ANALYTICAL SCIENCES AUGUST 1998, VOL. 14

Chemiluminescence Determination of Sulfite in Sugar and Sulfur Dioxide in Air Using $Ru(bipy)_3^{2+}$–$K_2S_2O_8$ System

Zhike He, Fengwu Wu, Hui Meng, Liangjie Yuan, Gongwu Song and Yun'E Zeng

Department of Chemistry, Wuhan University, Wuhan 430072, P. R. of China

A chemiluminescence (CL) detection method for the determination of sulfite is described. The light produced in the reaction of $Ru(bipy)_3^{2+}$(bipy=2,2′-bipyridyl)-SO_3^{2-}–$K_2S_2O_8$ is detected. The concentration of sulfite is proportional to the CL intensity in the range 1.5×10^{-7} – 1.0×10^{-4} mol/l. The limit of detection is 4.1×10^{-8} mol/l and the relative standard deviation is 4.3% for 2×10^{-5} mol/l sulfite solution in 9 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.

Keywords Sulfite, chemiluminescence, tris(2,2′-bipyridine)ruthenium(II), sugar, air

The determinations of sulfite and sulfur dioxide are very important because of their use as food preservatives to prevent oxidation and bacterial growth and a reducing agent in bleaching; they also show 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] however, 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 an alkaline solution, and reacts with the chemiluminescent reagent luminol.[10] In an acidic solution it can be 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 reaction with permanganate[13,14], and cerium[15], flavin mononucleotide for reaction with permanganate[16] and 3-cyclohexylaminopropanesulfonic acid (CAPS) for reaction with permanganate[14,17] and cerium[18], steroids for reaction with potassium bromate[19] and sodium cyclomate for a 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 the determination of 6-mercaptopurine[23] in alkaline media and oxalic, tartaric acids *etc*.[24,25] in sulfuric acid media.

This paper describes the CL properties of a reaction between potassium persulfate 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 and sulfur dioxide in air. The concentration of sulfite is proportional to the CL intensity in the range of 1.5×10^{-7} – 1.0×10^{-4} mol/l. The limit of detection is 4.1×10^{-8} mol/l and the relative standard deviation is 4.3% for the 2×10^{-5} mol/l sulfite solution (n=9). Triethanolamine (TEA) solution is a well-known sulfur dioxide absorbent.[2,26] We have used a TEA solution to collect sulfur dioxide in air and to successfully determined the contents in air.

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 (Seiko Epson Corp., Japan) 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.

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

Potassium persulfate stock solutions were prepared by dissolving a weighed amount of $K_2S_2O_8$ in water and 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.

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

Then, 1.0×10^{-2} mol/l solutions of sodium dodecylbenzene sulfonate (SDBS), tetradecylpyridine bromide (TPB), cetylpyridine bromide (CPB), and cetyltrimethylammonium 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, respectively.

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 5×10^{-4} mol/l SDBS and 0.2 ml sodium sulfite were mixed in order in sample cuvettes, and then transferred into the measuring chamber at a constant temperature of 25°C. After depressing the start button, 0.2 ml of 5.3×10^{-4} mol/l $K_2S_2O_8$ (5×10^{-2} mol/l H_2SO_4) was automatically injected and the peak height was recorded. The reagent blank was recorded using the same procedure, except that the sodium sulfite was replaced with doubly distilled water.

We then constructed a calibration graph of the emission intensity [*I*(mV)] *versus* the sulfite concentration [*C*(mol/l)] and determined the sulfite content of the samples. A standard sample solution was included for every 5 samples.

Determination of sulfite in sugar

A sample solution was prepared by dissolving 4.03 g of sugar in water and diluting with water to 100 ml. Then, 2.0 ml of the sample solution was transferred into a calibrated flask of 10 ml and dilute with water. The final solutions should contain 1×10^{-6} – 5×10^{-5} mol/l of sulfite. We then proceeded as with pure aqueous sulfite solutions.

Determination of sulfur dioxide in air

First, 10 ml of 0.1% TEA was transferred into the flasks of an air-sampling apparatus and pump, for example, air from outside room for 2 h at l.0 l/min. Any losses of the solution due to evaporation was restored by adding a 0.1% TEA solution after the termination of sampling. The standard solutions were prepared by 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.

Results and the Discussion

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

The emission intensity increases with increasing concentration of $Ru(bipy)_3^{2+}$. Since there is a wide range of linear response with 1.12×10^{-5} g/ml of $Ru(bipy)_3^{2+}$, it was used in this study.

