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CHEMILUMINESCENCE METHOD FOR SELECTIVE DETERMINATION OF IRON(II) AND CHROMIUM(III) WITH SINGLE REACTION SYSTEM

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A new chemiluminescence system, brilliant sulfoflavine-hydrogen peroxide-sodium hydroxide-acetonitrile, is described for continuous flow analysis for Fe(II) and Cr(III). This permits highly selective determination with detection limits of 1 x 10^{-9}M for Fe(II) and 3 x 10^{-8}M for Cr(III).

There have been an increasing number of investigations on the analytical use of solution chemiluminescence(CL) because the CL technique offers substantial advantages with respect to sensitivity, linearity, instrumentation, and speed of analysis.1) However, the CL method is not yet utilized widely in practice unlike other spectral methods. This is mainly due to the lack of selectivity and the paucity of CL reaction usable in analysis. In order to cope with these shortcomings, our efforts have been focussed on seeking new CL systems.2,3) This letter demonstrates a CL system, brilliant sulfoflavine(BSF)-hydrogen peroxide(H_2O_2)-sodium hydroxide(NaOH)-acetonitrile(CH_3CN), for selective determination of Fe(II) and Cr(III) by continuous flow method. The CL reaction is initiated by the Fenton or Fenton-like reaction, that is, the CL is considered to be BSF-sensitized emission which results from the energy transfer to BSF from singlet oxygen molecules produced through the reductive decomposition of H_2O_2 by Fe(II) and Cr(III) as described later.

Prior to flow experiments, a batch method as described previously4) was employed to examine CL characteristics of the present CL system. Each 0.2 ml of reagent solutions is transferred to a reaction vessel by a peristaltic pump. Sodium hydroxide and BSF(sodium 4-amino-N-(p-tolyl)naphthalimide-3-sulfonate) are co-dissolved in various reaction media as needed. Alkaline BSF, H_2O_2, and analyte solutions are transferred in that order unless otherwise stated.

Selection of reaction media is essential because CL reaction often proceeds more effectively in solutions containing organic solvent or surfactant assemblies than in water alone.2,3,5) Of reaction media tested, aqueous CH_3CN solution was found to be the best choice for sensitive detection of both analytes; the CH_3CN concentration in alkaline BSF solution providing maximum CL signal, 75% for Fe(II) and 10% for Cr(III), exhibited 8 and 6 times larger signal than those in water alone, respectively, under the conditions of 10^{-3}M(1 M=1 mol dm^{-3})BSF and NaOH, 0.6% H_2O_2, and 10^{-4}M analytes. Iron(II) gave emission not only in alkaline solution but also in acidic solution, whereas Cr(III) elicited light only in alkaline solution(Fig. 1). Emission intensity is often dependent on the mixing order of reagent solution. The results for the present CL system is shown in Table 1, indicating that the Cr(Ⅲ) solution should be first transferred but the Fe(II) solution finally for sensitive detection. Furthermore, the CL signal for Fe(II) depends strongly on the time from the transferring of the H_2O_2 solution until the last reagent solution is mixed(Fig. 2). Increase in the signal of ca.10 times was realized by the standing of 10 min at 10% CH_3CN when the Fe(II) solution was finally mixed; the standing time was reduced to ca.1 min at 75% CH_3CN. At 10^{-4}M NaOH, no change in signal was observed by the standing time of 1 min, the signal being about one-third that at 10^{-3}M NaOH. In the acidic region the standing time caused gradual decrease in signal. On the other hand, the first transferring of Fe(II) solution led to the CL disappearance within the standing time of 30 s. In contrast to Fe(II), the signal for Cr(Ⅲ) was not almost affected by the standing time.

