Determination of sulfite in sugar and sulfur dioxide in air by chemiluminescence using the Ru(bipy)$_3^{2+}$–KBrO$_3$ system

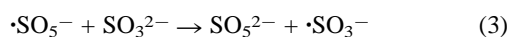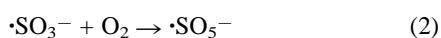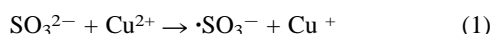**Fengwu Wu, Zhike He,* Hui Meng and Yun'e Zeng**

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A chemiluminescence (CL) detection method for the determination of sulfite using the reaction of Ru(bipy)$_3^{2+}$ (bipy = 2,2′-bipyridyl)–SO$_3^{2-}$–KBrO$_3$ is described. The concentration of sulfite is proportional to the CL intensity in the range 2.5×10^{-8}–9.5×10^{-5} mol l^{-1}. The limit of detection is 3.8×10^{-9} mol l^{-1} and the relative standard deviation is 4.6% for 5×10^{-5} mol l^{-1} sulfite solution with nine repeated measurements. This method was successfully applied to the determination of sulfite in sugar and sulfur dioxide in air by using triethanolamine as the absorbent material.

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 chromatography–chemiluminescence (CL),[6] HPLC–fluorescence detection[7] and ion chromatography.[8] However, 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 was produced by sulfite 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(IV).[12] The light-emission intensity can be enhanced by the presence of some compounds, *e.g.*, riboflavin for reaction with permanganate[13,14] and cerium(IV),[15] flavin mononucleotide for reaction with permanganate[16] and 3-cyclohexylaminopropanesulfonic acid (CAPS) for reaction with permanganate[14,17] and cerium(IV),[18] steroids for reaction with potassium bromate[19] and sodium cyclamate for reaction with cerium(IV).[20]

The kinetics and mechanism of sulfite oxidation were as follows:[9,21]

$$SO_3^{2-} + Cu^{2+} \rightarrow {}^{\bullet}SO_3^{-} + Cu^{+} \tag{1}$$

$$ {}^{\bullet}SO_3^{-} + O_2 \rightarrow {}^{\bullet}SO_5^{-} \tag{2}$$

$$ {}^{\bullet}SO_5^{-} + SO_3^{2-} \rightarrow SO_5^{2-} + {}^{\bullet}SO_3^{-} \tag{3}$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-} \tag{4}$$

These steps were supported by chemical evidence and are generally accepted.[22–24] A CL reaction scheme for sulfite has been described by Meiner and Jaeschke.[25] They thought the triplet state (^{3}SO$_2$*) can give luminescence from the intermediate $^{\bullet}$SO$_3^{-}$. The emission spectrum (450–600 nm) from the SO$_2$* has also been measured by Stauff and Jaeschke[26] using interference filters. This was supported by the idea that there is an emission only from the triplet state in the visible range.[27]

Ru(bipy)$_3^{2+}$ (bipy = 2,2′-dipyridyl) is an extremely versatile base reactant for a variety of CL processes.[28,29] It was used for the determination of oxalate and other organic acids,[30,31] pyruvate[32] and amino acids[33,34] by electrogenerated chemiluminescence (ECL). We have used it as a CL reagent for the determination of 6-mercaptopurine[35] in alkaline media and oxalic and tartaric acid, *etc.*,[36,37] in sulfuric acid media.

This paper describes the CL properties of the reaction of Ru(bipy)$_3^{2+}$–SO$_3^{2-}$–KBrO$_3$. 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 2.5×10^{-8}–9.5×10^{-5} mol l^{-1}. The limit of detection is 3.8×10^{-9} mol l^{-1} and the relative standard deviation is 4.6% for 5×10^{-5} mol l^{-1} sulfite solution with nine repeated measurements. Triethanolamine (TEA) solution is a well known sulfur dioxide absorbent.[2,38] We used a TEA solution to collect sulfur dioxide in air and to determine the content in air successfully.

