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### Chemiluminescence Determination of Sulfite and Sulfur Dioxide Using Tris(1,10-Phenanthroline)Ruthenium-KMnO<sub>4</sub> System

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## CHEMILUMINESCENCE DETERMINATION OF SULFITE AND SULFUR DIOXIDE USING TRIS(1,10-PHENANTHROLINE)RUTHENIUM- KMnO<sub>4</sub> SYSTEM

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The emission produced by sulfite after oxidation by potassium permanganate in acidic solution in the presence of Ru(phen)<sub>3</sub><sup>2+</sup> is used to determine 1.0×10<sup>-7</sup> to 2.5×10<sup>-5</sup> mol/L sulfite. The limit of detection is 4.5×10<sup>-9</sup> mol/L and the relative standard deviation is 3.1% for a 1×10<sup>-5</sup> mol/L sulfite solution (n=8). The method was also applied satisfactorily to the determination of sulfur dioxide in air by using triethanolamine (TEA) as absorbent material.

*Keywords:* Sulfite; chemiluminescence; tris(1,10-phenanthroline) ruthenium(II); air

### INTRODUCTION

Sulfur dioxide is the byproduct of various industrial reactions. It is a major air pollutant, and believed to be responsible for acidifying soil and water due to acid rain.

There are methods available for the determination of SO<sub>2</sub> and SO<sub>3</sub><sup>2-</sup> such as spectrophotometry<sup>[1,2]</sup>, potentiometry<sup>[3]</sup>, coulometry<sup>[4]</sup>, HPLC fluorescence<sup>[5]</sup> and ion chromatography<sup>[6]</sup>, but all suffer from either lack of sensitivity at ambient levels, lack of specificity, use of mercury or its salts, instrumental and procedural complications or long response times. In 1983, Yamada et al<sup>[7]</sup> described a method based on the oxidation of sulfite by permanganate in acidic solution in the presence of riboflavin phosphate to determine sulfite with chemiluminescence detection, and Burguera et al<sup>[8]</sup> used cerium(IV) as an oxidant to determine

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sulfite in wine. Some other compounds were also used as sensitizers such as 3-cyclohexylaminopropanesulphonic acid (CAPS)<sup>[9,10]</sup>, cyclootylamine<sup>[11]</sup>, cyclamate<sup>[12]</sup>, and steroids<sup>[13]</sup>.

Ru(bipy)<sub>3</sub><sup>2+</sup> is an extremely versatile base reactant for a variety of electrogenerated chemiluminescence (CL) processes<sup>[14]</sup> and has also recently become a useful CL reagent. Compared with Ru(bipy)<sub>3</sub><sup>2+</sup>, Ru(phen)<sub>3</sub><sup>2+</sup> has higher enhancement and sensitivity<sup>[15]</sup>. It has been used for the determination of some organic acids in the Ru(phen)<sub>3</sub><sup>2+</sup>-Ce(IV) chemiluminescence system<sup>[16,17]</sup>, but no other analytical application has been presented.

This paper describes the CL properties of the reaction between potassium permanganate and sulfite, in which the emission intensity is greatly enhanced by the presence of Ru(phen)<sub>3</sub><sup>2+</sup> and surfactant. Triethanolamine (TEA) solution was widely used as a sulfur dioxide absorbent<sup>[1,2,18]</sup>. We have used TEA solution to collect sulfur dioxide in air and determined the contents in air successfully with this chemiluminescence system.

## EXPERIMENTAL

### Apparatus

An LKB 1251 luminometer with a Dispenser SVD and a Dispenser controller DC (Pharmacia LKB Biotechnology AB, Sweden) and an Epson LX-800 printer were used.

### Reagents

All solutions were prepared from analytical-reagent grade materials in doubly distilled water. A  $1.0 \times 10^{-2}$  mol/L stock solution of sulfite was prepared daily by dissolving 0.630 g of sodium sulfite in water and diluting with water to 500 ml.

