Chemiluminescence determination of sulfite in sugar and sulfur dioxide in air using Tris(2,2′-bipyridyl)ruthenium(II)-permanganate system

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Abstract

A chemiluminescence (CL) detection for the determination of sulfite using the reaction of $Ru(bipy)_3^{2+}$ (bipy = 2,2′-bipyridyl) -SO_3^{2-}-$KMnO_4$ is described. The concentration of sulfite is proportional to the CL intensity from 5.0×10^{-8} to 1.25×10^{-4} mol l^{-1}. The limit of detection is 2.5×10^{-8} mol l^{-1} and the relative standard deviation is 4.9% for the 2×10^{-5} mol l^{-1} sulfite solution in six repeated measurements. This method has been successfully applied to the determination of sulfite in sugar and sulfur dioxide in air by using triethanolamine (TEA) as the absorbent material. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of sulfite and sulfur dioxide are very important because of their use as food preservatives to prevent oxidation and bacterial growth and reducing agents in bleaching, as well as their potential toxicity as pollutants in the atmosphere. Many methods are available for their determination such as spectrophotometry [1,2], potentiometry [3,4], coulometry [5], gas chromatographic chemiluminence (CL) [6], HPLC fluorescence [7] and ion chromatography [8], but each has some drawback such as lack of sensitivity,

selectivity, or simplicity. CL has been used for the determination of sulfite because of its high sensitivity and simplicity. The CL produced by sulfite was as follows: Sulfite can be oxidized by copper(II) [9] in alkaline solution, and reacts with chemiluminescent reagent luminol [10]. In acidic solution it was oxidized by potassium permanganate [11] or cerium(IV) sulfate [12]. The light emission intensity can be enhanced by the presence of some compounds, e.g. riboflavin for the reactions with permanganate [13,14] and cerium(IV) sulfate [15], flavin mononucleotide for the reaction with permanganate [16], 3-cyclohexylaminopropanesulphonic acid (CAPS) for the reaction with permanganate [14,17] and cerium(IV) sulfate [18], steroids for the reaction with potas-

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sium bromate [19] and sodium cyclamate for the reaction with cerium(IV) sulfate [20].

$Ru(bipy)_3^{2+}$ is an extremely versatile base reactant for a variety of electrogenerated CL processes [21,22], and has also recently become a useful CL reagent. It can be applied to determine 6-mercaptopurine [23] in alkaline medium, and to oxalic or tartaric acids etc. [24,25] in sulfuric medium with much higher sensitivity (the detection limit of oxalic acid is 2.7×10^{-8} mol l^{-1} [24]). It has been shown that $Ru(bipy)_3^{2+}$ is the luminophor in the above system [24] and it has been used in the sulfite–permanganate CL system to increase the sensitivity.

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 $Ru(bipy)_3^{2+}$ and a surfactant. The investigation was extended to the determination of sulfite in sugar. The concentration of sulfite is proportional to the CL intensity from 5.0×10^{-8} to 1.25×10^{-4} mol l^{-1}. The limit of detection is 2.5×10^{-8} mol l^{-1} and the relative standard deviation is 4.9% for the 2×10^{-5} mol l^{-1} sulfite solution in six repeated measurements. Triethanolamine (TEA) solution is a well-known sulfur dioxide absorbent [2,26]. We have used TEA solution to collect sulfur dioxide in air and determined the contents in air successfully.

2. Experimental

2.1. 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 (Seiko Epson, Japan) were used.

2.2. Reagents

All solutions were prepared from analytical-reagent grade materials in doubly distilled water.

A 1.0×10^{-2} mol l^{-1} stock solution of sulfite was prepared daily by dissolving 0.630 g of sodium sulfite in water and diluting with water to 500 ml.

