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Chemiluminescence determination of sulfite in sugar and of sulfur dioxide in air using the tris(2,2′-bipyridyl)ruthenium-KIO_4 system

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Abstract The chemiluminescence (CL) detection for the determination of sulfite using the reaction of $Ru(bipy)_3^{2+}$(bipy=2,2′-bipyridyl)-SO_3^{2-}-KIO_4 is described. The concentration of sulfite is proportional to the CL intensity from 1.0×10^{-7} to 1.0×10^{-4} mol/L. The limit of detection is 2.0×10^{-8} mol/L and the relative standard deviation is 4.4% for a 2×10^{-5} mol/L sulfite solution (n = 9). This method has successfully been applied to the determination of sulfite in powdered sugar (sucrose) and of sulfur dioxide in air by using triethanolamine (TEA) as absorbent material.

Introduction

The determination of sulfite and sulfur dioxide is 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 CL [6], HPLC fluorescence [7], and ion chromatography [8], but each has some drawbacks 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 used as follows: Sulfite was oxidized by copper(II) [9] in alkaline solution, and reacts with the chemiluminescent reagent luminol [10]. In acidic solution it was oxidized by potassium permanganate [11] or cerium [12]. The light emission intensity can be enhanced by the presence of some compounds, for example, riboflavin for the reactions with permanganate [13, 14] and cerium [15], flavin mononucleotide for the reaction with permanganate [16], 3-cyclohexylaminopropanesulfonic acid (CAPS) for the reaction with permanganate [14, 17] and cerium [18], steroids for the reaction with potassium bromate [19], and sodium cyclamate for the reaction with cerium [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 media, and oxalic or tartaric acids [24, 25] in sulfuric acid media with excellent sensitivity (the detection limit of oxalic acid is 2.7×10^{-8} mol/L [24]). It has been shown that $Ru(bipy)_3^{2+}$ is the luminophor in the above system [24] and it has been used in our previous study of the $Ru(bipy)_3^{2+}$-SO_3^{2-}-$K_2S_2O_8$ CL system [26]. Potassium periodate is a common oxidant in the laboratory, and it was used instead of $K_2S_2O_8$ in the above system because of its good results compared to $K_2S_2O_8$(linear range: 1.5×10^{-7} to 1.0×10^{-4} mol/L; DL: 4.1×10^{-8} mol/L; RSD: 4.3%).

This paper describes the CL properties of the reaction between potassium periodate and sulfite, in which the emission intensity is greatly enhanced by the presence of $Ru(bipy)_3^{2+}$ and surfactant. The investigation was extended to the determination of sulfite in powdered sugar (sucrose) and of sulfur dioxide in air. Triethanolamine (TEA) solution is a well-known sulfur dioxide absorbent [2, 27]. We have used it to collect sulfur dioxide in air and determined the contents in air successfully.

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 1.0×10^{-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.

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$Ru(bipy)_3^{2+}$ solutions were prepared by dissolving a weighed amount of $Ru(bipy)_3Br_2$ in water and diluting to volume. The concentration of stock solution is 4.48×10^{-3} g/mL.

Potassium periodate stock solutions were prepared by dissolving a weighed amount of KIO_4 in water, adding a certain volume of 1.0 mol/L H_2SO_4 and diluting to volume. Working solutions were prepared by dilution of the stock solution with 1.0 mol/L H_2SO_4 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 1.0×10^{-2} mol/L solutions of sodium dodecyl benzene sulfonate(SDBS), tetradecyl pyridine bromide (TPB), cetyl pyridine bromide (CPB) and 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