Experimental

Apparatus

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

Reagents

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

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

Ru(bipy)$_3^{2+}$ (prepared in our laboratory[35]) solutions were prepared by dissolving a weighed amount of Ru(bipy)$_3$Br$_2$ in water and diluting to volume. The concentration of the stock standard solution was 4.48×10^{-3} g ml^{-1}.

Potassium bromate stock standard solutions were prepared by dissolving a weighed amount of KBrO$_3$ in water, adding a certain volume of 1.0 mol l^{-1} H$_2$SO$_4$ and diluting to volume. Working standard solutions were prepared by dilution of the stock standard solution with 1.0 mol l^{-1} H$_2$SO$_4$ and water.

A 1.07×10^{-2} mol l^{-1} stock standard solution of sodium dodecylbenzene sulfonate (SDBS) was prepared by dissolving 374.4 mg of SDBS in water and diluting to 100 ml with water. Solutions of Tween-20, Tween-40, Tween-80 and Triton X-100 (all 2%) were prepared by dissolving 2.0 g of each in water and diluting to 100 ml with water. Solutions of tetradecylpyridine bromide (TPB), cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB) (all 1.0×10^{-2} mol l^{-1}) were prepared by dissolving 0.356, 0.384 and 0.364 g, respectively, in water and diluting to 100 ml with water. A 1.0% stock standard solution of triethanolamine (TEA) was prepared

by dissolving 1.0 g of TEA in water and diluting to 100 ml with water.

Procedure

A 0.2 ml portion of 4.48×10^{-5} mol l^{-1} Ru(bipy)$_3^{2+}$, 0.2 ml of 8.6×10^{-4} mol l^{-1} SDBS and 0.2 ml of 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 5.64×10^{-3} mol l^{-1} KBrO$_3$ (2.0×10^{-2} mol l^{-1} H$_2$SO$_4$) was automatically injected 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.

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

Determination of sulfite in sugar

A sample solution of sugar was prepared by dissolving 6.000 g of sugar in water and diluting to 50 ml with water. A 2.0 ml volume of the sample solution was transferred into a calibrated flask and diluted to 10 ml. The final solution should contain 1×10^{-3}–5×10^{-5} mol l^{-1} of sulfite, and proceeded as with pure aqueous sulfite solutions.

Determination of sulfur dioxide in air

A 10 ml volume of 0.1% TEA was added to the flasks of the air sampling apparatus and air, for example, from outside the room, was pumped through the flask for 2 h at l.0 l min^{-1}. Any losses of solution due to evaporation were restored by adding 0.1% TEA solution after termination of sampling. Standard solutions were prepared by using 0.1% TEA solution. The spiked samples were prepared by mixing equal volumes of the standard and the sample solution and proceeded as with pure aqueous sulfite solutions.

Results and discussion

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

The effect of the concentration of Ru(bipy)$_3^{2+}$ in the range 5.6×10^{-6}–1.12×10^{-4} mol l^{-1} was investigated. 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^{-1} of Ru(bipy)$_3^{2+}$, which was adopted in this study.

Effect of the concentration of KBrO$_3$ and sulfuric acid

The effect of the concentration of KBrO$_3$ in the range 2.8×10^{-5}–2.8×10^{-3} mol l^{-1} in 5×10^{-3} mol l^{-1} sulfuric acid was investigated (Fig. 1). The optimum concentration for the oxidant is 1.41×10^{-3} mol l^{-1} when 8.75×10^{-6} mol l^{-1} sulfite is used. KBrO$_3$ is a strong oxidant in sulfuric acid solution. The effect of the concentration of sulfuric acid in the range 2.5×10^{-4}–2×10^{-2} mol l^{-1} was investigated (Fig. 2). The optimum concentration of sulfuric acid was 5×10^{-3} mol l^{-1}.

