Abstract A novel chemiluminescence system for the determination of bismethiazol is first described in this paper. It is based on the chemiluminescence reaction of bismethiazol and Ce(IV) in nitric acid solution. The emission intensity could be enhanced greatly by Rhodamine B. The chemiluminescence intensity was proportional to bismethiazol concentration over the range 30–1000 μg/L. The detection limit was 12 μg/L (3σ) and the relative standard deviation is 2.4% for 500 μg/L of bismethiazol (n = 11). The proposed method was successfully applied to the determination of bismethiazol in water and in rice. The recovery was 96.4%–104.1%.

Keywords bismethiazol, flow injection analysis, rhodamine B, chemiluminescence

1 Introduction

Bismethiazol \((N,N'-\text{bis}-5\text{-mercapto}-1,3,4\text{-thiadiazole-}methylene)\) was manufactured by Chinese scientists and is widely used in the treatment of striped disease in rice and ulcer in citruses. Various methods have been developed to determine the residual quantity of bismethiazol in food and drinking water including potentiometric titration, spectrophotometry and high performance liquid chromatography. To the best of our knowledge, studies on bismethiazol based on flow injection chemiluminescence (CL) have not been reported.

In this work, a novel chemiluminescence method for the determination of bismethiazol was described. In acid medium, a weak CL was produced by the reaction of bismethiazol oxidized by Ce(IV). The weak CL can be enhanced by rhodamine B (RhB). The bismethiazol concentration was quantified by the enhanced CL intensity. The method has high sensitivity and good reproducibility. It was successfully applied to the determination of bismethiazol in water and in rice.

2 Materials and methods

An IFFM-D chemiluminescence system (Xi’an Rremax electronic science limited company) equipped with HL-2 peristaltic pumps (Huxi Instrument plant, Shanghai, China) was used.

All the reagents were of analytical grade and doubly distilled water was used for the preparation of solutions. Bismethiazol solution (0.1000 g/L) was prepared by dissolving the 10.00 mg bismethiazol (Zhejiang Longwan Chemicals Ltd. Co.) in 100 mL 0.2 mol/L NaOH solution. The stock solution of rhodamine B (0.005 mol/L) was prepared by dissolving 0.240 g RhB (Acros Organics) in 100 mL water. Ce\((\text{SO}_4)\)\(_2\) stock solution (0.010 mol/L) was prepared by dissolving 0.404 g Ce\((\text{SO}_4)\)\(_2\)-4H\(_2\)O in 100 mL 0.10 mol/L H\(_2\)SO\(_4\) solution.

As shown in Fig. 1, the flow lines were inserted into the sample solution, Ce\((\text{SO}_4)\)\(_2\) solution, RhB solution and carrier solution, respectively. First, when the pumps started to wash the whole flow system, the blank CL was measured and recorded. Then, an 80-μL portion of the sample solution was injected into the carrier stream by an eight-channel injector valve and the strengthened CL signal was recorded by PMT. The concentration of bismethiazol was quantified by the relative CL intensity.
3 Results and discussion

3.1 Effects of the fluorescent reagents

The preliminary studies show that the weak CL could be detected between the reaction of bismerthiazol and Ce(IV) in acid media. The CL intensity could be enhanced by some fluorescent reagents. The effects of the fluorescent reagents on the CL intensity such as Rhodamine 6G, Rhodamine B, fluorescein and dichlorofluorescein were studied. The results showed that the enhanced CL intensity was not detected for fluorescein and dichlorofluorescein. The enhanced CL intensity of Rh6G was lower than that of RhB's.

The effect of the concentration of RhB for the CL intensity was further investigated. The results show that increasing the RhB concentration gave an increasing CL intensity. The blank signal was also increased. When the concentration of RhB was 0.1 mmol/L, the signal was stable and a large S/N ratio could be obtained. So, 0.1 mmol/L RhB was used in all subsequent studies.

3.2 Effects of the acid medium

The CL intensity was detected only in acid medium. The acids HCl, HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4} were all investigated. The results show that the highest CL intensity could be detected in the HNO\textsubscript{3} solution. The CL intensity increased with increasing HNO\textsubscript{3} concentration. When the HNO\textsubscript{3} concentration was higher than 6.0 mol/L, the reproducibility of the CL signal decreased. Therefore, 6.0 mol/L HNO\textsubscript{3} was chosen as the optimum acid concentration.

3.3 Effects of concentration of Ce(IV)

The effect of Ce(IV) concentration was studied in the range of 0–2.0 mmol/L. Figure 2 shows that the relative CL intensity increased when the Ce(IV) concentration was increased up to 1.0 mmol/L but decreased at concentrations higher than 1.0 mmol/L. Therefore, 1.0 mmol/L Ce (IV) was used in all subsequent studies.

3.4 Performance of the system for bismerthiazol measurements

Under the optimum conditions described above, the CL response was linearly related to the concentration of bismerthiazol in the range of 30–1000 mg/L with a detection limit of 12 µg/L (3σ). The regression equation was $\Delta I = 1154.5C + 10.409$ (C: concentration of bismerthiazol mg/L, $r = 0.9996$). The relative standard deviation was 2.4% for 500 µg/L bismerthiazol ($n = 11$).

3.5 Interference study

The influence of other species was investigated by analyzing a standard solution of 100 µg/L bismerthiazol to which increasing amounts of interfering species were added. The tolerable limit of the other species was taken as a relative error not higher than 5%. Foreign substances which were found not to interfere with the test when present at up to 100 µg/L concentration include Mg\textsuperscript{2+}, Zn\textsuperscript{2+}, Cu\textsuperscript{2+}, Mn\textsuperscript{2+}, Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, NH\textsubscript{4}\textsuperscript{+}, glucose, pirimicarb, etrofolan, amyln, sucrose and dextrin. At concentrations of up to 50 µg/L, Al\textsuperscript{3+}, Co\textsuperscript{2+}, Pb\textsuperscript{2+}, Ni\textsuperscript{2+} and Cr\textsuperscript{3+} were found not to interfere with the test.

3.6 Applications

The concentration of bismerthiazol in water and rice was analyzed by the proposed method. The results are given in Tables 1, 2 and 3.