On the basis of these CL characteristics, a system as shown in Fig. 3 was assembled for continuous flow analysis for both analytes. That is to say, for the Fe(II) determination the H_2O_2 solution is mixed with the BSF solution and for the Cr(Ⅲ) determination with the Cr(Ⅲ) solution; a 2-m coil works not only as a mixing coil but also for the Fe(II) mode as a delay coil, the time delayed being correlated with the standing time stated above. A spiral flow cell D is the same as that previously used.[6] Under recommended conditions(as specified in Fig. 3), the logarithmic calibration graphs were linear over three decades with slopes of unity; the detection limits were 1×10^{-9}M for Fe(II) and 3×10^{-8}M for Cr(Ⅲ). For evaluation of the selectivity, various species

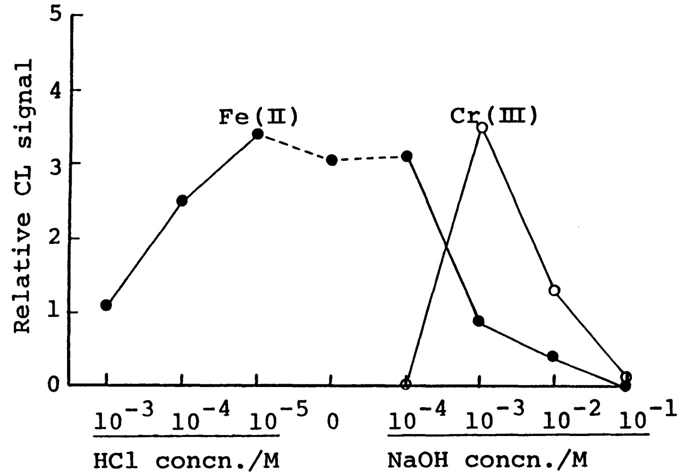

Fig. 1. Effect of the HCl and NaOH concentrations in BSF solution. 10^{-3}M BSF(75% CH_3CN for Fe,10% for Cr),0.3% H_2O_2,10^{-4}M Fe and Cr.

Table 1. Effect of the mixing order of reagent solution[a)]

Mixing order			Relative CL signal	
1	2	3	Fe(Ⅱ)	Cr(Ⅲ)
BSF +	H_2O_2 +	M	1.0	0.82
BSF +	M +	H_2O_2	0.52	0.27
M +	H_2O_2 +	BSF	0.20	1.0

a) 10^{-3}M BSF(10% CH_3CN,10^{-3}M NaOH), 0.6% H_2O_2, 10^{-4}M M(=Fe,Cr).

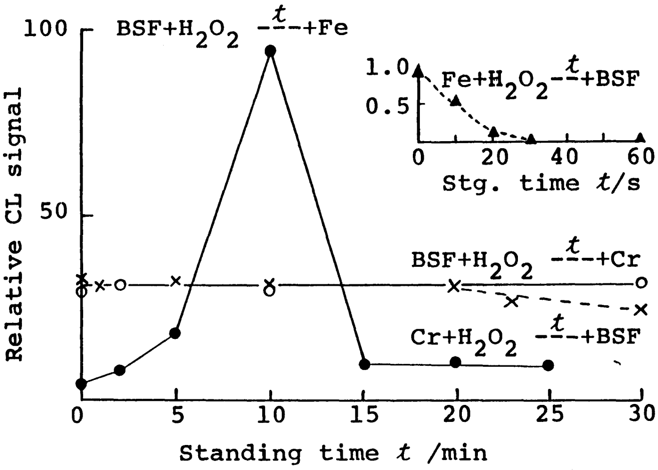

Fig. 2. Effect of the standing time(t in the figure). 10^{-3}M BSF(10^{-3}M NaOH,10% CH_3CN),0.6% H_2O_2,10^{-4}M Fe(II) and Cr(Ⅲ).