Effect of the concentration of $K_2S_2O_8$ and sulfuric acid

The effect of the concentration of $K_2S_2O_8$ in 1.25×10^{-2} mol/l sulfuric acid is shown in Fig. 1. The optimum concentration for the oxidant is 1.32×10^{-4} mol/l when 1.25×10^{-5} mol/l sulfite, 1.25×10^{-4} mol/l SDBS and 1.12×10^{-5} g/ml $Ru(bipy)_3^{2+}$ were used.

$K_2S_2O_8$ is a strong oxidant in a 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 1.25×10^{-2} mol/l.

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, and CTAB. SDBS has the highest enhancement among them, as shown in Table 1.

The effect of the concentration of SDBS in the system was shown in Fig. 3. The optimum concentration

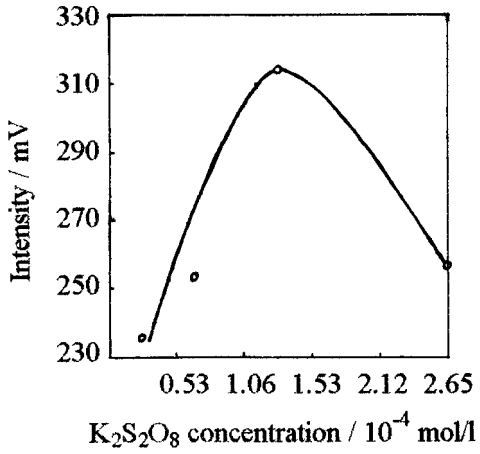

Fig. 1 Effect of the $K_2S_2O_8$ concentration in 1.25×10^{-2} mol/l sulfuric acid on the emission intensity from 1.25×10^{-5} mol/l sulfite in the presence of 1.12×10^{-5} g/ml $Ru(bipy)_3^{2+}$ and 1.25×10^{-4} mol/l SDBS.

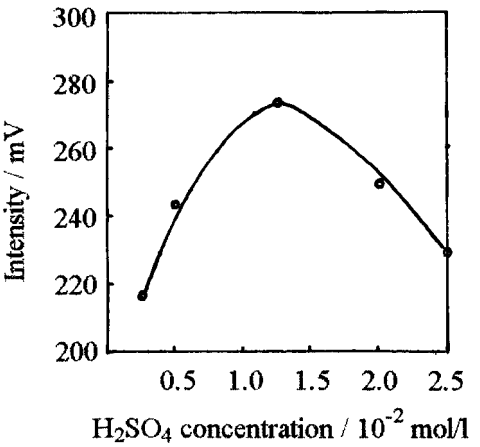

Fig. 2 Effect of the concentration of sulfuric acid on the emission intensity from 1.25×10^{-5} mol/l sulfite at 1.32×10^{-4} mol/l $K_2S_2O_8$ in the presence of 1.12×10^{-5} g/ml $Ru(bipy)_3^{2+}$ and 1.25×10^{-4} mol/l SDBS.

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	111.6	4.3	4.3	11.0	5.0	9.1	4.2	7.5

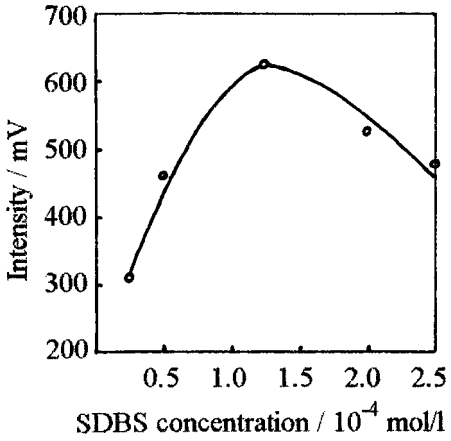

Fig. 3 Effect of the concentration of SDBS on the emission intensity from 1.25×10^{-5} mol/l sulfite at 1.32×10^{-4} mol/l $K_2S_2O_8$ in the presence of 1.12×10^{-5} g/ml $Ru(bipy)_3^{2+}$ and 1.25×10^{-2} mol/l sulfuric acid.

for SDBS is 1.25×10^{-4} mol/l.

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 greatest when $Ru(bipy)_3^{2+}$ and SDBS were put into a cuvette at first, and then sulfite just before the cuvette was put into the chamber, and $K_2S_2O_8$ was injected immediately.

