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$KMnO_4$-OP Chemiluminescence System for FIA Determination of Hydrogen Peroxide

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Abstract. A fast and simple $KMnO_4$-OP chemiluminescence system for flow-injection analysis of hydrogen peroxide is described. When a mixture of sample and OP is injected into acidic $KMnO_4$, solution in a flow-cell, strong chemiluminescence occurs. The response is linear to the concentration of hydrogen peroxide in the range of 1.0×10^{-8} to 6.0×10^{-5} mol/l with 0.1 mol/l permanganate, and the upper limit of linear response could be extended to 6×10^{-3} mol/l by increasing the permanganate concentration. The relative standard deviation of the method is between 1.6 and 2.3%. The detection limit is 6.0×10^{-9} mol/l. This method is suitable for automatic and continuous analysis and has been successfully tested for determination of hydrogen peroxide in rain water. The chemiluminescence intensity was found to be remarkably enhanced in the presence of the OP micellar system.

Key words: chemiluminescence, flow-injection, hydrogen peroxide, octylphenyl polyglycol ether (OP).

Hydrogen peroxide exists extensively in precipitation (rain water, snow) and as an oxidation metabolite and photochemical reaction product of biochemical substances. It is important to be able to determine hydrogen peroxide, in order to protect the environment and study biochemical and photochemical reactions. A number of chemical methods have been proposed, including absorbance [1], fluorescence [2, 3] and electrochemistry [4].

Determination of hydrogen peroxide based on chemiluminescence (CL) has been reported. Nabi and Worsfold [5] described a method based on the reaction between hydrogen peroxide and luminol with cobalt catalysis, obtaining a detection limit of fmol hydrogen peroxide. Eremin et al. [6] reported a similar system with peroxidase used in place of cobalt catalysis, with a detection limit of μmol/l. Katayama et al. [7] obtained a detection limit of 3.0 nmol/l hydrogen peroxide using a peroxyoxalate-sulforhodamine system in an organic phase. All these methods suffered some interference by metal ions.

In this paper, a new CL system, $KMnO_4$-OP, was investigated for determination of hydrogen peroxide. It was found that strong CL occurred when the mixture of sample and OP (octylphenyl polyglycol ether) was injected into acidic $KMnO_4$, solution. CL was hardly observed without OP, which tends to associate dynamically in aqueous solution to form micelles. Most of the common metal and non-metal ions in samples did not interfere. The results show that this system can perform simple, sensitive and rapid determination of hydrogen peroxide.

Experimental

Apparatus

The flow system used (Fig. 1) consisted of a peristaltic pump and a six-way injection valve. Because the CL reaction was fast, the mixing coil (PTFE tubing, 100 mm × 0.5 mm i. d.) after confluence points was used directly as the flow cell. The CL signal was detected with a R456 photomultiplier tube and recorded with a XWT-204 recorder

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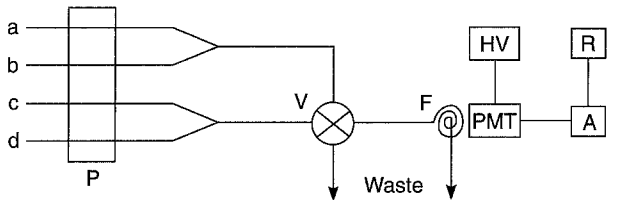

Fig. 1. Schematic diagram of the flow system. *a* sample solution; *b* OP solution; *c* H_2SO_4 solution; *d* $KMnO_4$ solution; *P* peristaltic pump; *V* six-way injection valve; *F* flow-cell; *PMT* photomultiplier tube; *A* amplifier; *R* recorder; *HV* negative high voltage

Reagents

Stock standard solution of hydrogen peroxide (10 mmol/l) was prepared by diluting 1 ml of 30% H_2O_2 to 100 ml with water and titrating with standard potassium permanganate. Working solution of hydrogen peroxide was prepared by further dilution of this stock solution. Octylphenyl polyglycol ether (OP) was purchased from Shanghai Number 1 Chemical Factory. Potassium permanganate solution was prepared by dissolving a weighed amount of $KMnO_4$ in water and diluting to volume. All other reagents were of analytical grade and used as received. Water used was deionized and distilled.

Procedures

As shown in Fig. 1, flow line (a) was connected to the sample solution, (b) to 5% (v/v) OP solution, (c) to 2 mol/l H_2SO_4 solution and (d) to the appropriate $KMnO_4$ solution. A mixture of sample and OP was injected into a mixed stream of the $KMnO_4$ and H_2SO_4 solutions. The flow-rate was controlled to 2.0 ml/min.

The concentration of hydrogen peroxide was quantified by the CL intensity.