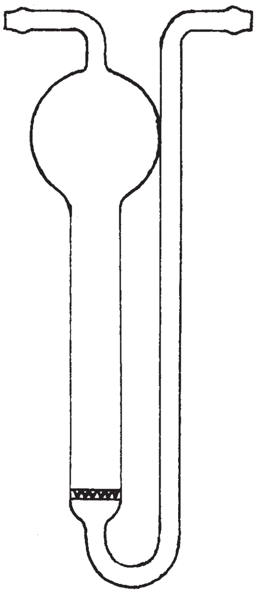
A 0.2 mL portion of 4.48×10^{-5} g/mL $Ru(bipy)_3^{2+}$ (prepared in our laboratory [23]) and 0.2 mL 8×10^{-4} mol/L SDBS and 0.2 mL sodium sulfite were mixed in this order in the sample cuvettes and then transferred into the measuring chamber at a constant temperature of 25 °C. After pressing the start button, 0.2 mL of 2×10^{-4} mol/L KIO_4 (5×10^{-2} mol/L H_2SO_4) was 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 sulfite in powdered sugar

A sample solution of powdered sugar (sucrose) was prepared by dissolving 4.0 g of powdered sugar in water and diluting with water to 100 mL. 2.0 mL of the sample solution were transfered into a calibrated flask and diluted to 10 mL with water. The final solutions contained 1×10^{-6} to 5×10^{-5} mol/L of sulfite. The spiked samples were prepared by adding 2 mL of sample solution and a certain amount of standard solution to a calibrated flask and diluting to 10 mL with water.

Fig. 1 SO_2 sampling device



Determination of sulfur dioxide in air

10 mL of 0.1% TEA were added into the flasks of the air sampling apparatus (see Fig. 1) and air (for example, from an outside room) was pumped through the flask for 2 h at l.0 L/min. Any losses of solution due to evaporation were restored by adding 0.1% TEA solution after termination of sampling. The standard solutions were prepared by using 0.1% TEA solution. The spiked samples were prepared by mixing the standard and the sample solution with equal volume.

Results and discussion

Stability of the sulfite standard solution

Sulfite solution of the same concentration were prepared every day and preserved for the determination. Seven solutions prepared in one week were measured. The decrease of intensity of the solution after one day is not more than 10% compared to the solution prepared freshly, as is shown in Fig. 2. Solutions prepared with water purged with Ar gas were also tested. It was shown that the decrease of intensity of the solution after two days is also

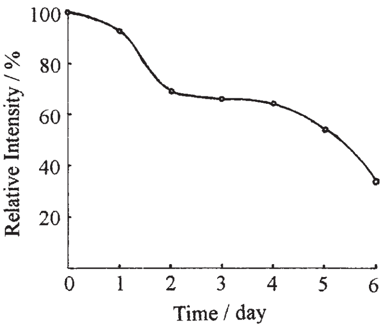


Fig. 2 Effect of deposit time of sulfite standard solution on the emission intensity from 1.25×10^{-5} mol/L sulfite at 1.25×10^{-5} mol/L KIO_4 in the presence of 1.25×10^{-2} mol/L H_2SO_4, 2.0×10^{-4} mol/L SDBS and 1.12×10^{-5} g/mL $Ru(bipy)_3^{2+}$

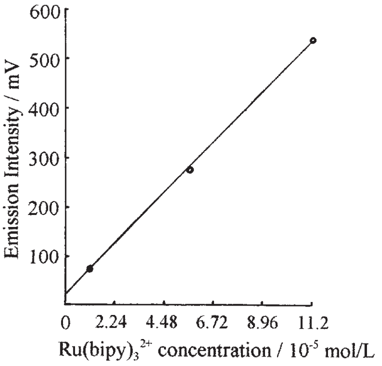


Fig. 3 Effect of the concentration of $Ru(bipy)_3^{2+}$ on the emission intensity from 2.5×10^{-6} mol/L sulfite at 1.25×10^{-5} mol/L KIO_4 in the presence of 1.25×10^{-2} mol/L H_2SO_4, 2.0×10^{-4} mol/L SDBS

not more than 10%. It is obvious that the oxygen content affects the stability of the sulfite solution. So the sulfite solution was prepared daily.

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

The emission intensity increases with increasing concentration of $Ru(bipy)_3^{2+}$. There is a wide range of linear response with 1.12×10^{-5} g/mL of $Ru(bipy)_3^{2+}$, so this was used in this study. The effect of the concentration of $Ru(bipy)_3^{2+}$ on the CL intensity is shown in Fig. 3.