Effect of sensitizers

Eight sensitizers were investigated, SDBS, Tween-20, Tween-40, Tween-80, Triton X-100, TPB, CPB and CTAB. The

interaction of Ru(bipy)$_3^{2+}$ photosensitizer with surfactants has been reported.[39,40] We have studied the effect of surfactants on the CL character of Ru(bipy)$_3^{2+}$.[41] SDBS shows the highest enhancement, as shown in Table 1. This is because Ru(bipy)$_3^{2+}$ exists as a cationic complex in aqueous solution, where it is surrounded by the anionic surfactant SDBS, which prevents the extinction of CL by water and increases the excited state lifetime of the complex of Ru(bipy)$_3^{2+}$. The effect of the concentration of SDBS in the system is shown in Fig. 3. The optimum concentration of SDBS was 2.15×10^{-4} mol l^{-1}.

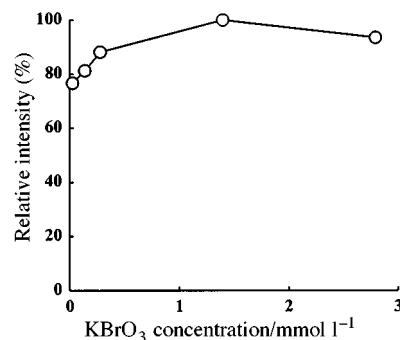**Fig. 1** Effect of KBrO$_3$ concentration in 5×10^{-3} mol l^{-1} sulfuric acid on the emission intensity from 8.75×10^{-6} mol l^{-1} sulfite in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ and 2.15×10^{-4} mol l^{-1} SDBS.
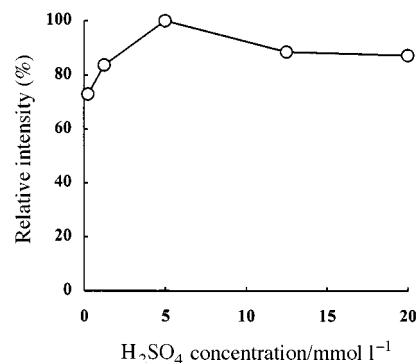

Fig. 2 Effect of H$_2$SO$_4$ concentration on the emission intensity from 8.75×10^{-6} mol l^{-1} sulfite at 1.41×10^{-3} mol l^{-1} KBrO$_3$ in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ and 2.15×10^{-4} mol l^{-1} SDBS.

Table 1 Effect of different sensitizers

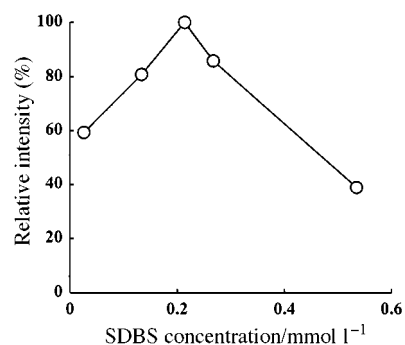| Sensitizer	Intensity/mV	Sensitizer	Intensity/mV
Water	3.8	Triton X-100	4.3
SDBS	126	TPB	7.7
Tween-20	7.9	CPB	5.6
Tween-40	7.7	CTAB	3.5
Tween-80	4.2		

Fig. 3 Effect of SDBS concentration on the emission intensity from 8.75×10^{-6} mol l^{-1} sulfite at 1.41×10^{-3} mol l^{-1} KBrO$_3$ in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$ and 5×10^{-3} mol l^{-1} sulfuric acid.
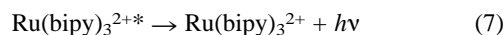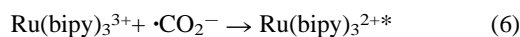
Effect of foreign compounds