The stock $Ru(bipy)_3^{2+}$ solutions were standardized by dissolving a weighed amount of $Ru(bipy)_3Br_2$ (prepared in our laboratory [23]) in water and diluting to volume. The concentration was 4.48×10^{-3} g ml^{-1}.
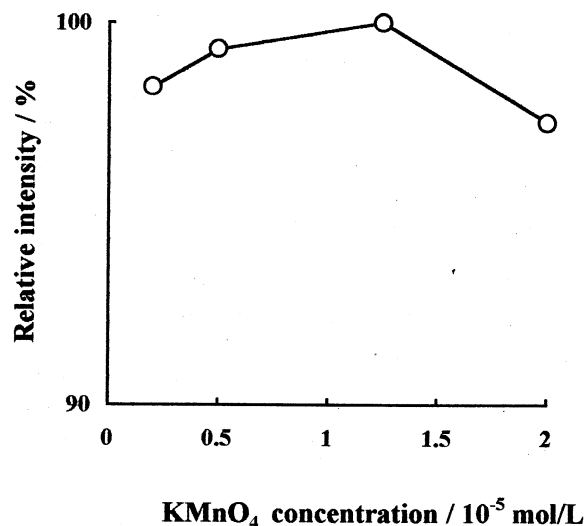

Fig. 1. Effect of $KMnO_4$ concentration in 2.5×10^{-3} mol l^{-1} sulfuric acid on the emission intensity from 8.0×10^{-6} mol l^{-1} sulfite in the presence of 1.12×10^{-5} g ml^{-1} $Ru(bipy)_3^{2+}$ and 5.0×10^{-4} mol l^{-1} SDBS.
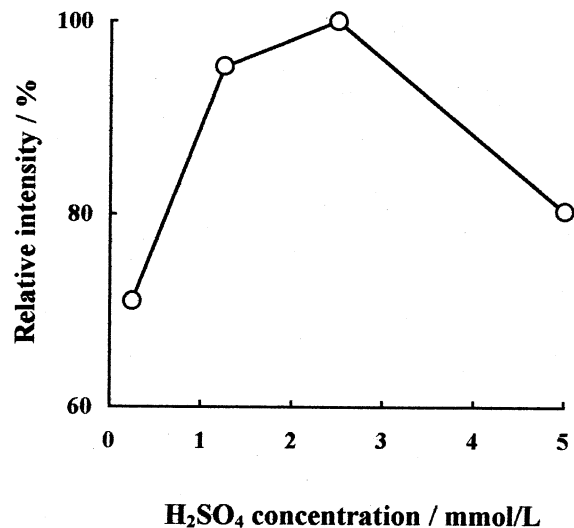

Fig. 2. Effect of H_2SO_4 concentration on the emission intensity from 8.0×10^{-6} mol l^{-1} sulfite at 1.25×10^{-5} mol l^{-1} $KMnO_4$ in the presence of 1.12×10^{-5} g ml^{-1} $Ru(bipy)_3^{2+}$ and 5.0×10^{-4} mol l^{-1} SDBS.

Table 1
Effect of different sensitizers

Sensitizer	Water	SDBS	Tween-20	Tween-40	Tween-80	Triton X-100	TPB	CPB	CTAB
Intensity (mV)	3.8	406	11.2	13.3	6.6	8.5	6.6	7.0	8.4

Potassium permanganate stock solutions were prepared by dissolving a weighed amount of $KMnO_4$ in water and adding a certain volume of 1.0 mol l^{-1} H_2SO_4 and diluting to volume. Working solutions were prepared by dilution of the stock solution with 1.0 mol l^{-1} H_2SO_4 and water.

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

The 1.0×10^{-2} mol l^{-1} solutions of sodium dodecyl benzene sulfonate (SDBS), tetradecyl 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, respectively 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.

2.3. Procedure

A 0.2 ml portion of 4.48×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ and 0.2 ml 2×10^{-3} mol $^{-1}$ SDBS and 0.2 ml sodium sulfite solution were mixed, in this order, in 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 5×10^{-5} mol l^{-1} $KMnO_4$ (1×10^{-2} mol l^{-1} H_2SO_4) was injected automatically and the peak height was recorded. The reagent blank (mV) was recorded using the same procedure, except that the sodium sulfite was replaced by doubly distilled water.