Effect of the concentrations of KIO_4 and sulfuric acid

The effect of the concentration of KIO_4 in 1.25×10^{-2} mol/L sulfuric acid is shown in Fig. 4. The optimum concentration for the oxidant is 5×10^{-5} mol/L when 2.5×10^{-6} mol/L sulfite, 2×10^{-4} mol/L SDBS and 1.12×10^{-5} g/mL $Ru(bipy)_3^{2+}$ were used.

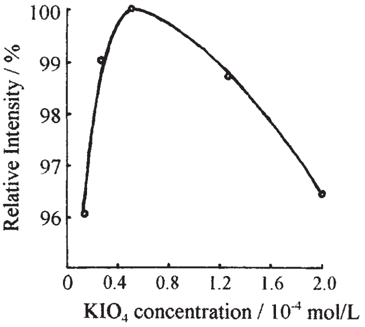


Fig. 4 Effect of KIO_4 concentration in 1.25×10^{-2} mol/L sulfuric acid on the emission intensity from 2.5×10^{-6} mol/L sulfite in the presence of 1.12×10^{-5} g/mL $Ru(bipy)_3^{2+}$ and 2.0×10^{-4} mol/L SDBS

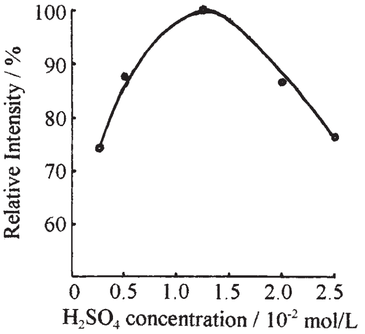


Fig. 5 Effect of the concentration of sulfuric acid on the emission intensity from 2.5×10^{-6} mol/L sulfite at 1.25×10^{-5} mol/L KIO_4 in the presence of 1.12×10^{-5} g/mL $Ru(bipy)_3^{2+}$ and 2.0×10^{-4} mol/L SDBS

KIO_4 is a strong oxidant in sulfuric acid solution and the CL intensity was affected by the concentration of the acid (see Fig. 5). The optimum concentration of sulfuric acid was 1.25×10^{-2} mol/L.

Effect of sensitizers

Eight sensitizers have been investigated in our study: SDBS, Tween-20, Tween-40, Tween-80, Triton X-100, TPB, CPB, CTAB. SDBS has the highest enhancement, as is shown in Table 1.

The effect of the concentration of SDBS in the system is shown in Fig. 6. The optimum concentration is 2×10^{-4} mol/L.

Effect of the mixing order of the reagents

The emission intensity is affected 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, then sulfite just before the cuvette was put into the chamber, and KIO_4 injected immediately. The major effect is caused by the oxidant; it should be added at last [23].

Calibration and detection limit

Under the recommended conditions, the calibration graph was stepwise linear from 1.0×10^{-7} to 1.0×10^{-4} mol/L sulfite. The maximum peak height increased linearly within two sulfite concentration ranges, as expressed by the equations $I = -2.702 + 4.304 \times 10^7 C$, $r = 0.9999$, $n = 7$ (C: 1.0×10^{-7} to 1.25×10^{-5} mol/L) and $I = -98.56 + 5.12 \times 10^7 C$, $r = 0.9997$, $n = 5$ (C: 1.25×10^{-5} to 1.0×10^{-4} mol/L), as is shown in Fig. 7. The detection limit is 2.0×10^{-8} mol/L and the relative standard deviation (RSD) is 4.4% for the 2×10^{-5} mol/L sulfite solution ($n = 9$).

Comparison with other methods

Under the optimum conditions, the proposed method allows the determination of sulfite with 1–4 orders of magnitude higher sensitivity than other reported methods based on various analytical techniques (see Table 2).