Ru(phen)<sub>3</sub><sup>2+</sup> (prepared in our laboratory<sup>[16]</sup>) solutions were prepared by dissolving a weighed amount of Ru(phen)<sub>3</sub>Br<sub>2</sub> in water and diluting to volume. The concentration of the stock solution was 0.01 g/ml.

Potassium permanganate stock solutions were prepared by dissolving a weighed amount of KMnO<sub>4</sub> in water and adding a certain volume of 1.0 mol/L H<sub>2</sub>SO<sub>4</sub> and diluting to volume. Working solution were prepared by dilution of the stock solution with 1.0 mol/L H<sub>2</sub>SO<sub>4</sub> and water.

The 2.0 % solutions of Tween-20, Tween-40, Tween-80, Triton X-100 were prepared by dissolving 2.0 g in water and diluting with water to 100 ml. The

$1.0 \times 10^{-2}$  mol/L solutions of sodium dodecyl benzene sulfonate (SDBS), tetracyl pyridine bromide (TPB), cetyl pyridine bromide (CPB), cetyl trimethyl ammonium bromide (CTAB) were prepared by dissolving 0.348, 0.356, 0.384, 0.364 g of them in water and diluting with water to 100 ml.

A 1.0% stock solution of Triethanolamine (TEA) was prepared by dissolving 1.0 g of TEA in water and diluting with water to 100 ml.

### Procedure

A 0.2 ml portion of  $4 \times 10^{-5}$  g/mL  $\text{Ru}(\text{phen})_3^{2+}$  and 0.2 ml  $5 \times 10^{-4}$  mol/L SDBS and 0.2 ml sodium sulfite were mixed in order in the sample cuvettes and then transferred into the measuring chamber at a constant temperature of 25° C. After pressing the start button, 0.2 ml of  $5 \times 10^{-3}$  mol/L  $\text{KMnO}_4$  ( $8 \times 10^{-2}$  mol/L  $\text{H}_2\text{SO}_4$ ) were injected automatically and the peak height was recorded. The reagent blank was recorded with the same procedure except that the sodium sulfite was replaced with doubly distilled water.

Calibration graphs of emission intensity [I(mV)] versus sulfite concentration [C(mol/L)] were prepared to determine the sulfite content of the samples. A standard sample solution was included after every 5 samples.

### Determination of sulfur dioxide in air

10 ml of 0.05 % TEA were added into the flasks of the air sampling apparatus and air was pumped through the flask for 2h at 1.0 L/min. Any losses of solution due to evaporation were restored by adding 0.05 % TEA solution after the sampling. The standard solutions were prepared by using 0.05 % TEA solution. The spiked samples were prepared by mixing equal volumes of the standard and the sample solutions.

## RESULTS AND DISCUSSION

### The stability of the sulfite standard solution

The sulfite solutions were prepared every day and preserved for determination. Seven solutions prepared in each day of one week were measured. The decrease of intensity of the solution prepared one day ago was no more than 10% compared to the freshly prepared solution. The solutions prepared with water purged with Ar gas were also tested. In this case the decrease of intensity of the solution