Various compounds commonly used in the laboratory were tested from high to low concentrations. It was found that the CL intensity remained almost unchanged for the determination of 5×10^{-5} mol l^{-1} sulfite when they were present in the system. Tolerated amounts of ions and solvents are as follows: 2000-fold, Na^+, Cl^-; 1000-fold, K^+, Ca^{2+}, Br^-, I^-, OAc^-, NO_3^-, CO_3^{2-}, $C_2O_4^{2-}$, PO_4^{3-}; 1 mol l^{-1} F^-; 0.01 mol l^{-1} Cu^{2+}; 0.001 mol l^{-1} EDTA; 50-fold, Al^{3+} (1000-fold Al^{3+} can be eliminated by adding F^-); 500-fold, NH_4^+; 10-fold, Fe^{2+}; 100-fold sucrose; 0.15%, phenanthroline; and 0.5%, methanol, ethanol, acetonitrile.

Effect of mixing order of reagents

The emission intensity is affected by the mixing order of reagents. It was found that the emission intensity was the greatest when $Ru(bipy)_3^{2+}$ and SDBS were placed in the cuvette first, then sulfite just before the cuvette was inserted into the chamber, and $KBrO_3$ was injected immediately.[35]
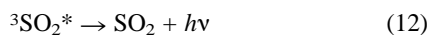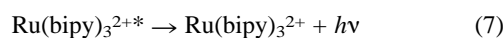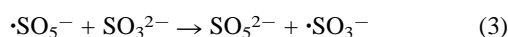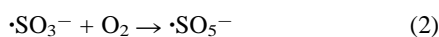
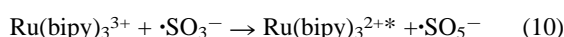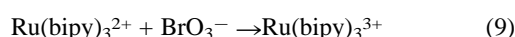## Kinetics and mechanism of the CL reaction

The emission intensities of $Ru(bipy)_3^{2+}$ + $Ce(SO_4)_2$ with and without $H_2C_2O_4$ are highest. The mechanism of $Ru(bipy)_3^{2+}$ oxidation with $Ce(SO_4)_2$ is as follows:[36,37]

$$Ru(bipy)_3^{2+} + Ce^{IV} \rightarrow Ru(bipy)_3^{3+} \quad (5)$$

$$Ru(bipy)_3^{3+} + \cdot CO_2^- \rightarrow Ru(bipy)_3^{2+*} \quad (6)$$

$$Ru(bipy)_3^{2+*} \rightarrow Ru(bipy)_3^{2+} + h\nu \quad (7)$$

The maximum emission wavelength of the excited state of $Ru(bipy)_3^{2+*}$ is 608 nm.[42] In this experiment, the emission intensities of $Ru(bipy)_3^{2+}$ + $KBrO_3$ and SO_3^{2-} + $KBrO_3$ are lower, but that of $Ru(bipy)_3^{2+}$ + SO_3^{2-} + $KBrO_3$ is higher.

According to the mechanisms of the oxidation of $Ru(bipy)_3^{2+}$ and SO_3^{2-} mentioned above, the mechanism of this system may be as follows:

$$SO_3^{2-} + BrO_3^- \rightarrow \cdot SO_3^- \quad (8)$$

$$Ru(bipy)_3^{2+} + BrO_3^- \rightarrow Ru(bipy)_3^{3+} \quad (9)$$

$$Ru(bipy)_3^{3+} + \cdot SO_3^- \rightarrow Ru(bipy)_3^{2+*} + \cdot SO_5^- \quad (10)$$

$$\cdot SO_3^- + O_2 \rightarrow \cdot SO_5^- \quad (2)$$

$$\cdot SO_5^- + SO_3^{2-} \rightarrow SO_5^{2-} + \cdot SO_3^- \quad (3)$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-} \quad (4)$$

$$Ru(bipy)_3^{2+*} \rightarrow Ru(bipy)_3^{2+} + h\nu \quad (7)$$

$$\cdot SO_3^- \rightarrow {}^3SO_2^* \quad (11)$$

$${}^3SO_2^* \rightarrow SO_2 + h\nu \quad (12)$$

$Ru(bipy)_3^{2+}$ and SO_3^{2-} may give luminescence in this system, as mentioned before. Because the emission intensity is proportional to the concentration of $Ru(bipy)_3^{2+}$ and SO_3^{2-} separately, there may be two luminophores in this system.