Results and Discussion

Chemiluminescence Kinetic Characteristics in Solution

The chemiluminescence kinetic characteristics of the reaction of hydrogen peroxide, OP and acidic $KMnO_4$ in solution were studied in detail. It was found that the rate of the reaction in solution was very fast; from the reagent mixing to the peak maximum only 2 s were needed and it took 6 s for the signal to return to zero.

Selection of Acid

Since the reaction between acidic potassium permanganate and some organic compounds yields measurable CL signals [8], the effects of various acids on the CL signal were studied. 0.5 mol/l HCl, H_2SO_4, HNO_3, H_3PO_4 and $H_6P_4O_{13}$ in 0.5 mmol/l $KMnO_4$ solutions were prepared and the light emission produced from 0.6 μmol/l hydrogen peroxide mixed with 5% OP was observed. Table 1 shows the results. The highest emission was observed from H_2SO_4-treated permanganate solutions and the signals were stable; hence, H_2SO_4 was chosen for further work. The concentration of H_2SO_4 in $KMnO_4$ solution was subsequently optimized (Fig. 2) and 2 mol/l H_2SO_4 was used for further experiments.

Organic acids (acetic acid and citrate-NaOH buffer) were also tested, but the CL was too weak to detect.

Table 1. Effect of acids on the permanganate-induced CL emission from a mixture of 0.60 μmol/l H_2O_2 and 5% OP

Acid (0.5 mol/l in aqueous 0.5 mmol/l $KMnO_4$)	HCl	HNO_3	H_2SO_4	H_3PO_4	$H_6P_4O_{13}$
Emission signal	30	24	39	32	35

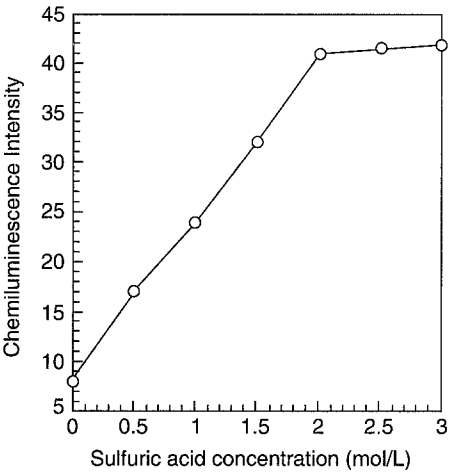

Fig. 2. Effect of sulfuric acid on the permanganate-induced hydrogen peroxide emission in aqueous 0.50 mmol/l $KMnO_4$. H_2O_2 concentration: 0.60 μmol/l; OP concentration: 5% (v/v)

Effect of Potassium Permanganate Concentration

The effect of potassium permanganate concentration on the CL emission within the range 0.05—7.5 mmol/l was investigated with different orders of magnitude of hydrogen peroxide concentration. The results are shown in Table 2: the higher the hydrogen peroxide concentration to be detected, the higher the $KMnO_4$ concentration required. Permanganate concentration had not only an effect on the sensitivity, but influenced the linear range for the assay. Higher permanganate concentration resulted in stronger CL, provided that $KMnO_4$ concentration was below 5.0 mmol/l. When the permanganate was above this level, the CL intensity decreased, at least partly because of the absorption of the emitted light by permanganate.

Table 2. Analytical characteristics for the determination of H_2O_2 by the proposed method

Linear concentration range (mol/l)	Regression equation	Correlation coefficient	$KMnO_4$ concentration (mmol/l)
1.0×10^{-8}–1.0×10^{-7}	$I = -0.3 + 1.1C$	0.9983	0.10
1.0×10^{-7}–1.0×10^{-6}	$I = 0.3 + 2.1C$	0.9987	0.10
1.0×10^{-6}–1.0×10^{-5}	$I = 0.8 + 2.3C$	0.9990	0.10
1.0×10^{-5}–1.0×10^{-4}	$I = 0.2 + 2.7C$	0.9994	0.50
1.0×10^{-4}–1.0×10^{-3}	$I = 1.2 + 6.2C$	0.9994	1.0
1.0×10^{-3}–6.0×10^{-3}	$I = 0.3 + 9.9C$	0.9995	5.0

I = relative peak-height intensity; C = concentration.

Selection of the Sensitizer

The characteristics of several different sensitizers including OP, β-cyclodextrin (β-CD), Tween 20, TritonX-100, SDS, SLS, CMC, CTMAB and SDBS were studied. It was found that only OP enhanced the CL emission intensity, and that CL was hardly observable without OP. Upon reaching a certain minimum concentration (the critical micelle concentration, CMC, 1.3×10^{-4} mol/l for OP [9]), amphiphilic surfactant molecules tend to associate dynamically in aqueous solution to form micelles [10]. The local micro-environment encountered by a solute associated with a micellar system can be drastically different from that which it experiences in a bulk homogeneous solvent system. Consequently, the CL intensity can be affected. The effect has been rationalized in terms of favorable alteration of such "solvent" properties as micro-polarity, micro-fluidity (viscosity) and dielectric constant for a solute associated with a micelle, in addition to the micellar effects upon the various photophysical rate processes [10]. The net result is that the micelle provides a protective environment for the excited singlet state, the micro-environment provided by the micelles should be ideal for the observation of enhanced CL.