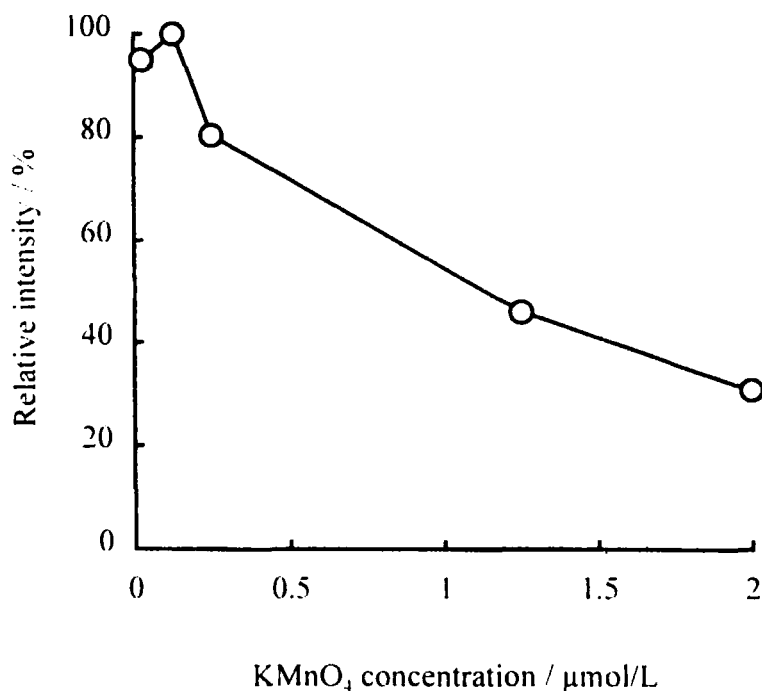


FIGURE 1 Effect of  $\text{KMnO}_4$  concentration in  $2.0 \times 10^{-2}$  mol/L sulfuric acid on the emission intensity from  $1 \times 10^{-5}$  mol/L sulfite in the presence of  $1 \times 10^{-5}$  g/ml  $\text{Ru}(\text{phen})_3^{2+}$  and  $1.25 \times 10^{-4}$  mol/L SDBS

prepared two days ago was no more than 10%. Obviously the oxygen contents of the solution affect the stability of the sulfite solution, so the solution was prepared daily.

#### Effect of concentration of $\text{Ru}(\text{phen})_3^{2+}$

The emission intensity increases with increasing the concentration of  $\text{Ru}(\text{phen})_3^{2+}$ . However, the linear response range was larger with lower concentration of  $\text{Ru}(\text{phen})_3^{2+}$ , so  $1 \times 10^{-5}$  g/ml  $\text{Ru}(\text{phen})_3^{2+}$  were used in this study.

#### Effect of concentration of $\text{KMnO}_4$ and sulfuric acid

The effect of the concentration of  $\text{KMnO}_4$  in  $2 \times 10^{-2}$  mol/L sulfuric acid is shown in Figure 1. The optimum concentration for the oxidant is

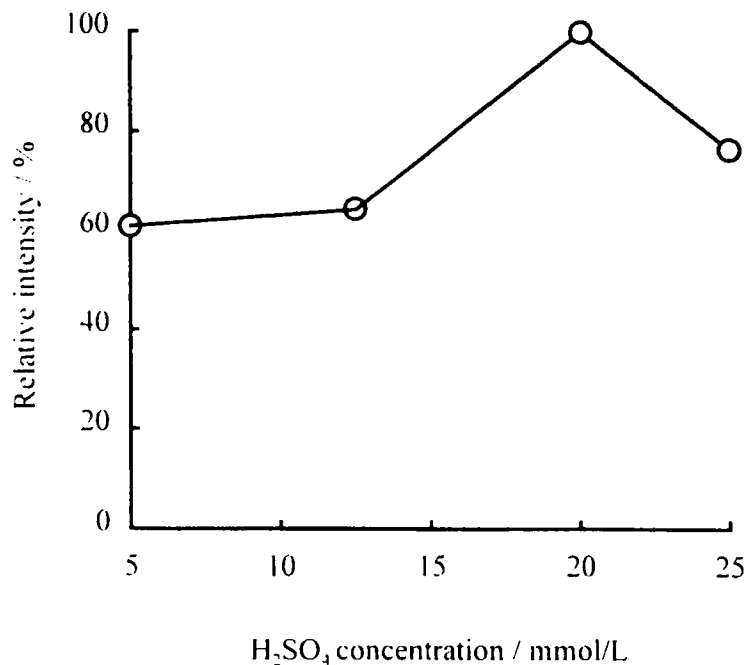


FIGURE 2 Effect of H<sub>2</sub>SO<sub>4</sub> concentration on the emission intensity from  $1 \times 10^{-5}$  mol/L sulfite at  $1.25 \times 10^{-7}$  mol/L KMnO<sub>4</sub> in the presence of  $1 \times 10^{-5}$  g/ml Ru(phen)<sub>3</sub><sup>2+</sup> and  $1.25 \times 10^{-4}$  mol/L SDBS