A calibration graph of emission intensity [I (mV)] versus the sulfite concentration [C (mol l^{-1})] were prepared to determine the sulfite content of the samples. A standard sample solution was included for every five samples.

2.4. Determination of sulfite in sugar

A sample solution of sugar was prepared by dissolving 3.42 g of sugar in water and diluting with water to 50 ml. Then 5.0 ml of the sample solution was transferred into a calibrated flask of 10 ml and diluted with water. The final solutions should contain $1 \times 10^{-6} - 5 \times 10^{-5}$ mol l^{-1} of sulfite. We then proceeded as with pure aqueous sulfite solutions.

2.5. Determination of sulfur dioxide in air

We transferred 10 ml of 0.1% TEA into the flasks of the air sampling apparatus and air, e.g. from outside room, was pumped through the flask for 2 h with a flow rate of 1.0 l min^{-1}. Any loss of solution due to evaporation was restored by adding 0.1% TEA solution after the termination
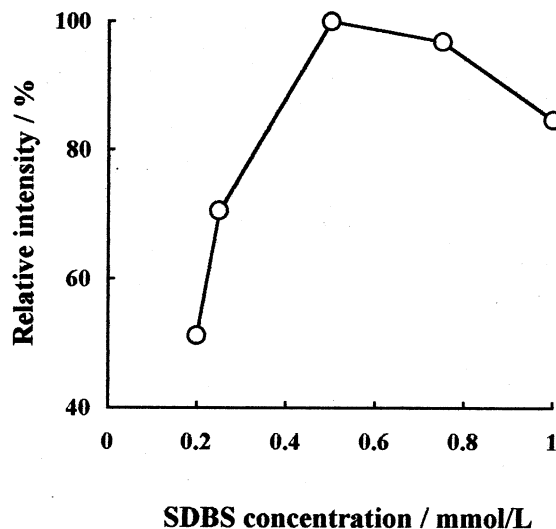

Fig. 3. Effect of SDBS concentration on the emission intensity from 8.0×10^{-6} mol l^{-1} sulfite at 1.25×10^{-5} mol l^{-1} $KMnO_4$ in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ and 2.5×10^{-3} mol l^{-1} sulfuric acid.

Table 2
The regression results of the calibration graph of sulfite in water solution and TEA solution.

Solution	Range of concentraton (mol 1^{-1})	n	a	b	r
Water	$5.0 \times 10^{-8} - 1.25 \times 10^{-6}$	4	5.348	3.133×10^7	0.9998
	$1.25 \times 10^{-6} - 2 \times 10^{-5}$	4	-29.07	5.9×10^7	0.9997
	$2 \times 10^{-5} - 1.25 \times 10^{-4}$	5	767.4	1.791×10^7	0.9999
TEA	$1 \times 10^{-7} - 2.5 \times 10^{-6}$	5	4.337	1.818×10^7	0.9995
	$2.5 \times 10^{-6} - 1.25 \times 10^{-5}$	4	-71.1	4.916×10^7	0.9999

$I = a + b * C$ (I, mV units; C, mol 1^{-1} units)

of sampling. The standard solutions were prepared using a 0.1% TEA solution. Spiked samples were prepared by mixing equal volume of the standard and sample solutions. We then proceeded as with pure aqueous sulfite solutions.

3. Results and discussion

3.1. The stability of the sulfite standard solution

The sulfite solutions of same concentration were prepared every day and preserved for determination. Seven solutions prepared in 1 week were measured. The intensity decreased along with time increases. The decrease of intensity of the solution prepared 1 day before was not more than 10% compared to the solution prepared freshly. It was obvious that the oxygen content of the solution affects the stability of sulfite solution. Therefore, the sulfite solution was prepared daily.