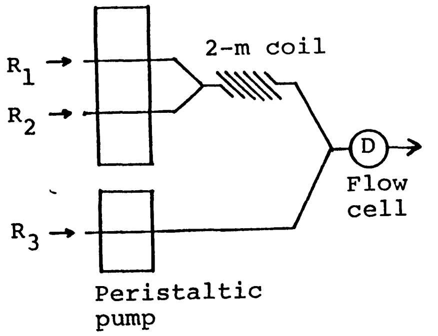

Fig. 3. Schematic diagram of the recommended flow system for Fe(II) and Cr(III) determinations. Fe(II) mode: $R_1=10^{-3}$M BSF(10^{-3}M NaOH,80% CH_3CN)(2 ml min^{-1}),R_2= 0.09% H_2O_2(2 ml min^{-1}),R_3=Fe(II) soln.(8 ml min^{-1}). Cr(III) mode: R_1=Cr(III) soln.(7 ml min^{-1}),$R_2=R_2$ for Fe(II) mode(7 ml min^{-1}),$R_3=R_1$ for Fe(II) mode(10 ml min^{-1}).

Table 2. Selectivity of the present CL system

Species[a]	Relative molar signal	Species[a]	Relative molar signal
Fe(II)[b]	100	Cr(III)[c]	100
Fe(III)	0.53	Fe(II)	0.03
$C_2O_4^{2-}$	0.04	Pb(II)	0.03
I^-	0.03	Ag(I)	0.03
Cr(III)	0.02	Fe(III)	0.02
Mn(II)	0.01	Hg(II)	0.01
S^{2-}	0.01	I^-	0.01

a) 10^{-4}M soln. of chloride or nitrate, or sodium or potassium salt except ammonium sulfate for Fe(II,III) and ammonium molybdate for Mo(VI). b) 10^{-8}M soln. c) 10^{-6}M soln. Species unspecified in each table, Cu(II), Ni(II),Co(II),Cr(VI),Zn(II),Pb(II),Mn(II),Hg(II), Ag(I),Sn(II),Mo(VI),Al(III),Ca(II),Mg(II),Cl^-, Br^-,NO_3^-,NO_2^-,CO_3^{2-},PO_4^{3-},ClO_4^-,CN^-,$Fe(CN)_6^{4-}$,SCN^-, S^{2-},SO_3^{2-},$S_2O_3^{2-}$,SO_4^{2-},EDTA,acetate,citrate, oxalate,and ascorbic acid, give rise to no emission.

were examined. The results are shown in Table 2, indicating that the present CL system is highly selective for both analytes. With the Fe(II) mode, the signal for Fe(III) which was based on the oxidative decomposition of H_2O_2 was greatly increased in the presence of complexing agents like triethylenetetramine(TETA) and tetraethylenepentamine(TEPA), whereas that for Fe(II) was slightly decreased. This suggests that Fe(III) can be determined with an sensitivity equal to that for Fe(II), resulting in the determination of total iron with no use of reductants.

The light emission is likely to arise through the following reactions. Both analytes decompose H_2O_2 reductively to produce OH radical(only in alkaline solution Cr(III) decomposes H_2O_2 to be oxidized to Cr(VI) with an appreciable reaction rate):

$$\mathrm{Fe(II)(or\ Cr(III))} + H_2O_2 \dashrightarrow \mathrm{Fe(III)(or\ Cr(IV))} + \cdot OH + OH^-.$$

The ·OH then reacts with H_2O_2 in alkaline solution:

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad (pKa=11.7)$$
$$\cdot OH + HO_2^- \dashrightarrow O_2^{\cdot -} + H_2O,$$

and also in acidic solution:

$$\cdot OH + H_2O_2 \dashrightarrow HO_2^{\cdot} + H_2O$$
$$HO_2^{\cdot} \rightleftharpoons O_2^{\cdot -} + H^+ \quad (pKa=4.8).$$