$1.25 \times 10^{-7}$  mol/L when  $1 \times 10^{-5}$  mol/L sulfite,  $1.25 \times 10^{-4}$  mol/L SDBS and  $1 \times 10^{-5}$  g/ml Ru(phen)<sub>3</sub><sup>2+</sup> were used.

KMnO<sub>4</sub> is a strong oxidant in sulfuric acid solution and the CL intensity was affected by the concentration of the acid (see Figure 2). The optimum concentration of sulfuric acid was  $2 \times 10^{-2}$  mol/L.

#### Effect of sensitizers

Eight sensitizers with two different concentrations were investigated in this study, namely SDBS, Tween-20, Tween-40, Tween-80, Triton X-100, TPB, CPB and CTAB. The enhancement of SDBS is much higher than that of the rest sensitizers.

The effect of the concentration of SDBS in the system is shown in Figure 3. The optimum concentration for SDBS was  $1.25 \times 10^{-4}$  mol/L.

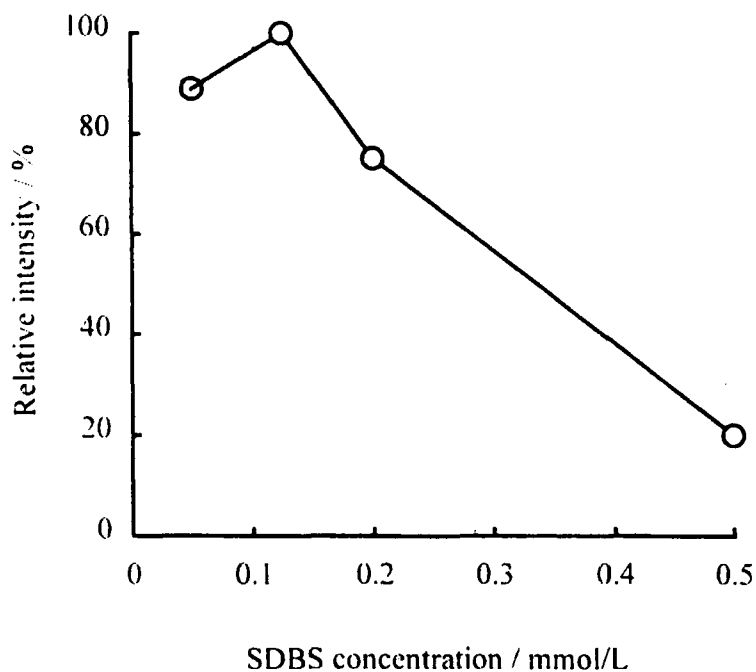


FIGURE 3 Effect of SDBS concentration on the emission intensity from  $1 \times 10^{-5}$  mol/L sulfite at  $1.25 \times 10^{-7}$  mol/L  $\text{KMnO}_4$  in the presence of  $1 \times 10^{-5}$  g/ml  $\text{Ru}(\text{phen})_3^{2+}$  and  $2 \times 10^{-2}$  mol/L sulfuric acid

#### Effect of various ions and solvents

Various ions and solvents commonly used in the laboratory were tested from high to low concentration. It was shown that the CL intensity was practically not changed for the determination of  $2 \times 10^{-5}$  mol/L sulfite when the following were present: 3000-fold  $\text{Na}^+$ , 1000-fold  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , 800-fold  $\text{K}^+$ ,  $\text{Cl}^-$ , 200-fold  $\text{Mg}^{2+}$ ,  $\text{Ac}^-$ ,  $\text{CO}_3^{2-}$ , 100-fold  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{NH}_4^+$ , 20-fold  $\text{Br}^-$ , 10-fold  $\text{SCN}^-$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$ , 8-fold  $\text{Zn}^{2+}$ , 1-fold  $\text{I}^-$ , 1.0 mol/L  $\text{F}^-$ ,  $3.0 \times 10^{-2}$  mol/L  $\text{Al}^{3+}$ .