3.2. Effect of the concentration of Ru(bipy)$_3^{2+}$

The emission intensity increases with increasing concentration of Ru(bipy)$_3^{2+}$. The increase is less at low SO_3^{2-} concentration, but large at high SO_3^{2-} concentration. The background has less change. In order to get a wide linear range, 1.12×10^{-5} g ml^{-1} of Ru(bipy)$_3^{2+}$ was used in this study.

3.3. Effect of the concentration of KMnO$_4$ and sulfuric acid

The effect of the concentration of KMnO$_4$ in 2.5×10^{-3} mol 1^{-1} sulfuric acid is shown in Fig. 1. The optimum concentration for the oxidant is 1.25×10^{-5} mol 1^{-1} when 8×10^{-6} mol 1^{-1} sulfite, 5×10^{-4} mol 1^{-1} SDBS and 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ were used. KMnO$_4$ is a strong oxidant in sulfuric acid solution, and the CL intensity was effected by the concentration of the acid (see Fig. 2). The optimum concentration of sulfuric acid was 2.5×10^{-3} mol 1^{-1}.

Table 3
Comparison of the dynamic linear range for sulfite afforded by the proposed CL method and other reported methods

Method	Dynamic linear range (mol 1^{-1})	Reference
Spectrophotometry	$1.5 \times 10^{-5} - 3.1 \times 10^{-4}$	[1]
	$7.8 \times 10^{-6} - 1.3 \times 10^{-4}$	[2]
Potentiometry	$3.9 \times 10^{-4} - 7.8 \times 10^{-3}$	[3]
	$5 \times 10^{-6} - 0.1$	[4]
Coulometry	$2.3 \times 10^{-7} - 3.9 \times 10^{-4}$	[5]
GC-CL	$3.1 \times 10^{-6} - 1.6 \times 10^{-4}$	[6]
HPLC-FLUOR	$5 \times 10^{-6} - 1 \times 10^{-3}$	[7]
Ion chromatography	$7.8 \times 10^{-6} - 1.6 \times 10^{-3}$	[8]
Proposed CL method	$5.0 \times 10^{-8} - 1.25 \times 10^{-4}$	

Table 4
Determination of sulfite in sugar

Sugar solution contents ($\times 10^{-6}$ mol 1^{-1})	Added ($\times 10^{-6}$ mol 1^{-1})	Found ($\times 10^{-6}$ mol 1^{-1})	Recovery (%)
6.13 ± 0.14	5.0	10.81 ± 0.09	93.6
		10.83 ± 0.09	94.0
		10.69 ± 0.09	91.2
	10.0	15.22 ± 0.15	90.9
		15.49 ± 0.15	93.6
		15.12 ± 0.15	89.9

Table 5
Determination of sulfur dioxide in air

Air solution contents ($\times 10^{-6}$ mol 1^{-1})	Added ($\times 10^{-6}$ mol 1^{-1})	Found ($\times 10^{-6}$ mol 1^{-1})	Recovery (%)
1.97 ± 0.12	2.0	1.94 ± 0.08	97.8
		1.88 ± 0.08	94.7
		1.90 ± 0.08	95.7
	6.0	4.20 ± 0.16	105.4
		3.77 ± 0.16	94.6
		3.88 ± 0.16	97.4

3.4. Effect of sensitizers

Eight kinds of sensitizers were investigated in our study. They were SDBS, Tween-20, Tween-40, Tween-80, Triton X-100, TPB, CPB, CTAB. At least two concentrations of the surfactants were tested. The enhancement of SDBS was much higher than that of the rest of surfactants in each condition. The value in Table 1 was obtained in one concentration condition. The effect of concentration of SDBS in the system is shown in Fig. 3. The optimum concentration for SDBS is 5×10^{-4} mol 1^{-1}.