It yields good results compared to the $Ru(bipy)_3^{2+}$-SO_3^{2-}-$K_2S_2O_8$ CL system we studied before [26]. The CL

Table 1 Effect of different sensitizers

Sensitizer	Water	SDBS	Tween-20	Tween-40	Tween-80	Triton X-100	TPB	CPB	CTAB
Intensity (mV)	5.0	96.5	2.9	4.4	2.4	1.6	5.1	4.9	2.8

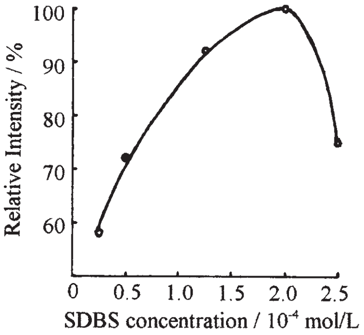


Fig. 6 Effect of the concentration of SDBS on the emission intensity from 2.5×10^{-6} mol/L sulfite at 1.25×10^{-5} mol/L KIO_4 in the presence of 1.12×10^{-5} g/mL $Ru(bipy)_3^{2+}$ and 1.25×10^{-2} mol/L sulfuric acid

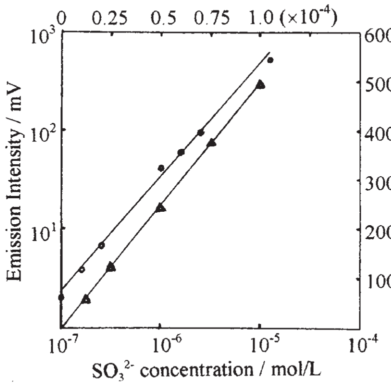


Fig. 7 Calibration graphs for sulfite in water under the recommended conditions. (○): $I = -2.702 + 4.304 \times 10^7 C$, $r = 0.9999$, $n = 7$, C: 1.0×10^{-7} to 1.25×10^{-5} mol/L; (△): $I = -98.56 + 5.12 \times 10^7 C$, $r = 0.9997$, $n = 5$, C: 1.25×10^{-5} to 1.0×10^{-4} mol/L

Table 2 Comparison of the dynamic linear range for sulfite obtained by the proposed CL method and other methods

Method	Dynamic linear range (mol/L)	Reference
Spectrophotometry	$1.5 \times 10^{-5} \sim 3.1 \times 10^{-4}$	[1]
	$7.8 \times 10^{-6} \sim 1.3 \times 10^{-4}$	[2]
Potentiometry	$3.9 \times 10^{-4} \sim 7.8 \times 10^{-3}$	[3]
	$5 \times 10^{-6} \sim 0.1$	[4]
Coulometry	$2.3 \times 10^{-7} \sim 3.9 \times 10^{-4}$	[5]
GC-CL	$3.1 \times 10^{-6} \sim 1.6 \times 10^{-4}$	[6]
HPLC-FLUOR	$5 \times 10^{-6} \sim 1 \times 10^{-3}$	[7]
Ion chromatography	$7.8 \times 10^{-6} \sim 1.6 \times 10^{-3}$	[8]
Proposed CL method	$1.0 \times 10^{-7} \sim 1.0 \times 10^{-4}$	

intensity of blank and the standard deviation of blank are lower than that of the $K_2S_2O_8$ system.

Effect of various ions and solvents

Various ions and solvents commonly used in the laboratory were tested from high to low concentrations. It was shown that the CL intensity was nearly not changed for the determination of 5×10^{-5} mol/L sulfite when the following were present: 1000-fold Na^+, K^+, NO_3^-, NH_4^+, Cl^-, Ba^{2+}; 500-fold Ca^{2+}, PO_4^{3-}, Mg^{2+}, SO_4^{2-}; 100-fold sucrose, HCO_3^-, Ac^-, Pb^{2+}, $C_2O_4^{2-}$, Ni^{2+}; 50-fold Cu^{2+}; 20-fold NH_4SCN; 10-fold Co^{2+}; 5-fold Zn^{2+}; 1-fold Mn^{2+}, Fe^{3+}, $KAl(SO_4)_2$; 0.1 mol/L F^-, 0.001 mol/L EDTA, 0.5% methanol, ethanol, acetonitrile.

Determination of sulfite in powdered sugar and of sulfur dioxide in air

The method was applied to the determination of sulfite in powdered sugar. Standard solutions of pure aqueous sulfite were used to analyze the sample solutions of powdered sugar, because 100-fold sucrose has no effect on the determination of 5×10^{-5} mol/L sulfite. The recoveries were sufficient for practical use and the results are listed in Table 3. The sulfite content in powdered sugar was 22.7 mg/kg.

