $\Delta I = I_0 - I_s$, where I_s and I_0 were CL signals in the absence and in the presence of hydrazine, respectively.

Results and Discussion

Time profile of CL reaction

The kinetic properties of the CL reaction is of great importance for the design of the flow system, thus, the time profile of the reaction was tested with a static system, using 1.0×10^{-7} mol L^{-1} luminol and 1.0×10^{-7} mol L^{-1} $K_3Fe(CN)_6$. The CL reached maximum intensity at 26 s and then became extinguished within 200 s after luminol and $K_3Fe(CN)_6$ had been mixed.

Effect of NaOH concentration in the luminol solution

The CL reaction of luminol and $K_3Fe(CN)_6$ takes place only in alkaline solution. The maximum intensity was found in range of the concentration 4.0×10^{-2} mol L^{-1} NaOH, and this concentration was then used in subsequent experiments.

Effect of luminol concentration

The CL intensity was also affected by luminol concentration. The maximal and constant intensity could be obtained at luminol concentrations higher than 8.0×10^{-4} mol L^{-1} . According to the result, 1.0×10^{-3} mol L^{-1} luminol was then employed in subsequent experiments.

Effect of NaOH concentration in the sample solution

The NaOH concentration in the sample solution has a significant influence on the decrease of CL intensity. The decreased CL intensity varied greatly with NaOH concentration in 50 ng mL^{-1} hydrazine. The best signal-to-noise ratio was found with a NaOH concentration of 0.6 mol L^{-1} .

Effect of $K_3Fe(CN)_6$ concentration

The effect of the concentration of $K_3Fe(CN)_6$ on CL intensity was also studied. It lays in two main aspects: one was that the inhibited effect of hydrazine on the CL reaction became weakened with the increase of the concentration of $K_3Fe(CN)_6$ and the accuracy and sensitivity then declined, another was the measurable range of hydrazine might be limited while using a lower concentration of reagents. An optimum concentration of $2.0 \times 10^{-6} \text{ mol L}^{-1}$ was considered for both of these aspects in the following procedures.

Performance of the system for hydrazine measurements

A series of standard solutions were determined under the optimized conditions to test the linearity of the calibration graph. The results are summarized in **Table 1**.

Table 1 Calibration graph of hydrazine

Hydrazine Conc. $\mu\text{g mL}^{-1}$	Equation $Y=aC+b$	Corr. Coe. $\tilde{a}$	RSD ($n=5$)%	LOD ng mL^{-1}
0.005~0.01	$Y=1750C-7.33$	0.9966	4.1	2.0 (3 σ)
0.01~0.1	$Y=284.4C+12.0$	0.9987	4.0	
0.1~1.0	$Y=88.9C+13.0$	0.9994	2.9	
1.0~10.0	$Y=31.5C+132.0$	0.9996	2.6	
10.0~40.0	$Y=7.7C+212.5$	0.9998	2.4	

Interference Study

An extensive interference study with a view to determining hydrazine in environment was performed by analyzing a standard solution of hydrazine to which increasing amounts of interfering species were added and the tolerable limit of a foreign species was taken if it caused a relative error of less than 5%. It was found that with respect to $0.05 \mu\text{g mL}^{-1}$ hydrazine, more than 1000 fold for Na^+ , K^+ , Cr^{3+} , Pb^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Cl^- , Br^- , I^- , NO_3^- , Ac^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , and PO_4^{3-} , 500 for Zn^{2+} , Ca^{2+} , SO_3^{2-} , and S^{2-} , 5 for Cu^{2+} , Mn^{2+} , and 0.1 for Fe^{3+} , Fe^{2+} , respectively. In terms of organic interferences, the tolerable ratios were more than 500 for methanol, ethanol, urea, and sodium benzosulfonate, 5 for benzenediol. The interference of metal ions could be masked by adding excess amount of EDTA.

Applications

The proposed method was applied for the determination of hydrazine in air samples. The recoveries obtained by adding a standard solution of hydrazine to each sample ranged between 96.0 and 101.0%. The results are shown in **Table 2**.

Conclusions

The proposed procedure is compact and simple from the technical point of view. The

combination of them has a potential value in on-line monitoring pollutants including hydrazine in environment.

Table 2 Results of hydrazine in different artificial samples

Sample No.	Results by proposed method				
	Found in air (mg m ⁻³)	Found in absorbent (μg mL ⁻¹)	Added (μg mL ⁻¹)	Total (μg mL ⁻¹)	Recovery (%)
1	2.02	2.91	2.00	4.93	101.0
2	1.92	2.77	1.00	3.76	99.0
3	0.13	0.19	0.20	0.38	96.1
4	0.12	0.17	0.10	0.27	101.0

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