3.5. Effect of mixing order of reagents.

The emission intensity is effected by the mixing order of the reagents. It was shown that the emission intensity is the greatest when Ru(-bipy)$_3^{2+}$ and SDBS were put into the cuvette at first, and then sulfite just before the cuvette was put into the chamber, and KMnO$_4$ was injected immediately. The major effect is caused by the oxidant [23].

3.6. Calibration and detection limit

Under the recommended conditions, the calibration graph was stepwise linear over the range $5.0 \times 10^{-8} - 1.25 \times 10^{-4}$ mol 1^{-1} sulfite. The regression results of the calibration graph was listed in Table 2. The detection limit is 2.5×10^{-8} mol 1^{-1} (DL $= 3s/r$), and the relative standard deviation (RSD) is 4.9% for the 2×10^{-5} mol 1^{-1} sulfite solution ($n = 6$).

3.7. Comparison with other methods

Under the optimum conditions, the proposed method allows for the determination of sulfite with one to four orders of magnitude higher sensitivity than other reported methods based on various analytical techniques (see Table 3).

3.8. Effect of foreign ions

Various compounds commonly used in laboratory were tested from high to low concentration. It was shown that the CL intensity was

almost unchanged for the determination of 5×10^{-5} mol 1^{-1} sulfite when they are present in the system. The list of ions and solvents is as follows: 2000-fold Na^+; 1000-fold K^+; 500-fold Ca^{2+}; 200-fold PO_4^{3-}; Ac^-; 100-fold sucrose; 10-fold Mn^{2+}; Al^{3+}; $C_2O_4^{2-}$; 1 mg ml^{-1} NH_4NO_3; 1 mol 1^{-1} F^-; 0.001 mol 1^{-1} Cu^{2+}; 0.001 mol 1^{-1} EDTA; 0.5% methanol; ethanol; acetonitrile.

3.9. Determination of sulfite in sugar and sulfur dioxide in air

The method was applied to the determination of sulfite in sugar. Standard solutions of pure aqueous sulfite were used for the calibration line to determine the sample solutions of sugar with this method, because 100-fold sucrose has no effect on the determination of 5×10^{-5} mol 1^{-1} sulfite. The recoveries were good enough for practical use. The determination results are listed in Table 4. The sulfite content in sugar is 22.7 mg kg^{-1}.

Several absorbing solutions have been investigated for the sampling of sulfur dioxide in the air (e.g. NaOH, Na_2CO_3, NaOH + citric acid etc.), but they are not suitable for this chemiluminescence system.

A TEA solution is a well-known, completely absorbing reagent for SO_2 [26]. It prevents the air oxidation of SO_3^{2-} formed from SO_2 absorbed by it. Previously, a $HgCl_2 \cdot NaCl$ solution was used to collect SO_2 stably, however, this method required that the $HgCl_2$ solution must be saved after use because it is toxic.

A TEA solution with a higher concentration severely reduced the CL intensity of the sulfite–permanganate solution. A 0.1% TEA solution has less emission itself, and a smaller effect on the CL intensity. Therefore, sulfur dioxide can be sampled if air is purged through a 0.1% TEA absorbing solution. Further, the slope of the calibration graph is constant for a given TEA solution.

The calibration graph was stepwise linear from 1×10^{-7} to 1.25×10^{-5} mol 1^{-1} of sulfite in the 0.1% TEA solution. The regression results of the calibration graph were listed in Table 2. It was used for analytical measurements of the air sam-

ples. The recoveries were good enough for practical use, and all of the determination results are listed in Table 5. The sulfur dioxide content in air is 10.5 μg m^{-3}.

In conclusion, the CL reaction of $Ru(bipy)_3^{2+}$-SO_3^{2-}-$KMnO_4$ can be satisfactorily applied to sensitive and reproducible determination of sulfite in sugar and sulfur dioxide in air. Our reported method is simple and easy. It has high sensitivity and wide linear range compared with other methods described in the introduction.

Acknowledgements

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