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

TEA solution is well-known to completely absorb SO_2. Previously $HgCl_2 \cdot NaCl$ solution was used to collect SO_2 stably, but this method required to reserve the $HgCl_2$ solution after use. The absorption of TEA solution is considered as follows. It prevents the oxidation by air of SO_3^{2-} formed from SO_2.

$$SO_2 + H_2O \rightarrow SO_2 \cdot H_2O$$

$$SO_2 \cdot H_2O \rightarrow HSO_3^- + H^+$$

$$HSO_3^- \xrightarrow{H_2O} SO_3^{2-} + H^+$$

$$N(CH_2CH_2OH)_3 + H_2O \rightarrow NH(CH_2CH_2OH)_3^+ + OH^-$$

$$2N(CH_2CH_2OH)_3^+ + SO_3^{2-} \rightarrow [N(CH_2CH_2OH)_3]_2(SO_3^{2-})$$

TEA solution with higher concentration severely reduces the CL intensity of sulfite-periodate. 0.1% TEA solution has less emission itself and less effect on the CL intensity. We used it in our study. 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.

Table 3 Determination of sulfite in powdered sugar (n = 5)

Sugar solution contents (× 10^{-6} mol/L)	Added (× 10^{-6} mol/L)	Found (× 10^{-6} mol/L)	Recovery (%)
1.38 ± 0.05	6.0	7.68 ± 0.37	105.0
		7.31 ± 0.37	98.8
		7.47 ± 0.37	101.5
	10.0	11.71 ± 0.80	103.3
		11.22 ± 0.80	98.4
		10.89 ± 0.80	95.1

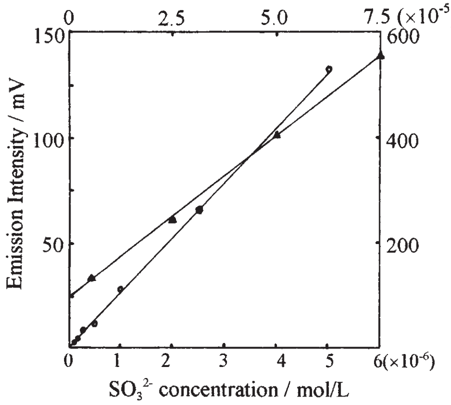


Fig. 8 Calibration graphs for sulfite in 0.1% triethanolamine under the recommended conditions. (○): $I = 0.3952 + 2.629 \times 10^7 C$, $r = 0.9994$, C: 1×10^{-7} to 5×10^{-6} mol/L; (△): $I = 98.25 + 6.056 \times 10^6 C$, $r = 0.9999$, C: 5×10^{-6} to 7.5×10^{-5} mol/L

Table 4 Determination of sulfur dioxide in air (n=5)

Air solution contents ($\times 10^{-6}$ mol/L)	Added ($\times 10^{-6}$ mol/L)	Found ($\times 10^{-6}$ mol/L)	Recovery (%)
2.05 ± 0.27	2.0	2.24 ± 0.16	110.4
		1.96 ± 0.16	96.9
		2.04 ± 0.16	100.7
	6.0	4.08 ± 0.13	101.4
		4.19 ± 0.13	104.1
		3.93 ± 0.13	97.6

The calibration graph was stepwise linear in the range 1×10^{-7} to 7.5×10^{-5} mol/L of sulfite in the 0.1% TEA solution ($I = 0.3952 + 2.629 \times 10^7 C$, $r = 0.9994$, C: 1×10^{-7} to 5×10^{-6} mol/L, $I = 98.25 + 6.056 \times 10^6 C$, $r = 0.9999$, C: 5×10^{-6} to 7.5×10^{-5} mol/L) (see Fig. 8), which was used for the analytical measurement of air samples. The recoveries were sufficient for practical use and the results are listed in Table 4. The sulfur dioxide content in air was 10.9 $\mu g/m^3$.

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