Calibration and detection limit

Under the recommended conditions, the calibration graph was linear over the range 2.5×10^{-8}–9.5×10^{-5} mol l^{-1} sulfur dioxide. The maximum peak height increased linearly with increase in sulfite concentration, as expressed by the equations $I = -0.03555 + 3.107 \times 10^7 C$, $r = 0.9994$ ($C = 2.5 \times 10^{-8}$–1.25×10^{-6}) and $I = -10.70 + 4.744 \times 10^7 C$, $r = 0.9998$ ($C = 1.25 \times 10^{-6}$–9.5×10^{-5}). The detection limit is 3.8×10^{-9} mol l^{-1} (DL = $3s/r$), and the relative standard deviation (RSD) is 4.6% for 5×10^{-5} mol l^{-1} sulfite solution with nine repeated measurements.
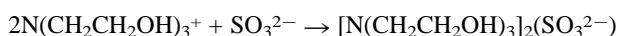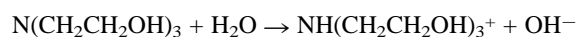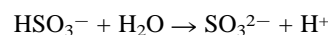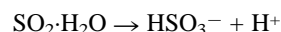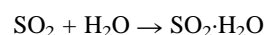
Comparison with other methods

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).

Determination of sulfite in sugar and sulfur dioxide in air

The method was applied to the determination of sulfite in sugar. Because no effect was observed from sucrose, we determined the sulfite contents of sugar solution as with pure aqueous sulfite solutions. The recoveries were good enough for practical use and all determination results are given in Table 3. The sulfite content in sugar is 22.8 mg kg^{-1}. Although several absorbing solutions were investigated for the sampling of sulfur dioxide in air (e.g., NaOH, Na_2CO_3, NaOH + citric acid), they are not suitable for this CL system.

A TEA solution is well known to absorb SO_2 completely. It prevents the air oxidation of SO_3^{2-} formed from SO_2 absorbed by it. Previously, an $HgCl_2$–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:[38]

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

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

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

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

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

A TEA solution with a higher concentration severely reduced the CL intensity of sulfite–bromate. The effect of various TEA concentrations on 2×10^{-5} mol l^{-1} sulfite is shown in Fig. 4 and the emission intensity of TEA solution of various concentrations is shown in Fig. 5. According to the emission itself and the effect of TEA concentration on sulfite, we selected 0.1% TEA solution as an absorbing solution. The CL intensity and the slope of calibration graph depend on the TEA concentration. TEA concentrations >0.1% severely reduce the intensity but at lower concentration the effect is less pronounced. The final concentration of TEA in the analyte solution should not exceed 0.1%. Therefore, sulfur dioxide can be sampled if air is purged through a 0.1% TEA absorbing

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}	Ref.
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–fluorescence	5×10^{-6}–1×10^{-3}	7
Ion chromatography	7.8×10^{-6}–1.6×10^{-3}	8
Proposed CL method	2.5×10^{-8}–9.5×10^{-5}	

Table 3 Determination of sulfite in sugar

Sugar solution content/ 10^{-6} mol l^{-1}	Added/ 10^{-6} mol l^{-1}	Found/ 10^{-6} mol l^{-1}	Recovery (%)
4.34	3.0	7.03	95.8
		7.16	97.5
		7.29	99.3
	15.0	19.0	98.2
		20.4	105.5
		21.2	109.6

solution. Further, the slope of the calibration graph is constant for a given TEA solution.