Calibration and detection limit

Under the recommended conditions, the calibration graph was linear over the range 1.5×10^{-7} – 1.0×10^{-4} mol/l sulfite. The maximum peak height increased linearly with the sulfite concentration, as expressed by the equations $I=-2.029+3.628\times10^7C$, $r=0.9998$, $n=4$ (C: 1.5×10^{-7} – 1.5×10^{-6} mol/l), $I=-17.72+4.488\times10^7C$, $r=0.9998$, $n=4$ (C: 1.5×10^{-6} – 1.25×10^{-5} mol/l), $I=88.09+3.91\times10^7C$, $r=0.9995$, $n=4$ (C: 1.25×10^{-5} – 1.0×10^{-4} mol/l). The detection limit is 4.1×10^{-8} mol/l (DL=3s/r), and the relative standard deviation (RSD) is 4.3% for 2×10^{-5} mol/l sulfite solution in 9 repeated measurements.

Comparison with other methods

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

It has a good result compared to the $Ru(bipy)_3^{2+}$–SO_3^{2-}–$KMnO_4$ CL system which we studied before. The CL intensity of a blank and the standard deviation of the blank were lower than that of the $KMnO_4$ system.

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

Method	Dynamic linear range/mol l^{-1}	Reference
Spectrophotometry	1.5×10^{-5} – 3.1×10^{-4}	1
	7.8×10^{-6} – 1.3×10^{-4}	2
Potentiometry	3.9×10^{-4} – 7.8×10^{-3}	3
	5×10^{-6} – 0.1	4
Coulometry	2.3×10^{-7} – 3.9×10^{-4}	5
GC-CL	3.1×10^{-6} – 1.6×10^{-4}	6
HPLC-Fluor.	5×10^{-6} – 1×10^{-3}	7
Ion chromatography	7.8×10^{-6} – 1.6×10^{-3}	8
Proposed CL method	1.5×10^{-7} – 1.0×10^{-4}	

Effect of various ions and solvents

The experimental results showed that 2000-fold Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, 1000-fold Ac^-, CO_3^{2-}, NH_4^+, 500-fold Pb^{2+}, Co^{2+}, 200-fold $C_2O_4^{2-}$, 100-fold sucrose, Ni^{2+}, PO_4^{3-}, NO_3^-, 50-fold Ba^{2+}, 25-fold SCN^-, 20-fold Al^{3+}, 10-fold Cu^{2+}, Mn^{2+}, 4-fold Zn^{2+}, 2-fold Fe^{3+}, 0.002 mol/l F^-, 0.001 mol/l EDTA, 0.5% methanol, ethanol, acetonitrile have no effect on the determination of 5×10^{-5} mol/l sulfite.

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 to determine the sample solutions of sugar in this method, because 100-fold sucrose has no effect on the determination of 5×10^{-5} mol/l sulfite. The recoveries were good enough for practical use; all of the determination results are listed in Table 3. The sulfite content in sugar is 29.3 mg/kg.

Although several absorbing solutions have been investigated for the sampling of sulfur dioxide in air (for example NaOH, Na_2CO_3, NaOH+ciric acid, *etc.*), they are not suitable for this chemiluminescence system. A TEA solution is well-known to completely adsorb SO_2. It prevents the air oxidation of SO_3^{2-} formed from SO_2 absorbed by it. Previously, a $HgCl_2$–NaCl solution was used to collect SO_2 stably; however, this method required that the $HgCl_2$ solution be saved after use. The absorption of a TEA solution is considered to occur as follows:

Table 3 Determination of sulfite in sugar

Sugar solution contents/10^{-6} mol l^{-1}	Added/ 10^{-6} mol l^{-1}	Found/ 10^{-6} mol l^{-1}	Recovery, %
1.88	3.0	5.03	105
		5.12	108
		4.94	102
	10.0	12.18	103
		12.07	102
		11.81	99.3

Table 4 Determination of sulfur dioxide in air

Air solution contents/ 10^{-6} mol l^{-1}	Added/ 10^{-6} mol l^{-1}	Found/ 10^{-6} mol l^{-1}	Recovery, %
3.53	2.0	2.73	98.7
		2.96	107.0
		3.25	117.5
	10.0	7.03	104.0
		6.50	96.2
		6.32	93.4

$$SO_2+H_2O \longrightarrow SO_2 \cdot H_2O,$$

$$SO_2 \cdot H_2O \longrightarrow HSO_3^- + H^+,$$

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

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

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

A TEA solution with a higher concentration severely reduced the CL intensity of sulfite–persulfate. A 0.1% TEA solution has less emission itself, and a smaller 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.