The $O_2^{\cdot -}(HO_2^{\cdot})$ takes part in the subsequent reactions for singlet oxygen molecule($^1O_2$) formation, although there are some controversies regarding the generation of $^1O_2$ by $O_2^{\cdot -}(HO_2^{\cdot})$ disproportionation reactions:7)

$$O_2^{\cdot -} + \cdot OH \dashrightarrow OH^- + {}^1O_2$$
$$O_2^{\cdot -} + O_2^{\cdot -} \dashrightarrow O_2^{2-} + {}^1O_2$$
$$O_2^{\cdot -} + HO_2^{\cdot} \dashrightarrow HO_2^- + {}^1O_2$$

$$HO_2^\bullet + HO_2^\bullet \dashrightarrow H_2O_2 + {}^1O_2$$

$$O_2^{\bar{\bullet}} + H_2O_2 \dashrightarrow OH^- + {\cdot}OH + {}^1O_2.$$

Then, a direct energy transfer from $^1O_2$ pairs to BSF molecules(λ_{fl}=ca.520 nm) occurs through the Khan-Kasha mechanism:[8)]

$$O_2^*({}^1\Delta_g)\cdot O_2^*({}^1\Sigma_g^+) + BSF \dashrightarrow BSF^* + 2O_2,$$

and thus BSF-sensitized emission is elicited:

$$BSF^* \dashrightarrow BSF + h\nu(ca.520\ nm).$$

The light emitted was not so strong as its spectrum could be measured by use of a monochromator. However, the above CL reaction scheme is supported by the following facts: (i)the addition of 2-propanol(a ·OH trapper), nitroblue tetrazolium(a $O_2^{\bar{\bullet}}$ trapper), or sodium azide or 1,4-diazabicyclo-[2,2,2]octane(a $^1O_2$ trapper) to the CL system leads to a pronounced decrease in signal; (ii)weak light chemiluminesces even in the absence of BSF; (iii)fluorescent compounds such as eosin Y and flavin mononucleotide also sensitize the emission; (iv) no change in absorption spectra of BSF is observed at various conditions; (v)the evolution of oxygen gas is observed during the CL reaction. Unlike Fe(II), the signal for Cr(III) was not affected by the presence of EDTA, 1,10-phenanthroline, TETA, or TEPA. This might exclude the possibility that Cr(IV) and/or Cr(V) are responsible for the catalytic decomposition of H_2O_2, because the complexation between both species(and also Fe(II)) and the above complexing agents[9)] alters the rate of the H_2O_2 decomposition but Cr(III) does not complex readily.

This preliminary results imply that Fe(II) and Cr(III) at sub-ppb and ppb levels, respectively, can be determined selectively by continuous flow method using a single reaction system with fewer interferences than any other CL system. The luminol CL system also permits very sensitive and selective determination of both analytes, but different reaction systems are required for separate determination.[10,11)] There is room for further development of the present flow system; better characteristics should be achieved by the mixing of the stream R_3 with the other stream(R_1+R_2) inside the flow cell because the light is emitted as soon as two streams join. This should provide increased sensitivity and reduced reagent-consumption due to lowered flow rates.

References

1) M.Yamada and S.Suzuki, Bunseki, 1985, 104.
2) M.Yamada and S.Suzuki, Anal.Lett., 17, 251(1984).
3) M.Kato, M.Yamada, and S.Suzuki, Anal.Chem., 56, 2529(1984).
4) M.Yamada, H.Kanai, and S.Suzuki, Bull.Chem.Soc.Jpn., 58, 1137(1985).
5) C.M.Paleos, G.Vassilopoulos, and J.Nikokavouras, J.Photochem., 18, 327(1982).
6) S.Nakahara, M.Yamada, and S.Suzuki, Anal.Chim.Acta, 141, 255(1982).
7) R.L.Arudi, B.H.J.Bielski, and A.O.Allen, Photochem.Photobiol., 39, 703(1984).
8) A.U.Khan and M.Kasha, J.Am.Chem.Soc., 88, 1574(1966).
9) K.Yamamoto and K.Ohashi, Bull.Chem.Soc.Jpn., 49, 2433(1976).
10) W.R,Seitz, W.W.Suydam, and D.M.Hercules, Anal.Chem., 44, 957(1972).
11) W.R.Seitz and D.M.Hercules, Anal.Chem., 44, 2143(1972).

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