#### Effect of mixing order of reagents

The emission intensity was affected by the mixing order of reagents. It was found that it was the greatest when  $\text{Ru}(\text{phen})_3^{2+}$  and SDBS were mixed first into the

cuvette, then sulfite was added, and finally  $\text{KMnO}_4$  was injected immediately after.

### Calibration and detection limit

Under the recommended conditions, the calibration graph was stepwise linear from  $1.0 \times 10^{-7}$  to  $2.5 \times 10^{-5}$  mol/L sulfite. The maximum peak height increased linearly within three sulfite concentration ranges, as expressed by the equations  $I = -2.882 + 4.408 \times 10^7 C$ ,  $r=0.9994$ ,  $n=4$  ( $C$ :  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-6}$  mol/L),  $I = -19.25 + 6.656 \times 10^7 C$ ,  $r=0.9999$ ,  $n=6$  ( $C$ :  $1.0 \times 10^{-6}$  to  $2.5 \times 10^{-5}$  mol/L). The detection limit was  $4.5 \times 10^{-9}$  mol/L ( $DL = 3s/r$ ), and the relative standard deviation (RSD) 3.1 % for the  $1 \times 10^{-5}$  mol/L sulfite solution ( $n=8$ ).

### Comparison with other methods

Under the optimum conditions, the proposed method allows the determination of sulfite with 1–3 orders of magnitude higher sensitivity than other reported methods based on various analytical techniques (Table I).

TABLE I Comparison of the dynamic linear range for sulfite afforded by the proposed CL method and other reported methods

Method	Dynamic linear range (mol/L)	Reference
Spectrophotometry	$7.8 \times 10^{-6}$ – $1.3 \times 10^{-4}$	1
	$1.2 \times 10^{-6}$ – $1.6 \times 10^{-4}$	2
Potentiometry	$3.9 \times 10^{-4}$ – $7.8 \times 10^{-3}$	3
Coulometry	$2.3 \times 10^{-7}$ – $3.9 \times 10^{-4}$	4
HPLC-Fluorescence	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	5
Proposed CL method	$1.0 \times 10^{-7}$ – $2.5 \times 10^{-5}$	

### Determination of sulfur dioxide in air

Several absorbing solutions have been investigated for sampling sulfur dioxide in air, for example NaOH,  $\text{Na}_2\text{CO}_3$ , NaOH+citric acid etc., but they are not suitable for this chemiluminescence system.

A TEA solution has been widely used to absorb  $\text{SO}_2$ . Higher concentrations of TEA severely reduces the CL intensity of sulfite-permanganate. A 0.05% TEA



solution has less emission itself and less effect on the CL intensity, and this was used in our study. Therefore, sulfur dioxide was sampled by purging air through a 0.05% TEA absorbing solution.

The calibration graph was linear in the range  $1.0 \times 10^{-7}$  to  $2.0 \times 10^{-4}$  mol/L of sulfite in the 0.05% TEA solution ( $I = -16.49 + 1.023 \times 10^8 C$ ,  $r = 0.9996$ ), which was used for the analytical measurement of air samples. The recoveries were sufficient for practical use and the results are listed in Table II.

TABLE II Determination of sulfur dioxide in air (n=5)

Sample solution ( $SO_3^{2-}/10^{-6}$ mol/l)	Added ( $10^{-6}$ mol/l)	Found ( $10^{-6}$ mol/l)	Recovery (%)
17.37	2.0	9.49	97.99
		9.35	96.54
		9.04	93.34
	10.0	12.36	90.32
		12.54	91.63
		12.93	94.48

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