The calibration graph was stepwise linear over the range 1.5×10^{-7} – 1.0×10^{-4} mol/l of sulfite in the 0.1% TEA solution (I=0.6767+3.14×10^7C, r=0.9995), which was used for analytical measurements of air samples. The recoveries were good enough for practical use; all of the determination results are listed in Table 4. The sulfur dioxide content in air is 9.4 μg/m^3.

The authors thank the Chinese Natural Science Foundation and the Hubei Provincial Natural Science Foundation for financial support.

References

1. L. G. Decnop-Weever and J. C. Kraak, *Anal. Chim. Acta*, **337**, 125 (1997).
2. M. Pandurangappa and N. Balasubramanian, *Analusis*, **24**, 225 (1996).
3. C.-Y. Chiou and T.-C. Chou, *Electroanalysis*, **8**, 1179 (1996).
4. I. Ibrahim, Y. Cemal and B. Humeyra, *Analyst*[London], **121**, 1873 (1996).
5. N. Ekkad and C. O. Huber, *Anal. Chim. Acta*, **332**, 155 (1996).
6. A. Lavigne-Delcroix, D. Tusseau and M. Proix, *Sci. Aliments*, **16**, 267 (1996).
7. J. Rethmeier, A. Rabenstein, M. Langer and U. Fischer, *J. Chromatogr.*, **760**, 295 (1997).
8. E. Ruiz, M. I. Santillana, M. De Alba, M. T. Nieto and S. Garcia-Castellano, *J. Liq. Chromatogr.*, **17**, 447 (1994).
9. J. M. Lin and T. Hobo, *Anal. Chim. Acta*, **323**, 69 (1996).
10. Y. L. Huang, J. M. Kim and R. D. Schmid, *Anal. Chim. Acta*, **266**, 317 (1992).
11. F. Meixner and W. Jaeschke, *Fresenius' Z. Anal. Chem.*, **317**, 343 (1984).
12. K. Takeuchi and T. Ibusuki, *Anal. Chim. Acta*, **174**, 359 (1985).
13. M. Yamada, T. Nakada and S. Suzuki, *Anal. Chim. Acta*, **147**, 401 (1983).
14. S. A. Al-Tamrah, A. Townshend and A. R. Wheatley, *Analyst*[London], **112**, 883 (1987).
15. J. L. Burguera and M. Burguera, *Anal. Chim. Acta*, **214**, 429 (1988).
16. M. Kato, M. Yamada and S. Suzuki, *Anal. Chem.*, **56**, 2529 (1984).
17. D. A. Paulls and A. Townshend, *Analyst*[London], **121**, 831 (1996).
18. I. I. Koukli, E. G. Sarantonis and A. C. Calokerinos, *Analyst*[London], **113**, 603 (1988).
19. A. B. Syropoulos, E. G. Sarantonis and A. C. Calokerinos, *Anal. Chim. Acta*, **239**, 195 (1990).
20. I. M. Psarellis, E. G. Sarantonis and A. C. Calokerinos, *Anal. Chim. Acta*, **272**, 265 (1993).
21. L. L. Shultz, J. S. Stoyanoff and T. A. Nieman, *Anal. Chem.*, **68**, 349 (1996).
22. W. Y. Lee and T. A. Nieman, *Anal. Chem.*, **67**, 1789 (1995).
23. Z. K. He, X. L. Liu, Q. Y. Luo, X. M. Yu and Y. E. Zeng, *Anal. Sci.*, **11**, 415 (1995).
24. Z. K. He, H. Gao, L. J. Yuan, Q. Y. Luo and Y. E. Zeng, *Analyst*[London], **122**, 1343 (1997).
25. Z. K. He, R. M. Ma, Q. Y. Luo, X. M. Yu and Y. E. Zeng, *Acta Chim. Sinica*, **54**, 1003 (1996).
26. T. Korenaga, "*Development of a passive sampler for sulfur oxide monitoring in China*", pp. 53 – 54, The University of Tokushima, Japan, Mar. 1996.

(Received January 30, 1998)
(Accepted April 13, 1998)