The calibration graph was linear in the range 5×10^{-8}–5×10^{-6} mol l^{-1} of sulfite [$I = 2.903 + 1.381 \times 10^{-7}C, r = 0.9902$ ($C = 5 \times 10^{-8}$–5×10^{-7} mol l^{-1}); $I = -1.691 + 2.336 \times 10^7C, r = 0.9991$ ($C = 5 \times 10^{-7}$–5×10^{-6} mol l^{-1})] in the 0.1% TEA solution, which was used for the analytical measurement of air samples. The recoveries were good enough for practical use and all of the determination results are listed in Table 4. The sulfur dioxide content in air is 11.6 µg m^{-3}.

Conclusion

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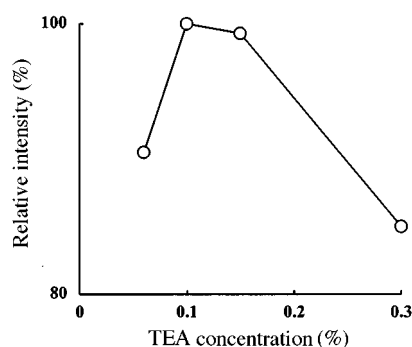

Fig. 4 Effect of TEA concentration on the emission intensity from 8.75×10^{-6} mol l^{-1} sulfite at 1.41×10^{-3} mol l^{-1} KBrO$_3$ in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$, 5×10^{-3} mol l^{-1} sulfuric acid and 2.15×10^{-4} mol l^{-1} SDBS.
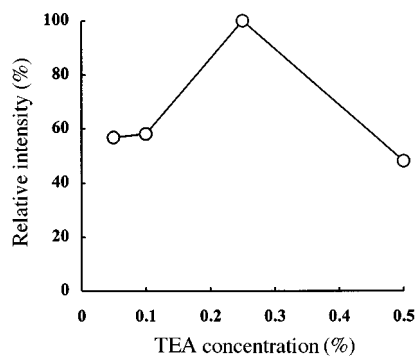
Fig. 5 Emission intensity of various concentrations of TEA at 1.41×10^{-3} mol l^{-1} KBrO$_3$ in the presence of 1.12×10^{-5} g ml^{-1} Ru(bipy)$_3^{2+}$, 5×10^{-3} mol l^{-1} sulfuric acid and 2.15×10^{-4} mol l^{-1} SDBS.

Table 4 Determination of sulfur dioxide in air

Air solution content/ 10^{-6} mol l^{-1}	Added/ 10^{-6} mol l^{-1}	Found/ 10^{-6} mol l^{-1}	Recovery (%)
2.18	2.0	2.01	96.2
		2.12	101.4
		2.14	102.4
	6.0	3.82	93.4
		3.95	96.6
		4.02	98.3