Figure 3 shows the effect of OP. If its concentration was above the CMC (from 1 to 10%), the CL intensity was remarkable improved, 5% (v/v) OP was considered to be the optimum concentration and was used for further experiments.

Response to Hydrogen Peroxide

The hydrogen peroxide gave rise to CL under the optimized conditions. The analytical parameters for hydrogen peroxide examined are summarized in Table 2. At a flow-rate of 2.0 ml/min, it took less than 1 min to complete one measurement, and the injection frequency was 60 h^{-1}. The relative standard deviations

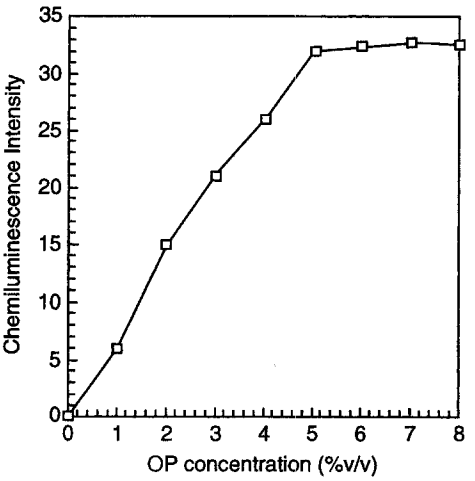

Fig. 3. Effect of OP concentration on hydrogen peroxide CL emission in acid $KMnO_4$ medium. $KMnO_4$ concentration: 0.50 mmol/l; H_2SO_4 concentration: 2.0 mol/l; H_2O_2 concentration: 0.60 μmol/l

of 7 repetitive measurements of 4×10^{-n} (n = 8, 7, 6, 5, 4, 3) mol/l hydrogen peroxide were 2.3, 2.0, 1.8, 1.6, 1.6, and 1.8%, respectively. The detection limit (3σ) was 6.0 nmol/l.

Interferences

The effect of foreign ions was studied using the above procedure. A foreign ion was considered not to interfere if it caused a relative error of less than 5% for the determination of 0.60 μmol/l hydrogen peroxide. The tolerated molar ratio of foreign ions to 0.60 μmol/l hydrogen peroxide was 1000 for F^-, Br^-, Cl^-, acetate, NO_3^-, Al^{3+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-}, HPO_4^{2-}, Na^+, K^+ and HCO_3^-; 100 for Zn^{2+}, Fe^{3+}, Cu^{2+}, Ag^+, Mn^{2+}, Pb^{2+}, Ta(VI), Zr^{4+}, Au^{3+} and Bi^{3+}; 10 for Cr^{3+}, Cr (VI), $S_2S_8^{2-}$, ClO^-, CrO_4^{2-}, S^{2-}, Nd^{3+}, Fe^{2+}, Co^{2+}, V^{6+}, MoO_4^{2-}, Ni^{2+}, La^{3+}, Sb^{3+}, and MnO_4^-. The effects of some organic compounds

Table 3. Hydrogen peroxide measurements in rain water samples

Sample	Content (μmol/l)	RSD (%)	Calibration range (mol/l)	Fluorescence method (μmol/l)
1	0.080	2.9	1.0×10^{-8}–1.0×10^{-7}	0.085
2	0.13	2.5	1.0×10^{-7}–1.0×10^{-6}	0.14
3	0.21	2.3	1.0×10^{-7}–1.0×10^{-6}	0.22

were also tested; the tolerated molar ratio of these compounds to 0.60 μmol/l hydrogen peroxide was 10 for phenol, EDTA and oxalic acid. 5% methanol and ethanol and 0.60 μmol/l of ascorbic acid, methyl nitrile and ethyl nitrile interfered with the determination of 0.60 μmol/l hydrogen peroxide.

Sample Analysis

The proposed method was applied to the determination of hydrogen peroxide in rain water collected at different times on the same day. The results are listed in Table 3 and quite comparable with those by a fluorescence method [11].

Conclusions

The proposed method has been successfully applied to the determination of hydrogen peroxide in rain water with RSDs between 2.3 and 2.9%. Study revealed that OP can strongly enhance the CL when its concentration exceeds the CMC, therefore OP-micelles are the key for strong enhancement of CL. Some organic compounds, especially those that affected micelle formation, interfered with the determination.

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