References

1 L. G. Decnop-Weever and J. C. Kraak, *Anal. Chim. Acta*, 1997, **337**, 125.
2 M. Pandurangappa and N. Balasubramanian, *Analusis*, 1996, **24**, 225.
3 C.-Y. Chiou and T.-C. Chou, *Electroanalysis*, 1996, **8**, 1179.
4 I. Ibrahim, Y. Cemal and B. Humeyra, *Analyst*, 1996, **121**, 1873.
5 N. Ekkad and C. O. Huber, *Anal. Chim. Acta*, 1996, **332**, 155.
6 A. Lavigne-Delcroix, D. Tusseau and M. Proix, *Sci. Aliments*, 1996, **16**, 267.
7 J. Rethmeier, A. Rabenstein, M. Langer and U. Fischer, *J. Chromatogr.*, 1997, **760**, 295.
8 E. Ruiz, M. I. Santillana, M. De Alba, M. T. Nieto and S. Garcia-Castellano, *J. Liq. Chromatogr.*, 1994, **17**, 447.
9 J. M. Lin and T. Hobo, *Anal. Chim. Acta*, 1996, **323**, 69.
10 Y. L. Huang, J. M. Kim and R. D. Schmid, *Anal. Chim. Acta*, 1992, **266**, 317.
11 F. Meixner and W. Jaeschke, *Fresenius' Z. Anal. Chem.*, 1984, **317**, 343.
12 K. Takeuchi and T. Ibusuki, *Anal. Chim. Acta*, 1985, **174**, 359.
13 M. Yamada, T. Nakada and S. Suzuki, *Anal. Chim. Acta*, 1983, **147**, 401.
14 S. A. Al-Tamrah, A. Townshend and A. R. Wheatley, *Analyst*, 1987, **112**, 883.
15 J. L. Burguera and M. Burguera, *Anal. Chim. Acta*, 1988, **214**, 429.
16 M. Kato, M. Yamada and S. Suzuki, *Anal. Chem.*, 1984, **56**, 2529.
17 D. A. Paulls and A. Townshend, *Analyst*, 1996, **121**, 831.
18 I. I. Koukli, E. G. Sarantonis and A. C. Calokerinos, *Analyst*, 1988, **113**, 603.
19 A. B. Syropoulos, E. G. Sarantonis and A. C. Calokerinos, *Anal. Chim. Acta*, 1990, **239**, 195.
20 I. M. Psarellis, E. G. Sarantonis and A. C. Calokerinos, *Anal. Chim. Acta*, 1993, **272**, 265.
21 H. L. J. Backstrom, *Z. Phys. Chem.*, 1934, **B25**, 122.
22 G. C. Mishra and R. D. Srivastava, *Chem. Eng. Sci.*, 1975, **30**, 1387.
23 N. N. Semenov, *Some Problems in Chemical Kinetics and Reactivity*, Princeton University Press, Princeton, NJ, 1985, Vol. I.
24 W. A. Waters, *The Chemistry of Free Radicals*, Oxford University Press, Oxford, 1946.
25 F. X. Meiner and W. A. Jaeschke, *Int. J. Environ. Anal. Chem.*, 1981, **10**, 51.
26 J. Stauff and W. A. Jaeschke, *Naturforschung B.*, 1978, **33B**, 293.
27 R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 4th edn., 1976, pp. 297–298.
28 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Ven Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
29 H. S. White and A. J. Bard, *J. Am. Chem. Soc.*, 1982, **104**, 6891.
30 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 512.
31 I. Rubinstein, C. R. Martin and A. J. Bard, *Anal. Chem.*, 1983, **55**, 1580.
32 A. W. Knight and G. M. Greenway, *Analyst*, 1995, **120**, 2543.
33 A. W. Knight and G. M. Greenway, *Analyst*, 1996, **121**, 101R.
34 S. N. Brune and D. R. Bobbitt, *Talanta*, 1991, **38**, 419.
35 Z. K. He, X. L. Liu, Q. Y. Luo, X. M. Yu and Y. E. Zeng, *Anal. Sci.*, 1995, **11**, 415.
36 Z. K. He, H. Gao, L. J. Yuan, Q. Y. Luo and Y. E. Zeng, *Analyst*, 1997, **122**, 1343.
37 Z. K. He, R. M. Ma, Q. Y. Luo, X. M. Yu and Y. E. Zeng, *Acta Chim. Sin.*, 1996, **54**, 1003.
38 T. Korenaga, Thesis, University of Tokushima, Tokushima, 1996, pp. 53–54.
39 S. W. Snyder, S. L. Buell and J. N. Demas, *J. Phys. Chem.*, 1989, **93**, 5265.
40 S. W. Snyder, J. N. Demas and B. A. Degraff, *Chem. Phys. Lett.*, 1988, **145**, 434.
41 Z. K. He, L. J. Yuan, R. M. Ma, Q. Y. Luo, X. M. Yu and Y. E. Zeng, *J. Wuhan Univ. (Nat. Sci. Ed.)*, 1997, **43**, 191.
42 X. Chen and M. Sato, *Anal. Sci.*, 1995, **11**, 749.

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